Publication No. U-3237

FINAL REPORT

STUDY OF THE AUTOMATED BIOLOGICAL LABORATORY PROJECT DEFINITION

VOLUME V OF VI
EXOBIOLOGY BIBLIOGRAPHY

Prepared for:
Bioscience Programs Division
Office of Space Science and Applications
NASA Headquarters
Washington, D. C.

Under Contract: NASw-1065

Reporting Period: 10 August 1964 - 10 August 1965

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10 September 1965

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FOREWORD

This bibliography contains 425 annotated references dealing with various aspects of the problem of detecting extraterrestrial life. Due to the wide range of material that can be included in a bibliography of this kind, no attempt has been made to do an exhaustive study of any one phase of the problem. Rather, the emphasis has been on the variety of techniques and instruments that could prove useful in detecting life outside our planet. The references cited are mainly those compiled from September 1964 to April 1965.

The majority of abstracts are those of the authors themselves. When no author abstract was available, one was prepared from the text of the paper cited.

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PROCEDURES, INSTRUMENTS AND INFORMATION APPROPRIATE TO THE PROBLEM OF THE DETECTION OF EXTRA-TERRESTRIAL LIFE

AN ANNOTATED BIBLIOGRAPHY

SECTION 1

ANALYTICAL METHODS - GENERAL

Cassidy, W., NONDESTRUCTIVE NEUTRON ACTIVATION ANALYSIS OF SMALL PARTICLES, Ann. N. Y. Acad. Sci. 119, 318-338, (1964).

This report describes procedures and results for the nondestructive neutron activation analysis of particles from various sources.

Clifford, W. E., H. Irving, AN ABSORPTIOMETRIC DETERMINATION OF PERCHLORATE BY MEANS OF A NOVEL COLOURED LIQUID ANION EXCHANGER, Anal. Chim. Acta, 31 No. 1, 1-10 (1964).

A novel liquid anion exchanger can be prepared from tetra-n-hexylammonium iodide and Erdmann's salt, $(NH_4)[Co(NH_3)_2(NO_2)_4]$. When a solution of this quaternary erdmannate in a suitable organic solvent (ϵ_{max} = 15,700 at 355 mμ) is equilibrated with an aqueous solution of a salt, the coloured ermannate ion is displaced to a greater or less extent: the effect decreases in the order $ClO_4^- \gg ClO_3^- > NO_3^- > Cl^- \gg SO_4^{2-}$ etc. The effects of changes in the organic solvent composition, of ionic strength, and of other variables on the position of equilibrium have been studied with a view to defining the optimum conditions for the absorptiometric determination of perchlorate ion ($\geqslant$25μg) in the presence of chlorate and other ions. Methods are proposed for eliminating those ions that form insoluble silver salts and to allow for the presence of substantial proportions of chlorate or nitrate ions.

Davies, C. W. and A. Narebska, THE BEHAVIOR OF ION-EXCHANGE RESINS WITH MIXED SOLVENTS. PART III. DIOXAN-WATER MIXTURES, J. Chem. Soc., 800, 4169-4172, (1964).

Measurements are reported of the uptake of dioxan and water by sulphonic acid resins of varying degrees of cross-linking in the sodium, potassium, and nickel forms. At low molar fractions of water in the solvent, the sorption of water is less the more lightly cross-linked is the resin. Virtually no dioxan is taken up by a resin containing less than one mole of water per equivalent.

Espinosa, E., QUICK TWO-DIMENSIONAL ELECTROPHORESIS FOR SIMULTANEOUS ANALYSIS OF SEVERAL SERUM PROTEIN SAMPLES. STUDY OF VARIOUS SPECIES SERUM, Anal. Biochem., 9, No. 2, 146-149, (1964).

A two-dimensional agar hydrolyzed-starch electrophoresis technique facilitating simultaneous analysis of several serum protein samples in 5 to 6 hr. is described. Results obtained with human, rabbit, dog, rat, mouse, and guinea pig serum proteins are shown.

Fester, J. I., W. E. Robinsen, METHOD FOR DETERMINING CARBOXYL CONTENT OF INSOLUBLE CARBONACEOUS MATERIALS, Anal. Chem., 36, No. 7, 1392-1394, (1964).

A revision of an ion exchange method for determining carboxyl groups in insoluble carbonaceous materials is described. Addition of a steam distillation step to remove acetic acid as it is formed results in increased speed, better reproducibility and less mineral interference. The authors suggest application of this technique in analysis of pulp, coal, lignin and of other natural and synthetic polymers.

Fleck, A., H. N. Munro, THE DETERMINATION OF ORGANIC NITROGEN IN BIOLOGICAL MATERIALS, Clin. Chim. Acta, 11, No. 1, 2-12, (1965).

Methods of estimating nitrogen in samples of biological material have been reviewed. Under almost all circumstances, some form of the KJELDAHL method is the most suitable procedure to apply to biological material. The digestion of the sample in concentrated sulphuric acid is a critical stage in the KJELDAHL method, and optimal conditions for this step have been defined. The most convenient means of estimating the ammonia formed by digestion will depend on the amount of nitrogen in the sample. When the sample contains more than 0.3 mg nitrogen, steam distillation into standard acid is the most suitable procedure. Samples containing smaller amounts of nitrogen can be assayed by colorimetric procedures applied directly to the digest, provided that certain precautions are taken.

Frank, W. A., H. D. Kutsche, MOLECULAR DISTILLATION OF THERMALLY SUPERSENSITIVE LIQUIDS, Anal. Chem., 36, No. 11, 2167-2170 (1964).

By using an all-glass apparatus with a special device to distribute the film of the liquid to be distilled, it is possible to distill and separate thermally supersensitive liquids up to a molecular weight of approximately 2000. The apparatus is briefly described. New results of distillation experiments are reported. The reasons for the unusual separating power at higher molecular weights are discussed.

Freeland, L. T. A LOW-LEVEL CARBON-14 COUNTING TECHNIQUE, Anal. Chem., 36, No. 11, 2055-2057 (1964).

Liquid scintillation spectrometry has proved very useful in the dating of carbon-14 containing artifacts. However, most carbon-14 dating methods involve a tedious and usually low yield preparation of a suitable solvent for liquid scintillation spectrometry. The possibility of isotope effects is present in some of these procedures. This paper describes a technique which circumvents the before mentioned limitations. The method requires the combustion of the sample to CO_2, absorption of the CO_2 in sodium hydroxide solution, followed by reaction with phenylmagnesium bromide to form benzoic acid. The benzoic acid-C^{14} is esterified to methyl benzoate. This methyl benzoate is the solvent used in the assay of the sample by liquid scintillation spectrometry.

Freeman, R. R., SEPARATION OF CELLS FROM FLUIDS, Biotechnol. Bioeng., 6, 87-125 (1964).

The selection of a method for the separation of cells from fluids depends on various factors such as the character of the cells, the scale of the operation and the quality of the purified product. The author describes the following methods of cell separation: centrifugation, flotation, filtration, flocculation, freeze, spray and other drying methods, use of ion exchange resins and electrophoresis.

Guinn, V. P., ACTIVATION ANALYSIS, Ind. Res., 6, No. 9, 30-36 (1964).

The principles of neutron activation are discussed. The author cites the advantages and applications of this method of analysis.

Hodge, Paul W., F. W. Wright, C. C. Langway, Jr., STUDIES OF PARTICLES FOR EXTRATERRESTRIAL ORIGIN. 3. ANALYSES OF DUST PARTICLES FROM POLAR ICE DEPOSITS, J. Geophys. Res., 64, No. 14, 2919-2931 (1964).

A total of 166 dust particles collected principally from Greenland and antarctic ice has been subjected to chemical analysis by the electron-beam microanalyzer technique. Several have Ni/Fe ratios indicative of a meteoritic origin. The remainder are probably also primarily cosmic in origin. The rate of deposit of opaque spherules is found to be nearly, but not exactly, the same at all geographical locations sampled.

Howe, A. F, T. Groom, R. G. Carter, USE OF POLYETHYLENE GLYCOL IN THE CONCENTRATION OF PROTEIN SOLUTIONS, Anal. Biochem., 9, 443-453, (1964).

Protein solutions were concentrated quickly, conveniently, and inexpensively using osmotic ultrafiltration against Carbowax 20-M (polyethylene glycol). A small amount of material counter-dialyzed and contaminated the samples being concentrated. This material was eluted from DEAE-cellulose columns in two peaks (one at low ionic strength and one at high ionic strength), had an absorption maximum at 286 mu, and interfered with the Lowry protein determination but not with the biuret determination. Antigen and antibody concentrated with Carbowax 20-M showed no differences from controls in the quantitative precipitin test or on immunoelectrophoresis.

Jevons, F. R., DETECTION OF NON-REDUCING CARBOHYDRATE WITH ORCINOL IN PHOSPHORIC ACID, J. Chromatog., 16, 252-253, (1964).

Methods to detect non-reducing carbohydrate using periodate depend on the availability of pairs of free vicinal hydroxyl groups, and the only really general type of procedure is to use a reagent such as orcinol in a strong acid such as sulphuric acid which breaks down the polysaccharide. In the modification described here, sulphuric acid is replaced by phosphoric acid and the reaction is done on spot tiles instead of test tubes. This increases sensitivity (down to 0.2 μg) and ease of handling a large number of samples.

Kateman, G., L. L. M. Willemsen, J. B. G. Wijenberg, P. J. Stornebrink, RAPID NEW METHODS FOR THE DETERMINATION OF NITROGEN IN FERTILISERS AND OTHER COMPOUNDS. PART 2. AUTOMATIC ANALYSIS, Anal. Chem. Acta, 31, No. 2, (1964).

The determination of ammonia nitrogen, or the sum of nitrate and ammonia nitrogen in fertilisers as described in a previous article, has been automated. In routine work one operator can analyse 50 samples (including grinding, weighing, distillation and titration) within one hour; the total time of analysis per sample does not exceed 3.5 min.

Lublin, P., ELECTRON PROBE ANALYSIS IN THE ELECTRONICS INDUSTRY, Norelco Reporter, 11, No. 2, 47-50 (1964).

Several applications of electron probe analysis to the special analytical problems of the electronics industry such as diffusion studies, phase identification and analysis of thin films are discussed.

Lyman, D. J., B. H. Loo, R. W. Crawford, NEW SYNTHETIC MEMBRANES FOR DIALYSIS. I. A COPOLYETHER-ESTER MEMBRANE SYSTEM, Biochem., 3, No. 7, 985-990, (1964).

Block copolymers based on polyoxyethylene glycol and polyethylene terephthalate were synthesized, and the effects of varying the molecular weight and the molar composition of the macroglycol on the membrane properties of these copolymers were determined. Membranes from the copolymer containing 0.3 mole % of polyoxyethylene glycol, molecular weight of 1540, dialyzed compounds such as urea, creatinine, and uric acid at a faster rate than did a Cuprophane membrane. However, sugar molecules such as glucose and sucrose showed relatively slower escape rates through the copolyester membrane than through the Cuprophane membrane. A dialysis cell suitable for laboratory studies on new polymeric membranes is described.

McCrone, W. C., J. S. Martin, IDENTIFYING COLORLESS TRANSPARENT PARTICLES BY MICROSCOPY, Res. Develop., 15, No. 11, 28-31, (1964).

In using the dispersion staining technique with microscopy to solve identification as well as other problems, the authors outline several modifications that increase speed and accuracy while reducing the amount of specialized technical background necessary.

Moser, H. C., P. Nordin, J. K. Senne, LABELING CARBOHYDRATES BY EXPOSURE TO ENERGETIC TRITIUM ATOMS, Intern. J. Appl. Radiation Isotop., 15, 557-559, (1964).

An apparatus for bombarding carbohydrates with energetic tritium atoms is described. The system was found to give about the same yield of tritium labeled carbohydrates as the gas exposure technique while using less tritium and a shorter time period.

Noel, A. R. A., A STAINING AND MOUNTING COMBINATION FOR SECTIONS OF PLANT TISSUES, Stain Tech., 30, No. 5, 324-325, (1964).

A further modification for Berkeley's combination of aniline blue and basic fuchsin in lactophenol as a stain and temporary mountant for plant tissue is suggested. The author recommends the addition of iodine which allows the observation of starch grains and heightens the color of the lignified walls by fuchsin.

Peetoom, F., P. S. Gerald, A SIMPLE AND INEXPENSIVE METHOD FOR THE CONCENTRATION OF PROTEIN SOLUTIONS BY MEANS OF ULTRFILTRATION, Clin. Chim. Acta, 10, No. 4, 375-376, (1964).

The method requires two glass plates and weights of approximately 10-15 kg. The protein solution to be concentrated is put into a dialysis bag which is in turn placed on one of the glass plates which is covered with a piece of filter paper. Two microscope slides are placed on each side of the bag and another sheet of filter paper covers the bag and slides. The second glass plate is on top covered by the weights. A significant loss of fluid from the bag will be observed by 4 hours.

Přibyl, M., Z. Slovák, COULOMETRIC DETERMINATION OF SMALL AMOUNTS OF WATER BY THE PRINCIPLE OF THE KARL-FISHER REACTION, Mikrochim. Acta, No. 6, 1097-1105, (1964).

A coulometric method for the determination of water on the principle of the Karl Fischer reaction has been developed. It permits the determination of around 10 μg of water as a minimum in small samples of liquids. The error in the determination is approximately ± 2 μg in the range from 10 to 550 μg water. All-glass specimen holders were successfully used for taking the samples for analysis; the transfer of a measured volume of the sample into the titration vessel is by means of a special pipette.

Rakovic, M., COMBINATION OF NEUTRON ACTIVATION ANALYSIS WITH PAPER CHROMATOGRAPHY, Chem. Listy, 58, 1141-1146, (1964).

In this review article the author shows the advantages of neutron activation analysis in combination with paper chromatography.

Roe, D. K., ELECTROCHEMICAL FRACTIONATION: POTENTIOSTATIC CHROMATOGRAPHY AND ELUTION VOLTAMMETRY, Anal. Chem. 36, No. 12, 2371-2372, (1964).

This paper reviews recent developments of column electrolysis both from the literature and from the author's laboratory.

Ryan, D. P., A. Kolin, CONTINOUS TURBIDIMETRIC ANALYSIS OF pH DEPENDENT BIOLOGICAL COALESCENCE PROCESSES, IEEE Trans. Bio-Med. Eng. BME-11, No. 3, 109-113, (1964).

The method described allows rapid analysis, by pH modulation, of the coalescence of small samples of biological materials in dilute suspensions. Specifically, agglutination of various species of viruses and bacteria at their isoelectric points, and the polymerization process of the muscle protein actin are investigated. A typical time of analysis is 20 sec, and 5 ml of suspensions as dilute as 0.2 mg/ml are sufficient for most viruses investigated.

Salvage, T., J. P. Dixon, THE COLORIMETRIC DETERMINATION OF PHOSPHORUS IN ORGANIC COMPOUNDS ON THE MICROGRAM SCALE, Analyst, 90, 1-8 (1965).

A method is described for determining phosphorus in 30- to 500µg samples of organic compounds, The sample is wet oxidised in a 1-ml calibrated flask, the yellow molybdovanadophosphate complex is developed in situ and its concentration is measured at 430 mµ in a micro cell with a Unicam SP600 spectrophotometer. Techniques for weighing solid and liquid samples are described, and our results for the calibration of an Oertling Decimicro balance Model QOI are included.

Smith, D. R., J. J. Pieroni, MEASUREMENT OF ELECTRON SPIN RESONANCE DIFFERENCE SPECTRA AT 77°K. APPLICATIONS OF THE METHOD IN LOW-TEMPERATURE RADIATION CHEMISTRY, Can. J. Chem., 42, 2209-2214, (1964).

The technique of measuring e.s.r. difference spectra has been extended to 77°K. This enables elimination of the main signal due to irradiated silica sample tubes and of about 90% of the hydrogen atom signal from the same source. Under certain conditions, e.g. when the e.s.r. spectrum due to one species can be photochemically bleached, the method permits resolution of two superimposed spectra. This has been demonstrated by measurements which resolve the e.s.r. singlet due to trapped electrons in irradiated tetrahydro-2-methylfuran from the underlying septet. These developments have rendered the e.s.r. difference method very useful for the study of paramagnetic species formed in systems which have been γ-irradiated at 77°K.

Smithies, O., STARCH-GEL ELECTROPHORESIS, Metabolism, 13, No. 10, Part II, 974-984 (1964).

The author discusses the use of starch-gel electrophoresis to study the structural differences in the human hemoglobin binding serum proteins (hoptoglobins).

Steim, J. M., A. A. Benson, DERIVATIVE ACTIVATION CHROMATOGRAPHY, Anal. Biochem., 9, No. 1, 21-34 (1964).

Although most biologically important compounds do not contain atoms which produce a useful radionuclide by thermal neutron capture, activation analysis has been extended to these cases by the use of easily formed derivatives which do contain activatable atoms, such as bromine. Sensitive qualitative and quantitative analyses for mixtures of many compounds were obtained by paper chromatography of such derivatives, followed by neutron activation of the chromatograms in a nuclear reactor. p-Bromophenacyl esters of carboxylic acids, p-bromophenylsulfonamides of amino acids, p-bromophenylhydrazones of keto acids and sugars, and mercuriated fatty acids were separated and activated. Induced activities were located by radioautography and measured by appropriate detectors. Comparisons of radioactivities in separated compounds with those in suitable standards allowed quantitative estimations. The method is generally more sensitive than conventional chemical spray methods, and quantification is less troublesome.

Stempak, J. G., R. T. Ward, AN IMPROVED STAINING METHOD FOR ELECTRON MICROSCOPY, J. Cell Biol. 22, No. 3, 697-701, (1964)

A solution of uranyl acetate in methanol was used in staining tissue components for electron microscopy. This stain has several advantages. It stains in a shorter time than the aqueous stain, it yields an image with greater contrast and the increased contrast may be obtained more consistently and stain contamination is extremely small in amount or lacking altogether.

Strehler, B. L., J. R. Totter, DETERMINATION OF ATP AND RELATED COMPOUNDS: FIREFLY LUMINESCENCE AND OTHER METHODS, Methods of Biochem. Anal., V. I, p. 341-356, ed. by D. Glick, Interscience Publ., N. Y. (1954).

A discussion of the principles involved in various methods of ATP determination has been presented. While each method has advantages for certain problems, the firefly enzyme method not only offers a rapid and specific assay procedure for ATP, but also has certain advantages, in sensitivity, and in the fact that the basic elements of the apparatus and the enzyme necessary can be applied to many allied assays.

Tauber, L. F., CONCENTRATION OF SMALL VOLUMES OF BIOLOGICAL FLUIDS USING A MICRO-ULTRAFILTRATION APPARATUS, Am. J. Med. Technol., 30, 181-182 (1964).

A modified micro-ultrafiltration apparatus to handle small volumes of biological fluids was devised. This apparatus has made it possible not only to concentrate spinal fluid, urine, transudates, joint and serous cavity effusions for various analytical procedures, but also to remove excess fluid from fractions obtained by continous flow electrophoresis.

Van Kampen, E. J., NEW DEVELOPMENTS IN CLINICAL ANALYSIS, Anal. Chem., 205, 381-393 (1964).

The revolutionary development of clinical chemistry finds expression in the fact, that the total number of analyses doubles nearly every five years. The only solution of this problem is automation. Some examples of new developments in the fields of enzyme, protein and amino-acid chemistry are given. These few examples can be extended almost ad infinitum. It is clear however, that analytical chemical technique development goes hand in hand with modern instrumentation development. A short survey of some of the major points concerning spectrophotometry, gas chromatography and radioactive isotopes is given. Attention is finally drawn to a very important aspect of these new developments, which may easily be overlooked, namely standardization. A survey is given of the Dutch work on the standardization of haemoglobinometry (HiCN-method).

SECTION 2

AUTOMATIC TECHNIQUES

Bitner, E. D., H. J. Dutton, AUTOMATED MANOMETRIC APPARATUS, Amer. Oil Chem. Soc. J., 41, 720-723, (1964).

A manometric system has been developed for automatically performing hydrogenations, autoxidations and similar gas-liquid phase reactions. Incorporation of an ion chamber permits radioactive isotope experiments. Nonradioactive isotopes (such as deuterium and O^{18}) are monitored by attaching the apparatus to a mass spectrometer. Automatic recording of gas volume and radioactivity establishes a permanent record and allows unattended operation. Use of a servomotor-driven syringe eliminates all mercury, including mercury leveling bulbs. The flow-through construction of the syringe permits circulation of the gas phase and, as required in isotopic experiments, obviates the dead space inherent in classical manometers. Basic electronics and readily available components enhance operation and construction. Typical hydrogenations with accompanying graphs showing gas uptake, reaction time and radioactivity concentration illustrate the utility of the apparatus and the ease of collecting data.

Cadavid, N. G., A. C. Paladini, AUTOMATIC AMINO ACID ANALYSIS: REAGENT AND INSTRUMENTAL IMPROVEMENTS, Anal. Biochem., 9, 170-174 (1964).

A procedure for the automatic analysis of amino acids using the Auto-Analyzer apparatus in combination with a modified Rosen reagent is described. With the use of a narrow column (0.6 cm i.d.) it is possible to estimate 0.03 μ mole of a single amino acid with a standard deviation not higher than 5%. Amounts ten times less than the above lower limit can be detected.

Callahan, P. X., A STREAM DIVISION VALVE FOR USE IN AUTOMATIC COLUMN CHROMATOGRAPHY, J. Chromatog., 15, 1-4 (1964).

A stream division valve which allows the division of a column effluent for analysis and collection in automatic column chromatography is described. Details of the construction of this valve as well as the results obtained in using it are presented.

Catanzaro, E. W., SOME FUNDAMENTAL ASPECTS OF THE TECHNICON AUTOMATIC KJELDAHL ANALYZER...DIGESTION TECHNIQUES, Paper #23 presented at Technicon Internatl. Symposium on Automated Analytical Chemistry, Sept. 16-18, 1964, N.Y.

The effects of digestion temperature, media and catalysts in use of the Technicon automatic Kjeldahl analyzer have been investigated along with the associated phenomenon of nitrogen loss. Conditions have now been established whereby nitrogen loss is kept to a minimum and digestion efficiency is excellent.

Catravos, G. N., AN AUTOMATIC METHOD FOR SEPARATION, HYDROLYSIS AND DETECTION OF PEPTIDES, Paper #46 at the Technicon International Symposium on Automated Analytical Chemistry, Sept. 16-18, 1964, N.Y.

A method and apparatus has been developed for the separation and hydrolysis of peptides from enzymatic hydrolysates of proteins and subsequent continuous alkaline hydrolysis as the peptides are eluted from the chromatographic column. By comparing the ninhydrin peaks before and after hydrolysis one obtains a good idea of the size of the individual peptides.

Cooper, Daniel I., THE AUTOMATED LABORATORY, Int. Sci. and Tech., No. 36, 20-29 (1964).

The machines aren't publishing papers...yet. But in many laboratories rather complex experiments run themselves and data are taken and reduced automatically. In a few cases, computers decide on the optimum way to proceed in an experiment. Most commonly it is manipulation that is automated: machines do complicated wet-chemical analyses on large numbers of samples, or x-ray counters are positioned by serro controls in response to punched-tape instructions. The now familiar chart recorder has been supplemented by digital readout devices that speak to small computers which subtract backgrounds, calculate areas under peaks and otherwise reduce and analyze the raw data. The trend is to the use of computers, closely coupled to the experiment, to: (1) direct its progress, (2) analyze the data as they are taken, (3) display the data in the form most useful to the experimenter, (4) put alongside the data the predictions of theory. The general effect of laboratory automation is to make experimentation faster--by something like a factor of ten. This encourages more experiments, more complicated experiments, and, hopefully, better experiments.

Druzhinin, F. G., V. P. Mityanin, AUTOMATIC ANALYSIS OF BLAST-FURNACE GASES BY GAS CHROMATOGRAPHY, Ind. Lab., <u>30</u>, 663-664 (1964).

Gas chromatography has been used for automatic analysis of blast-furnace gas (CH_4, CO, H_2). Purified air was used as the carrier gas. A full automatic analysis takes 3 minutes.

Dwiggins, C. W. Jr., AUTOMATED DETERMINATION OF ELEMENTS IN ORGANIC SAMPLES USING X-RAY EMISSION SPECTROMETRY, Anal. Chem., <u>36</u>, 1577-1582 (1964).

New automated x-ray methods for determining elements in organic materials, including petroleum and petrochemicals, use both x-ray emission and scatter methods. Methods for matrix effect and background corrections suitable for automated analyses were investigated in detail. When possible, correction methods were based only on x-ray data, and more generalized methods capable of simplification for less complex analyses were developed. Specific analytical applications illustrate the utility of the direct and ashing methods for determining vanadium and nickel and direct methods for determining sulfur, carbon, and hydrogen. Direct-reading analyses for some of the more routine determinations were achieved. The use of the new correction methods and techniques speeds analyses and requires much less operator attention for both routine and special analyses.

Flannery, R. L., J. E. Steckel, SIMULTANEOUS DETERMINATION OF CALCIUM, POTASSIUM, MAGNESIUM AND PHOSPHORUS IN SOIL ELECTRODIALYZATES BY AUTO ANALYSIS, Paper #17, Tech. Internatl. Symposium on Automated Analytical Chemistry, Sept. 16-18, 1964, N. Y.

A satisfactory AutoAnalysis procedure was developed that permits quantitative determinations of Ca, K, Mg and P simultaneously in soil electrodialyzates at the rate of 40 samples per hour. This method permits the determination of these four elements in soil electrodialyzates within the following solution concentration ranges: Ca 2.5 to 150 ppm, K 0.5 to 25 ppm, Mg 0.5 to 10 ppm and P 0.10 to 4 ppm without preliminary concentration or dilution. The AutoAnalyzer results obtained for Ca, K, Mg and P agree very closely with Ca, K, and Mg results determined by atomic absorption method and P determined by manual method.

Holmström, B., C.-G. Hedén, FLEXIBILITY IN CULTIVATION EQUIPMENT. I. A SMALL-SCALE CONTINUOUS CULTURE APPARATUS FOR THE STUDY OF COMPLEX PROCESSES, Biotechnol. Bioeng., 6, 419-439 (1964).

A cultivation apparatus made up from six small (80-800 ml.) glass units with independent pH-, aeration-, and foam control is described. Exchangeable attachments made it possible to run the unit both batchwise and continuous and to connect up the units in various fashions.

Hoober, J. K., I. A. Bernstein, AUTOMATIC CONTINUOUS MONITORING OF ENZYMIC ACTIVITY IN COLUMN EFFLUENT, Anal. Biochem. 9, 467-473 (1964).

A procedure has been described using the flow system of analysis for continuous monitoring of enzymic activities in column effluents. The system exhibits a high degree of sensitivity. Greater than 90% of the enzyme in the effluent can be recovered for further use.

Jones, R. T., G. Weiss, LONG-PATH FLOW CELLS FOR AUTOMATIC AMINO ACID ANALYSIS, Anal. Biochem., 9, 377-382 (1964).

The sensitivity of a Spinco model 120 amino acid analyzer was increased up to 10-fold by use of photometer flow cells with path lengths longer than used by previous workers. No loss in quantitative accuracy or resolution of amino acids was observed.

Junge, H. D., A NEW TYPE OF AUTOMATIC TITRATING APPARATUS FOR OPERATING CONTROL, Chem. Tech, Berlin, 16, No. 6, 357-395 (1964).

A new method for automatic titration is described. Titration solution and the substance to be determined enter the mixing vessel through magnetic valves. Value of pH in the mixing vessel is measured by a glass electrode; this value is then amplified and controlled by magnetic valve relays in such a manner that the pH value fluctuates around a final point of titration. Certain values of two feed times during one switching period are taken as a measure of concentration of the material under investigation. Comparison of the feed times is achieved with a pneumatic RC member in such a way that the apparatus delivers a pneumatic output pressure which corresponds to the concentration of the substance under investigation. Patents for this method and apparatus are applied for in East Germany, West Germany, Czechoslovakia and Hungary.

Lee, S., D. McMullen, G. L. Brown, A. R. Stokes, METHODS FOR AUTOMATIC NUCLEOTIDE-SEQUENCE ANALYSIS. MULTICOMPONENT SPECTROPHOTOMETRIC ANALYSIS OF MIXTURES OF NUCLEIC ACID COMPONENTS BY A LEAST-SQUARES PROCEDURE, Biochem. J., 94, 314-322 (1965).

1. A theoretical analysis of the errors in multicomponent spectrophotometric analysis of nucleoside mixtures, by a least-squares procedure, has been made to obtain an expression for the error coefficient, relating the error in calculated concentration to the error in extinction measurements. 2. The error coefficients, which depend only on the 'library' of spectra used to fit the experimental curves, have been computed for a number of 'libraries' containing the following nucleosides found in s-RNA: adenosine, guanosine, cytidine, uridine, 5-ribosyluracil, 7-methylguanosine, 6-dimethylaminopurine riboside, 6-methylaminopurine riboside and thymine riboside. 3. The error coefficients have been used to determine the best conditions for maximum accuracy in the determination of the compositions of nucleoside mixtures. 4. Experimental determinations of the compositions of nucleoside mixtures have been made and the errors found to be consistent with those predicted by the theoretical analysis. 5. It has been demonstrated that, with certain precautions, the multicomponent spectrophotometric method described is suitable as a basis for automatic nucleotide-composition analysis of oligonucleotides containing nine nucleotides. Used in conjunction with continuous chromatography and flow chemical techniques, this method can be applied to the study of the sequence of s-RNA.

Lindley, G., APPARATUS FOR ROUTINE ANALYSIS. PART IV. CHROMATOGRAPHY COLUMN FEEDER, Lab. Practice, 9, 176-177 (1960).

A simple feeder which automatically supplies liquid to the top of a chromatography column bed is described. The feeder has been used for column work with cellulose powder, silica gel and ion exchange resins as well as in filtering large volumes of reagent solutions.

Maizel, J. V. Jr., PREPARATIVE ELECTROPHORESIS OF PROTEINS IN ACRYLAMIDE GELS, Ann. N.Y. Acad. Sci., 121, Art. 2, 382-390 (1964).

(1) A simple apparatus is described for adaption of the "disc" electrophoresis techniques to a preparative procedure that permits analytic and radioactive monitoring of the effluent fractions automatically.

(2) The efficiency of the procedure for separating a model system consisting of ribonuclease, trypsin, and chymotrypsin has been demonstrated. In addition, preliminary results concerning the separation of the unexpected multiple proteins of poliovirus are presented.

Naughten, M. A., H. N. Dentzis, A RAPID AUTOMATIC METHOD FOR THE ANALYSIS OF NUCLEOTIDES FROM RNA, Tech. Internatl. Symposium on Automated Analytical Chemistry, Sept. 16-18, 1964, N. Y.

The autophoresis machine (described in this paper) has been modified for the analysis of nucleotides and this suggests that any small molecular weight substance which is colored or has a UV absorption and, of course is electrophoretically mobile, can be analyzed in a similar manner.

Roubal, W. T., A. L. Tappel, AN AUTOMATED SEPHADEX COLUMN FOR THE SEPARATION AND MOLECULAR WEIGHT DETERMINATION OF PROTEINS, Anal. Biochem., 9, 211-216 (1964).

An automated column chromatographic apparatus is described for use in separation and measurement of soluble protein. A novel, easily constructed, leak-proof connector for capillary Teflon tubing is described. The relationship between retention volume and protein molecular weight is presented and an example of the determination of molecular weight by this relationship is shown.

Spratt, J. L., J. W. Ende, AUTOMATIC LIQUID DISPENSING APPARATUS, Anal. Chem. 36, 2223-2224 (1964).

An automatic liquid dispensing apparatus with contact surfaces of glass and teflon has been developed. Unattended operation can be performed by concurrent use of a fraction collector.

Starbuck, W. C., W. J. Steele, LARGE-SCALE NINHYDRIN RESERVOIR SYSTEM FOR AUTOMATIC AMINO ACID ANALYSIS, Anal. Biochem., 8, 325-327 (1964).

This paper deals with the description and operation of a large-scale ninhydrin system (a reservoir of 20 liters sufficient for 2½ months of continuous operation) employing constant nitrogen pressure without use of a hydrostatic system. Adaptation to commercial instruments costs about $100.

Stefanye, D., L. Spero, AUTOMATIC AMINO ACID ANALYSIS OF REPLICATE SAMPLES, Anal. Biochem., 8, 265-268, (1964).

This report describes a method for analyzing replicate samples of certain simple mixtures of amino acids automatically and simultaneously. The method has been used advantageously in the determination of C-terminal residues of proteins degraded with hydrozine by the method of Akabori *et al*.

Sterling, R. E., A. A. Wilcox, A. G. Ware, M. K. Umehara, AN AUTOMATED DETERMINATION OF ALKALINE PHOSPHATASE UTILIZING p-NITROPHENOL PHOSPHATE, Clin. Chem., 10, 1112-1116, (1964).

A technic is described for the automated determination of serum alkaline phosphatase. This method permits a production rate of 60 determinations per hour on 0.2 ml. of serum per determination. Calculations are simplified since no serum blank is required.

Sturgeon, P., D. T. McQuiston, A FULLY AUTOMATED SYSTEM FOR THE SIMULTANEOUS DETERMINATION OF WHOLE BLOOD RED CELL COUNT AND HEMOGLOBIN CONTENT, Paper #35, Technicon International Symposium on Automated Analytical Chemistry, Sept. 16-18, 1964, N. Y.

The AutoAnalyzer continuous flow instrument system has been adapted to test for hemoglobin and red count; it can be operated by one technician at the rate of forty samples per hour. These studies indicate that the system has relatively good precision, accuracy and reliability with normal bloods and most of those exhibiting quantitative and qualitative abnormalities. It should find a substantial field of application in routine blood counting, laboratory hematology and mass surveys for hematological abnormalities.

Večerek, B., L. Kolařík, AUTOMATION IN ANALYTICAL CHEMISTRY. AN AUTOMATIC REMOTE CONTROLLED APPARATUS FOR DOSING FLUIDS, Chem. Listy., 58, No. 8, 950 (1964).

An automatic device is described which is equipped with a remote control. This device has many other applications. It can be used as a separate dosing unit; in combination with elaborate analyzers; as titration device with visual or automatic control; in work with solutions without the access of air; in work with radioisotopes; for slow gradual addition of reagents; in combination with recording devices.

Zubkov, V. I., A DEVICE FOR AUTOMATIC SWITCHING OF MASS SPECTROMETER RANGES, Instr. Exper. Tech., March/April 1964, pp. 392-393.

The proposed device enables automatic recording of the mass spectrum over the entire range of the mass spectrometer. Devices previously designed record the mass spectrum only over one subrange.

SECTION 3

CALORIMETRY

Anonymous, METTLER COMBINES THERMAL ANALYSIS SYSTEMS, Chem. Eng. News, 71, No. 24, 52-53 (1964).

An instrument for simultaneous thermogravimetric analysis and differential thermal analysis has been developed by Mettler Instrument Corp. This instrument enables a user to make direct and exact comparison of the curves showing the extent of gain or loss in weight of a sample and the transformations involving energy changes.

Barrall II, E. M., R. S. Porter, J. F. Johnson, THERMAL EXPANSION APPARATUS FOR USE WITH DIFFERENTIAL THERMAL ANALYSIS EQUIPMENT, Anal. Chem., 36, No. 12, 2316-2318 (1964).

Auxiliary apparatus is described for use in conjunction with differential thermal analysis (DTA) instruments to measure thermal expansion of solids. By use of the temperature programmer, amplifiers, and recorder in DTA equipment, the necessary additional apparatus is minor. Sample expansion is mechanically and electrically amplified and recorded automatically with excellent accuracy. This instrument can determine coefficients of thermal expansion of solid samples over a wide temperature range. For polymers, it provides a measurement of both the glass transition temperature (T_g) and, through use of expansion coefficients above and below T_g, measurements of crystallinity in some cases. Considerably less effort is required to obtain results that are equivalent to dilatometric data than with previously reported methods.

Barrall II, E. M., R. S. Porter, J. F. Johnson, CALORIMETRIC STUDIES BY DIFFERENTIAL THERMAL ANALYSIS, Anal. Chem., 36, No. 11, 2172-2174, (1964).

A differential thermal analysis cell has been developed which permits precision calorimetry on polymer and inorganic samples irrespective of initial aggregation state. The apparatus is contrasted with differential thermal analysis cells of conventional design using centrally located thermocouples. Calorimetric errors which arise from changes in sample thermal conductivity are demonstrated to exist in cells of conventional design and to be almost totally removed by the new cell design. The effect of using the new cell is illustrated by tests on a polymer sample with two fusion points and on blends of ethylene and propylene polymers. The necessity of calibrating differential thermal analysis cells at more than one temperature for calorimetry is demonstrated.

Chesters, G., O. N. Allen, O. J. Attoe, DIFFERENTIAL THERMOGRAMS OF SELECTED ORGANIC ACIDS AND DERIVATIVES, Soil Sci. Soc. Amer. Proc., 23, 454-457 (1959).

Thirty-eight organic acids and derivatives were characterized by differential thermal analysis (DTA) employing free access of air. Each thermogram was readily distinguished from the others, inclusive of such closely related acids as fumaric and maleic (cis-trans isomers), and pyrogallic acid (1:2:3 trihydroxy-benzene) and phloroglucinol (1:3:5 trihydroxy-benzene). In general, the peaks were sharp and duplication of the thermograms was highly satisfactory. Although the mechanism involved was not clearly elucidated, the thermograms evidenced fundamental differences in molecular structure.

David, D. J., DETERMINATION OF SPECIFIC HEAT AND HEAT OF FUSION BY DIFFERENTIAL THERMAL ANALYSIS. STUDY OF THEORY AND OPERATING PARAMETERS, Anal. Chem., 36, No. 11, 2162-2166 (1964).

Utilization of differential thermal analysis under nearly equilibrium conditions permits the determination of heat of fusion and specific heat on a variety of inorganic and organic compounds from a single calibration of an easily handled material like tin. Variables such as sample size, heating rate, and sample state were studied for their effect upon the heat of fusion. These variables did not exhibit effects upon the results within the limits of error of the determination. The theory and equations underlying the specific heat determination are discussed and a practical method is presented which is applicable to a wide range of materials. The standard deviation at the 95% confidence level for the heat of fusion and specific heat was found to be 1.5 cal./gram and 0.02 cal./gram/°C., respectively.

Kolaion, J. H., P. F. Low, DETERMINATION OF UNFROZEN WATER IN MONTMORILLONITE PASTES, Soil Sci., 95, 376-384 (1963).

A calorimetric method was used to determine the unfrozen water in pastes of Li-, Na-, and K-montmorillonite at -5° and -15°C. As much as 55 per cent of the water remained unfrozen at -5° and as much as 45 per cent at -15°C. The unfrozen-water content was greatest in the Na-montmorillonite and least in the K-montmorillonite. Reasons, based on thermodynamic equations, were given for the lack of freezing. It was concluded that forces at the particle surfaces were a significant factor.

O'Neill, M. J., THE ANALYSIS OF A TEMPERATURE-CONTROLLED SCANNING CALORIMETER, Anal. Chem., 36, No. 7, 1238-1245 (1964).

The features of various types of scanning calorimeters are described and compared. It is shown that proportional temperature control of a sample-holding surface, with simultaneous measurement of the heat flow rate into or out of the sample, is a superior technique with respect to instrumental criteria such as analysis time and applicability to reversible and regenerative thermal phenomena. After an analysis of the performance of a temperature-controlled calorimeter with a sharp sample transition, such as fusion, it is further concluded that the small thermal source resistance inherent in such a system is ideally suited for the resolution of such phenomena. A figure of merit is derived, with which different instrument designs may be evaluated.

Sekiguchi, K., T. Yotsuyanogi, S. Mikami, STUDIES ON THE METHOD OF THERMAL ANALYSIS OF ORGANIC MEDICINALS. V. SEMI-MICRO APPARATUS FOR THE DIFFERENTIAL THERMAL ANALYSIS PERMITTING DIRECT OBSERVATION, Chem. & Phar. Bull. Tokyo, 12, No. 9, 994-1004 (1964).

A convenient DTA apparatus using two matched thermistors was designed and was easily and inexpensively constructed. Because of sensitivity of the thermistors for detecting temperature difference and of the advantage of the double cell consisting of a inner tube and a jacket, the sample size is much reduced even to a few milligrams. The arrangement of the cell is also effective for making the base line flatten. Another characteristic point of the apparatus is that it permits direct viewing of the sample during the course of measurement. Since it is often desirable to compare peaks in the DTA curve with visual changes, the arrangement is found very useful for the study of phase reactions of organic materials. Tests concerning the experimental conditions show that analysis can be performed with accuracy and reproducibility. Applications were done for the studies of thermal behaviors of ammonium nitrate, bromo-diethylacetylurea and α-bromoisovalerylurea. Direct transformation of ammonium nitrate from the modification of IV to II was occasionally noticed. It was also confirmed that there was clear correspondence between the fall and rise of the DTA curve of copper sulfate pentahydrate and the changes in color observed with eye.

As a general application of DTA, a simple method for evaluating the heat of transition was proposed. It is based on direct comparison of two peaks by conducting DTA with a mixture of the sample and the inert substance of known heat of transition. The heat of polymorphic transition of potassium nitrate at 128~129° was found to be 1.20 kcal./mol. by using benzoic acid as an internal standard. It is thought that the method will have wide application, especially to organic materials. Also discrimination of pyrabital from the corresponding mixture of aminopyrine and barbital was successfully done by DTA. The curve of the former shows two peaks which is due to the stable eutectic liquefaction and to melting, while that of the latter exhibits in addition to these peaks, one pair of endothermic and exothermic ones which is attributed to the metastable eutectic liquefaction and to the molecular compound formation, respectively. These results will suggest that DTA is generally applicable to the detection of molecular compound between organic medicinals.

Watson, E. S., M. J. O'Neill, J. Justin, N. Brenner, A DIFFERENTIAL SCANNING CALORIMETER FOR QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS, Anal. Chem., <u>36</u>, No. 7, 1233-1238 (1964).

An instrument for differential thermal analysis has been developed which directly measures the transition energy of the sample analyzed. The instrument performs thermal analyses of milligram level samples at high speeds (scan rates up to 80°C per minute) and in a temperature range of 173° to 773°K. (-100° to +500° C). Analytical data are recorded in a fashion graphically similar to that of traditional DTA, but peak amplitude directly represents millicalories per second of transition energy and peak area directly represents total transition energy in millicalories. Direct temperature marking is also displayed. Atmosphere control and vacuum operation are also provided. Samples may be run in closed-cup or open-cup configurations and are conveniently handled in powder or sheet form. Quantitative performance is independent of specific heat of sample, sample geometry, and temperature scanning rate. Qualitative information is equivalent or superior to conventional DTA in terms of speed, sensitivity, resolving power, and operational convenience. However, the principal innovation of the unit is the capability for direct, convenient, and precise quantitative measurement of transition energy.

SECTION 4

CARBON ANALYSIS

Eng, K. Y., R. A. Meyer, C. D. Bingham, DETERMINATION OF CARBON IN SODIUM BY ISOTOPE DILUTION MASS SPECTROMETRY, Anal. Chem., 36, No. 9, 1832-1834 (1964).

A method utilizing isotope dilution mass spectrometry has been developed for the determination of carbon in sodium. The details of the method are described for the determination of "elemental" carbon employing Van Slyke oxidation, although, by choice of spike material, other forms of carbon may be determined. Accuracy and precision in the ranges 50 ± 10 μg. to 150 ± 25 μg. of carbon have been demonstrated. The determination is not affected by loss of generated carbon dioxide or by contamination from any source except carbon.

Frazer, J. W., R. W. Crawford, THE HANDLING OF VOLATILE COMPOUNDS FOR THE SIMULTANEOUS DETERMINATION OF CARBON, HYDROGEN, AND NITROGEN, Mikrochim. Acta, No. 5, 676-678 (1964).

A technique is described, which permits obtaining the correct weight of a volatile substance, vapor pressure not exceeding four atmospheres at ambient temperature, previous to combustion in a vacuum system.

Kainz, G., F. Scheidl, COMBUSTION AT A JET, A VERY EFFICIENT OXIDATION METHOD FOR THE DETERMINATION OF CARBON, HYDROGEN, FLUORINE, CHLORIDE, BROMINE, IODINE, SULFUR, AND PHOSPHORUS IN ORGANIC COMPOUNDS, Mikrochim. Acta, No. 6, 998-1018 (1964). (In German)

The bases of combustion at a burner tip are elucidated. The reactions at the tip are related to the temperature of the tip, the dilution of the sample with the purging gas, to the heat of combustion of the sample, and to the dimensions of the space surrounding the tip. The oxygen fed in reacts completely during the actual combustion. The exchange at the tip is greater than in the "empty tube" under like conditions.

Combustion at the tip is suitable for determining the elements C, H, F, Cl, Br, I, S, and P. Supplementary priming gas (hydrogen) is necessary only for highly halogenated compounds with a halogen: carbon ratio ≥ 1. Priming gas is unnecessary with all other compounds. The determinations can be conducted with either micro- or semimicro amounts.

Lakemy, J., L. Lehar, M. Vecera, QUANTITATIVE ORGANIC ANALYSIS. XXXV. MICRODETERMINATION OF CARBON IN ORGANIC SUBSTANCES, USING A NEW CONDUCTIVITY CELL, Khimicheskykh. Rabot, 28, No. 12 (1963).

By using a new conductivity cell and a simple apparatus for the conductometric microdetermination of carbon in organic substances, the conditions for the automation of these determinations were established. The complete absorption of CO_2 even at high momentary concentrations permits flash combustion of the sample, and the rapid homogenization of the absorption solution permits carrying out a carbon determination in 15-20 minutes. The conductivity change caused by long-lasting fluctuations of the bath temperature was eliminated by means of an empirical factor. The accuracy of the determination was $s = \pm 0.19\%$ C.

Lewis, L. L., M. J. Nardozzi, A COMBUSTION, THERMAL-CONDUCTIVITY ANALYZER FOR CARBON IN STEEL, Anal. Chem., 36, No. 7, 1329-1331 (1964).

For carbon determinations, steel samples are burned in an induction furnace in which carbon is converted to carbon dioxide in a stream of oxygen. The gaseous mixture is swept from the furnace and through a molecular-sieve trap, which collects the carbon dioxide at ambient temperature. After all of the carbon dioxide has been collected, the trap is placed in an oxygen carrier-gas stream of a gas chromatograph and heated to desorb the carbon dioxide. The desorbed carbon dioxide then passes through a thermal-conductivity detector that gives an electrical signal, which indicates the carbon content of the sample. The analysis is complete 30 seconds after the end of the flush and combustion period, which requires 95 seconds. Data obtained on a group of different steels containing from 0.01 to 0.9% carbon showed a relative standard deviation of 2.5%, the maximum being 4.3%. The relative standard deviation at the 0.001% level was 10%.

Miller, C. D., J. D. Winefordner, AN EFFICIENT INSTRUMENTAL PROCEDURE FOR THE RAPID DETERMINATION OF CARBON AND HYDROGEN IN THE SUBMILLIGRAM RANGE, AND ITS EXTENSION TO THE DETERMINATION OF NITROGEN, Microchem. J., 8, No. 4, 334-348 (1964).

Details of an instrumental method providing an extremely rapid, efficient and economical means for the microdetermination of carbon and hydrogen are presented in this paper. Based upon a thermal conductivity detection of combustion and conversion products in an oxygen carrier gas, the system allows an analysis to be completed within 90 seconds after introduction of the sample, With slight modifications, a separate nitrogen analysis may be conducted in approximately 45 seconds.

Newman, D. G., C. Tomlinson, THE MICRODETERMINATION OF CARBON AND HYDROGEN IN ORGANOMETALLIC COMPOUNDS. I. ALKALI AND ALKALINE EARTH METAL COMPOUNDS, Mikrochim. Acta, 6, 1023-1028 (1964).

21 alkali and alkaline earth metal salts have been analysed with and without tungstic oxide to determine the influence of the latter and the significance of the residues formed without this additive. The usefulness of potassium persulphate as an additive is also discussed.

Oda, N., G. Tsuchihashi, S. Ono, NEW APPARATUS FOR RAPID DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC COMPOUNDS, Microchem. J., 8, 69-78 (1964).

A new and simple type of apparatus in which a sample is burned explosively is proposed for the rapid determination of carbon and hydrogen in organic compounds. The development of the apparatus has been achieved with a special construction of an inclined combustion tube attached with a sample-boat guide-tube, and connecting the absorption train by means of spherical ground-glass joints and a modified holder. The analytical procedure with this apparatus is extremely simple and rapid. A sample of 2-10 mg. is dropped into the combustion tube which has been heated at 800°-850°C and burned explosively. Combustion of the sample and the elimination of the resultant gas can be completed in 5 minutes at an oxygen flow-rate of 50 ml per minute. The total time required for an analysis is normally 20 minutes. This apparatus is applicable to the analysis of organic compounds containing halogen, sulfur, and nitrogen, as well as those that explode or sublimate. Accuracy of the analysis with this apparatus is comparable to that of conventional methods.

Pella, E., NEW COMBUSTION METHOD FOR THE CARBON HYDROGEN MICRO DETERMINATION, Mikrochim. Acta, No. 6, 943-953 (1964). (In German)

A method is described for the rapid, reliable and step-wise gasification of the sample in C-H-microdeterminations. It is likewise applicable for very volatile, easily inflammable or explosive substances. It is based on shielding the sample from the stream of oxygen during the pyrolysis by housing it in a quartz capsule that can be shifted from the outside. The combustion occurs automatically by means of a furnace that is advanced at a constant speed. Several sources of error are pointed out along with ways to overcome them.

Rittner, R. C., R. Culmo, RAPID MULTIPLE MICRODETERMINATION OF CARBON AND HYDROGEN, Mikrochim. Acta, No. 5, 631-640 (1964).

A technique has been developed for the simultaneous determination of carbon and hydrogen in at least four independent samples. A large-diameter furnace and small combustion tubes make it possible to position at least four combustion tubes in the furnace at one time. An operator can analyze eight samples in one hour (7½ minutes per analysis). The low cost of the apparatus and the relatively small amount of bench space needed make this technique especially advantageous for low-budget industrial, governmental, and academic laboratories.

Starr, R. I., C. W. Ross, A METHOD FOR DETERMINATION OF CARBON IN PLANT TISSUE, Anal. Biochem., 9, No. 2, 243-252 (1964).

The method of Baker et al. involving the Van Slyke Folch oxidation mixture for ^{14}C analysis was adapted for plant tissues. The reproducibility and precision of the method appear to be satisfactory.

West, D. L., DETERMINATION OF TOTAL CARBON IN WATER BY COMBUSTION-GAS CHROMATOGRAPHY, Anal. Chem., 36, No. 11, 2194-2195 (1964).

A method is described that allows determination of as low as 0.004 wt % carbon in a 10 µl. sample with adequate reliability for many applications. The analysis rate is about 10 to 12 samples per hour.

Young, J. L., M. R. Lindbeck, CARBON DETERMINATION IN SOILS AND ORGANIC MATERIALS WITH A HIGH-FREQUENCY INDUCTION FURNACE, Soil Sci. Soc. of Amer. Proc., 28, No. 3, 377-381,(1964).

Application of established procedures for determination of carbon (C) in metals yielded about 60 to 90% C recovery from soils and pure organics. Systematic instrument and procedural changes showed that low recovery was due to escape of pyrolysis products or other volatile organic materials. Complete C recovery from dry soils and pure organics was achieved by adaptations employing an internal quartz-enclosed graphite ignitor or an external auxiliary resistance furnace. The procedures also permit analysis of total C in residues from soil extracts or other solutions and for inorganic C and organic C in soils.

SECTION 5

CHROMATOGRAPHY

5.1 GENERAL

Arurdi, B., O. Samuelson, SUGAR SEPARATIONS ON ION EXCHANGE RESINS IN MIXTURE WITH CELITE, Anal. Chim. Acta, 31, No. 5, 462-466 (1964).

The chromatographic separation of sugars in ethanol-water solutions by means of anion-exchange resins can be improved markedly by using extremely fine resin particles. To avoid an excessively high pressure drop in the column when crushed resin particles are employed the resin can be used in mixture with Celite. Working at elevated temperature results in improved separations and a considerable saving of time.

Ayres, J. T., COLUMN CHROMATOGRAPHY WITH A POLYNITROSTYRENE RESIN STATIONARY PHASE, Anal. Chem., 36, No. 11, 2185-2186 (1964).

Preparation and use of a polynitrostyrene resin as chromatographic adsorbent for electron denor molecules is discussed. The resin is recommended as a stationary phase for fractionation of mixtures of such molecules as naphthalene, anthracene, pyrene, carbazoli, naphthylamine, aniline, transtilbene and dimethylphenol.

Badami, R. C., REVERSED PHASE PARTITION COLUMN CHROMATOGRAPHY: A METHOD FOR THE QUANTITATIVE ANALYSIS OF FATTY ACIDS, Chem. & Ind., No. 46, 1920-1921 (1964).

Reversed phase partition column chromatography is most useful for the separation and estimation of milligram quantities of fatty acids. No elaborate apparatus is required.

Barker, P. E., R. W. Boaz, J. L. Gregory, THE SEPARATION OF BIOLOGICAL MIXTURES BY A LIQUID-LIQUID CHROMATOGRAPHY COLUMN CONTAINING DIFFERENTIALLY PERMEABLE PARTITIONS, Biotechnol. Bioeng., 6, No. 2, 235-240 (1964).

The operation and construction of a liquid-liquid chromatography apparatus containing differentially permeable partitions is described. The method is of value for the separation of heat sensitive and nonvolatile solutes.

Bombaugh, K. J., J. N. Little, AN INVESTIGATION OF LIQUID-LIQUID CHROMATOGRAPHY WITH A RECORDING DETECTOR, J. Chromatog., 16, 47-54 (1964).

A liquid-liquid chromatography system patterned after the gas chromatography model was built and investigated. Liquid-liquid chromatography and gas-liquid chromatography were found to have many principles in common. Much of the gas chromatography instrument technology was applicable to liquid-liquid chromatography. The system built for this investigation afforded simplified operation and provided rapid separations which were not readily attainable by other methods. Although problems remain to be solved, the results warrant continued investigation. The subtle differences which separate the techniques were found to result from basic differences between gas-liquid equilibrium and liquid-liquid equilibrium. When properly treated, however, these differences may be used to advantage.

In the unitized system, water was shown to be a desirable stationary phase, particularly when working with surfactants. Both chromosorb and the polydextran Sephadex G-25 were found to be desirable solid supports. Multifunctional copolymers showed promise as stationary phases and warrant further investigation.

Brooks, A., CHROMATOGRAPHIC DATA PROCESSING, Paper #45 presented at Technicen International Symposium on Automated Analytical Chemistry, Sept. 16-18, 1964, N. Y.

This paper discusses various devices which eliminate the necessity for tedious and time consuming manual interpretation of chromatograms produced by automatic amino acid analyzers. A whole spectrum of devices from labor saving aids through semi-automatic systems to full automation is described.

Determann, H., CHROMATOGRAPHIC SEPARATIONS ON POROUS GELS, Angew. Chem. Intern. ed. Engl., 3, No. 9, 608-617 (1964).

Over the past few years, fractionation of mixtures of substances on the basis of differences in their molecular weights has become an important method in chemistry and biochemistry. A survey is given of the theory and practice of separations applying porous gels, and the multifarious uses of such gels are indicated.

Farmer, T. H. CHROMATOGRAPHY ON STARCH COLUMNS, J. Chromatog., 16, 264-265, (1964).

A starch column and .1N hydrochloric acid were used to quantitatively and easily resolve phenylalanine, tyrosine, tryptophan, monoiodotyrosine and diiodotyrosine. Other mixtures have also been separated by means of this system.

Flodin, P., J. D. Gregory, L. Rodén, SEPARATION OF ACIDIC OLIGOSACCHARIDES BY GEL FILTRATION, Anal. Biochem., 8, 424-433 (1964).

Gel filtration has been used for the separation of the acidic oligosaccharides obtained by testicular hyaluronidase treatment of hyaluronic acid and of chondroitin 4-sulfate. In each series, the four lower members have been isolated and characterized by analysis before and after reduction with sodium borohydride.

Funatsu, G., SEPARATION OF TRYPTIC PEPTIDES OF TOBACCO MOSAIC VIRUS AND STRAIN PROTEINS BY AN IMPROVED METHOD OF COLUMN CHROMATOGRAPHY, Biochem., 3, 1351-1355 (1964).

A chromatographic-elution schedule for the separation of peptides is described which gives reproducible patterns for a given mixture. The location of each peptide is affected in predictable manner by its net charge, content of tyrosine and phenylalanine residues, and chain length. The exact location of amino acid exchanges in mutants is facilitated by this procedure.

Giles, C. H., I. A. Easton, R. B. McKay, MECHANISM OF ADSORPTION OF CATIONIC DYES BY ALUMINA, AND A NOTE ON HEAT CHANGES IN SOLUTION ADSORPTION, J. Chem. Soc., 858, 4495-4503 (1964).

A range of cationic dyes has been applied to (alkaline) chromatographic alumina powder. The nature of the adsorption has been interpreted from the shape of the adsorption isotherms, the ease of desorption, the effect of temperature on the equilibrium, and the "coverage factor", i.e., the factor by which the maximum adsorption exceeds the theoretical value for a monolayer of flatwise close-packed molecules. In most cases adsorption occurs by ion exchange of ionic micelles of dye, giving coverage factors >unity and the dye is completely desorbable by water alone. Rhodamine 6GB, which has hydrogen-donor groups, is adsorbed edgewise in a vertically close-packed monolayer, and is not completely desorbed by water; it thus appears to be held to the surface by hydrogen bonds; another hydrogen-bonding solute, p-nitrophenol, is also not completely desorbable. The triphenylmethane dyes show anomalous effects with rise in temperature: the amount adsorbed increases considerably. As the temperature approaches b. p. a marked change in adsorption occurs: adsorption of monodisperse dye molecules, oriented edge-on, appears to replace adsorption of ionic dye micelles.

The heat change in solution adsorption in general is discussed. This can be exothermic, temperature-independent ("athermic"), or endothermic, and it is shown that the sign and magnitude of the change can depend upon the nature of association of the solute on adsorption.

Hjertén, S., THE PREPARATION OF AGAROSE SPHERES FOR CHROMATOGRAPHY OF MOLECULES AND PARTICLES, Biochim. Biophys. Acta, 79, No. 2, 393-398 (1964).

A method is described for preparation of spherical agarose or agar grains, to be used as bed material for chromatographic "sieving" of molecules and particles. Due to a comparatively great hardness of these grains, they give high flow rates even if they are made small in order to increase the resolving power of the column.

Hori, M., E. Konishi, CHROMATOGRAPHY OF NUCLEIC ACID COMPONENTS, J. Biochem., 56, 375-376 (1964).

Chromatographic separation of the common components of nucleic acids together with some other bases and nucleosides was achieved by modification of the method of Anderson, et al.

Innes, W. B., W. E. Bambrick, RAPID HYDROCARBON ANALYSIS BY CHROMATOGRAPHY AND CHEMICAL ABSORPTION, J. Gas Chromatog., 2, No. 10, 309-313 (1964).

A new chromatographic approach to the analysis of complex hydrocarbon mixtures containing different hydrocarbon classes is used for various complex samples. The method combines chemical absorption with chromatography and flame ionization detection in such a way that different hydrocarbon classes are separately recorded.

A variety of high surface area inorganic oxides as well as conventional supported absorbents are tried for column purposes using wet nitrogen as a carrier gas under various conditions and mercuric sulfate-sulfuric acid as an olefin absorber. Moisture is used to improve reproducibility and reduce tailing particularly with silica gel.

For rapid hydrocarbon analysis of device treated auto exhaust, silica gel is preferred for the C1 to C4 fraction while alkalized alumina serves well for analysis of C5 to C8's. Silica gel gives almost no isomer separation while alumina gives partial isomer separation.

Rapid and complete analysis of C1 to C5 hydrocarbons from catalytic cracking is achieved with a supported diisodecylphthalate column.

Janák, J., MULTI-DIMENSIONAL CHROMATOGRAPHY USING DIFFERENT DEVELOPING METHODS, J. Chromatog., 15, No. 1, 15-28 (1964).

A new multi-dimensional chromatographic technique is described. µg to mg quantities from the gas chromatogram are placed on the start-line of a thin layer of adsorbent or of a sheet of chromatographic paper, which is moved past the orifice of the gas chromatograph and then developed in the usual manner. Thus, separation of the materials is obtained by exploiting the two most extreme possibilities given by the existing chromatographic methods, viz. gas-liquid chromatography, which separates according to the relative volatility of compounds (in the direction of the time-axis along the start), and thin-layer chromatography or paper chromatography, which separate according to the type of the functional group (in the vertical direction). After the extraction of the separated materials from the thin-layer or paper, GLC, on a suitably selected stationary phase, may be repeated if necessary. The theory for separation and experimental details are given. Further possibilities are obtainable by programming the driving velocity of the plate (paper) which acts in the same manner as temperature programming of a GC column.

The method described was used successfully in the research on the composition of coal tar, but can be applied to other complex mixtures of compounds of different chemical character.

Janák, J., MULTI-DIMENSIONAL CHROMATOGRAPHY USING DIFFERENT DEVELOPING METHODS. II. MICROSCOPIC AND COLORIMETRIC INVESTIGATION OF COMPOUNDS SEPARATED BY GAS CHROMATOGRAPHY IN SUBMICRO-QUANTITIES, J. Chromatog., 16, No. 3, 494-501 (1964).

Many classical colorimetric and crystallographic methods can be applied to the identification of nano- to picogram quantities of compounds obtained after separation by gas chromatography, if the compounds are examined under a microscope.

Techniques of handling crystals are described. The method is useful for the investigation of capillary gas chromatographic effluents.

Kurozumi, T., M. Itoh, K. Shibata, CHROMATOGRAPHIC SEPARATION OF DIFFERENT SPECIES OF CELLS WITH ION EXCHANGE RESIN, Arch. Biochem. & Biophys., 109, No. 2, 241-247 (1965).

A technique to separate different species of cells chromatographically with anion exchange resins as the adsorbent was developed and applied to mixtures of several species of cells to examine the degree of separation. Resin granules adsorbing cells on the surface were placed on the top of a resin column without cells, and the elution of cells was made with salts (NaCl, sodium acetate, KI, or phosphates); the resin granules were stirred with a square rod inserted into the column in a cylindrical glass tube. The concentration gradient elution of mixed cells gave a separation pattern with peaks, each of a single species of cells. The separation was complete between baker's yeast and *Escherichia coli* or *Chlorella* cells, less satisfactory between baker's and wine yeast cells, and partial between baker's yeast and *Trigonopsis* cells. Rapidity in practicing the separation is one of the characteristics of this new technique, since the whole process of separation could be completed within an hour. The applicabilities of the technique for analysis or separation of mixed cells in suspension were discussed.

Laurent, T. C., E. P. Laurent, AN ELECTRICAL ANALOGY TO THE GEL FILTRATION PROCESS, J. Chromatog., 16, 89-98 (1964).

An electrical analog computer has been constructed to study the process of gel filtration. The gel phase is represented by a series of condensors and the liquid phase by one condensor connected to a wiper shaft which moves along the row of condensors. The time for diffusion equilibrium between the phases is regulated by a resistor. The elution curve for a solute can be simulated if the partition coefficient and the time factor for the equilibration of the substance between the gel and liquid phases are known.

Pfann, W. G., ZONE MELTING CONSIDERED AS A CHROMATOGRAPHIC SEPARATION TECHNIQUE, Anal. Chem., 36, 2231-2234 (1964).

Zone melting can be adapted to perform separations of the kind achieved in chromatography. A mixture of solutes is placed at a point in a long column of solid solvent, and molten zones are passed in one direction. The solutes separate into bands, each of which travels at a rate determined by the distribution coefficient of the solute. Idealized theory shows that the solute distribution in a band has the form of a modified Poisson distribution, and that the number of zone-passes required to separate two solutes depends only on the ratio of their distribution coefficients. Typically, some hundreds of zone-passes, and columns hundreds of zone-lengths long, are required. Since the permissible rate of zone-travel is relatively low, practical realization of zone chromatography requires techniques for producing very short and very closely-spaced molten zones.

Pressey, P., R. S. Allen, PAPER CHROMATOGRAPHY OF OLIGOGALACTURONIDES, J. Chromatog., 16, 248-251 (1964).

This paper describes the separation of oligogalacturonides with a degree of polymerization as high as 12. The relationship between chromatogram mobility and molecular size for this group of oligosaccharides is discussed.

Squire, P. G., A RELATIONSHIP BETWEEN THE MOLECULAR WEIGHTS OF MACROMOLECULES AND THEIR ELUTION VOLUMES BASED ON A MODEL FOR SEPHADEX GEL FILTRATION, Arch. Biochem. Biophys., 107, 471-478 (1964).

Equations relating the elution volume in Sephadex gel filtration to the molecular weight and the molecular radius of a given solute have been derived on the basis of a model in which the elements of volume available to solvent within the gel are approximated by a combination of cones, cylinders, and crevices. The equations are based on the assumption that the volume of liquid passing through the column between the application of a macromolecular solute and emergence of the solute in maximal concentration is equal to the volume within the Sephadex bed which is available to macromolecules of a given size. The volume which for steric reasons is unavailable to the macromolecular solute is explicitly described in terms of the model.

These equations are tested and two parameters are evaluated by means of data relating molecular weights and elution volumes taken from the literature. One of the parameters can also be evaluated from the ratio of the bed volume to the void volume. The good agreement between values calculated in these two ways provides support for the notion that the simple model is essentially equivalent to the Sephadex gel.

Molecular weights calculated from the elution volume by means of the equations derived here in most instances agree rather well with values calculated by conventional means. A few serious discrepancies in the data, however, suggest that caution be used in applying this or perhaps any other simple relationship between molecular weights and elution volume to the estimation of molecular weights.

Storeffer, J. E., T. E. Kersten, P. M. Krueger, A NEW METHOD FOR THE DETECTION OF SUBSTANCES SEPARATED BY LIQUID-CHROMATOGRAPHIC SYSTEMS, Biochim. Biophys. Acta, 93, 191-193 (1964).

The detector described here was developed as a modification of the hydrogen flame detection system of Haahti and Nikkari. It was found to have a sensitivity comparable to that of flame unization detectors in gas chromatography. The range of usefulness of this system is illustrated by the separation of a protein from an amino acid and a mucopolysaccharide from a monosaccharide.

Sunderwirth, S. G., G. G. Olson, G. Johnson, PAPER CHROMATOGRAPHY-ANTHRONE DETERMINATION OF SUGARS, J. Chromatog., 16, 176-180 (1964).

Mixtures of glucose, fructose and sucrose were successfully analyzed by a method employing separation on paper, elution and colorimetric determination with the anthrone reagent. Since the anthrone reagent is employed as the colorimetric reagent, prior hydrolysis of sucrose is not necessary. The method, which requires very simple apparatus, may be used for the rapid and accurate determination of sugars in plant materials.

Thomson, A. R., B. J. Miles, ION-EXCHANGE CHROMATOGRAPHY OF AMINO-ACIDS: IMPROVEMENTS IN THE SINGLE COLUMN SYSTEM, Nature, 203, 483-484 (1964).

Modification of the system of Pilz and Morris for the analyses of amino acids permits completion of chromatograms in a shorter time period.

Vining, L. C., W. A. Taber, ANALYSIS OF THE ENDOGENOUS SUGARS AND POLYOLS OF CLAVICEPS PURPUREA (FR.) TUL. BY CHROMATOGRAPHY ON ION EXCHANGE RESINS, Can. J. Microbiol., 10, 647-657 (1964).

A method has been developed for the quantitative analysis of sugars and polyols accumulated in the mycelium of fungi. The constituents of the neutral, water-soluble material extracted from the cells with hot water were separated as their borate complexes on a column of strongly basic anion exchange resin. Alternate fractions were analyzed for sugars and the rest for polyols. The separation of polyols on a sulphonic acid type of cation exchange resin was also examined.

Cultures of two strains of *Claviceps purpurea* grown on a variety of nutrient media always stored trehalose and mannitol in the mycelium. The accumulation of other carbohydrates depended upon the medium in which the fungus was grown and the strain used.

Welford, G. A., SUBMICROANALYSIS BY RADIOCHROMATOGRAPHY, Anal. Chem., 36, 2350 (1964).

S^{35} labeled sulfates, P^{32} labeled phosphates and improved radiometric techniques allowed achievement of sensitivities as low as 0.001 μg for Ca, Sr, Ba, Be and Zr.

Welford, G. A., E. L. Chiotis, THE PAPER CHROMATOGRAPHIC ISOLATION OF NUCLIDES IN AIR SAMPLES, Anal. Chim. Acta, 31, 378-381 (1964).

A method is outlined for the quantitative transfer of nuclides of strontium, barium, cerium, zirconium, lanthanum, yttrium, and niobium from solution to a paper for chromatographic separation. Carrier quantities of iron are precipitated as the hydroxide from a carbonate solution and filtered directly onto the chromatographic paper. A two-dimensional development is utilized to isolate the individual nuclides.

This separation procedure is applied to air dust samples containing nuclear debris. Radiometric determinations may be conveniently made by γ-spectrometric or conventional low-background β-measurements.

5.2 GAS CHROMATOGRAPHY

Bayer, E., R. Widder, GAS CHROMATOGRAPHIC DETERMINATION OF THE CARBONYL FORMS OF SUGARS, Anal. Chem., 36, 1452-1455 (1964).

The different isomeric forms of sugars in solution were investigated by formation of glycosides followed by methylation and chromatographic separation of methyl ethers. It was demonstrated that the seven-membered-ring septanose occurs in solutions of galactose. The question concerning the presence of carbonyl forms in equilibrium with ring isomers in solution was resolved by detecting 3.4% in the case of fructose, 0.7%, in galactose, and lesser quantities, (0.3%), in arabinose and glucose solutions.

Bentley, R., C. C. Sweeley, M. Makita, W. W. Wells, GAS CHROMATOGRAPHY OF SUGARS AND OTHER POLYHYDROXY COMPOUNDS, Biochem. Biophys. Res. Comm., 11, 14-18, (1963).

A major development of this work has been to extend the useful range of gas chromatography of carbohydrates from the present upper limit of disaccharides to tetrasaccharides and to complex glycosides such as phloridzin. It is expected that this method will be effective in the preparative gas chromatography of carbohydrates.

Beroza, M., R. Sarmiento, CARBON SKELETON CHROMATOGRAPHY USING HOT-WIRE THERMAL-CONDUCTIVITY DETECTION, Anal. Chem, 36, 1744-1750 (1964).

The catalytic apparatus previously used with a flame ionization gas chromatograph to determine the chemical structure of minute amounts of compounds has been modified for use with gas chromatographs having hot-wire thermal-conductivity detectors. Chromatograms of different types of compounds are presented. Peaks are usually sharp and well resolved. Sample size is between 0.05 and 2 µl. and the effect of varying sample size is illustrated. The modified apparatus produces enough product for spectral analysis, from which identifications made on the basis of retention time may be confirmed or denied. The effect of catalyst temperature on the yield of aromatics and cycloaliphatics from 6-membered carbocyclic structures was studied. With the catalyst temperature at 200°C. cycloaliphatics are favored; at 360°C. the aromatics predominate. Features of the apparatus design that contribute to maximum performance, advantages, and disadvantages of the flame ionization and katharometer catalytic units are discussed. The analysis is rapid and is as broadly applicable as the one previously advanced for use with flame ionization.

Cacace, F., LABELED ORGANICS IN GAS CHROMATOGRAPHY, Nucleonics, 19, 45-50 (1961).

Discusses general principles of gas chromatographic analysis as well as various techniques developed for gas chromatography of labeled substances.

Camin, D. L., R. W. King, S. D. Shawhan, CAPILLARY GAS CHROMATOGRAPHY USING MICROVOLUME THERMAL CONDUCTIVITY DETECTORS, Anal. Chem. 36, 1175-1178 (1964).

Two capillary chromatographs that utilize microvolume thermal conductivity detectors have been designed and constructed. Experience with these instruments has shown that such detectors are capable of producing a usable signal from as little as 10^{-10} gram of material, and have sufficiently low dead volume and rapid response to permit their use with 0.02-inch i.d. capillary columns. When used in a well designed capillary system for quantitative analysis, microvolume cells will, without prior calibration produce data that are within 10% of the true value. In addition, they are nondestructive and exhibit a response for materials that escape ionization detection. Examples of the practical application of these instruments for the separation of complex hydrocarbon mixtures demonstrate that thermal conductivity detectors can be used to construct simple, inexpensive and reliable capillary chromatographs that exhibit excellent operating characteristics at temperatures up to 250°C.

Cruickshank, P. A., J. C. Sheehan, GAS CHROMATOGRAPHIC ANALYSIS OF AMINO ACIDS AS N-TRIFLUOROACETYLAMINO ACID METHYL ESTERS, Anal. Chem., 36, 1191-1197 (1964).

Trifluoroacetylated amino acid methyl esters have been analyzed by gas liquid chromatography. Procedures for rapid esterification and acylation of individual or mixtures of amino acids have been developed for 21 naturally occurring amino acids. The derivatives were separated on a 2-foot stainless steel column packed with neopentyl glycol succinate coated on Gas Chrom P. Preparation of derivatives and chromatography has required approximately 2 hours. Determination of amino acid ratios in peptides as well as qualitative determination of amino acids in proteins has been demonstrated.

Dijkstra, A., C. C. M. Fabrie, G. Kateman, C. J. Lamboo, J. A. L. Thissen, A RECORDING CONDUCTOMETER FOR THE DETERMINATION OF SMALL AMOUNTS OF CARBON DIOXIDE AND ITS USE IN COMBINATION WITH THE COMBUSTION TECHNIQUE IN GAS CHROMATOGRAPHY, J. Gas Chromatog., 2, 180-183 (1964).

Detection of carbon dioxide formed upon oxidation of organic components in the effluent of a gas chromatographic column is carried out by absorbing carbon dioxide in sodium hydroxide and measuring the change in conductivity of the solution. A recording conductometer to be used with a four-electrode conductivity cell and a novel absorption vessel are described.

Esposito, G. G., QUANTITATIVE PYROLYTIC GAS CHROMATOGRAPHY BY INTERNAL STANDARD, Anal. Chem., 36, 2183-2185 (1964).

The primary objective of this investigation was to demonstrate the applicability of the internal standardization technique used with pyrolytic gas chromatography, for quantitative purposes, to the analysis of some coating materials. The technique and its accuracy are described and illustrated by application to the semiquantitative determination of some polymethacrylates and polystyrene in various coating systems and comparison is made to the total area method.

Giddings, J. C., THEORY OF GAS-SOLID CHROMATOGRAPHY. POTENTIAL FOR ANALYTICAL USE AND THE STUDY OF SURFACE KINETICS, Anal. Chem., 36, 1170-1174 (1964).

The theory of gas-solid chromatography in packed and capillary columns has been developed and discussed. Particular emphasis has been placed on expressing the important plate height coefficient, C_k, in terms of known parameters. The accommodation coefficient, α, a parameter which has often been measured in connection with surface studies, is used to express the rate of adsorptive-desorptive mass transfer. The theory shows that C_k is very small, the order of 10^{-7} second, for typical packed columns with uniform adsorptive sites. Nonuniform surfaces exhibit a C_k which is larger by a heterogeneity factor, σ. The equation for σ provides the first quantitative basis for the effects of nonuniformity, and indicates the energy difference between sites required for column deterioration. An examination of the analytical potential of gas-solid chromatography indicates real advantages in terms of column efficiency and high speed analysis. A great potential is shown to exist for enhancing selectivity by making use of the steric nature of the adsorption forces. Finally, gas-solid chromatography is shown to have a real potential for the measurement of surface kinetics.

Grant, D. W., AUTOMATIC CAPILLARY GAS CHROMATOGRAPHY AND SAMPLING OF DISTILLATION PRODUCTS, Anal. Chem., 36, 1519-1522 (1964).

An automatic sampling valve has been developed which, when inserted at a single point into a gas or vapor system, extracts small repeatable samples and transfers them to a capillary column gas chromatograph for analysis. Details of the valve and associated equipment are given together with results of laboratory tests with benzene, toluene, xylenes, pyridine, picoline, phenol, and cresols. Minor impurities in these products can be continuously determined during distillation and this is considered to be the main potential application of the apparatus. The valve has been successfully operated at temperatures of up to 200°C. and results are given for a vapor system at sub-atmospheric pressures. The limitations of the valve in the latter connection are demonstrated.

Groten, B., APPLICATION OF PYROLYSIS-GAS CHROMATOGRAPHY TO POLYMER CHARACTERIZATION, Anal. Chem., 36, 1206-1212 (1964).

Pyrolysis-gas chromatography has been applied to several phases of polymer analysis. Qualitative fingerprinting conditions have been defined so that a large number (>150) of polymers can be identified using essentially singular pyrolysis and chromatograph conditions. Quantitative analytical schemes have been devised for ester types in cellulosics, and for styrene content in SBR vulcanizates. Finally, the technique has been applied to the elucidation of polymer microstructure, where it is useful for differentiating blends from true copolymers of ethylene and propylene, and for indicating major differences in stereoregularity in polypropylene.

Halász, I., C. Horváth, POROUS LAYER GLASS BEAD COLUMN PACKING IN GAS ADSORPTION LAYER CHROMATOGRAPHY, Anal. Chem., 36, 2226-2229 (1964).

The applicability of porous layer glass beads (PLGB) coated with highly disperse ferric oxide or zirconium oxide and impregnated with triethylene glycol (TEG) will be demonstrated for the separation of aliphatic and aromatic hydrocarbons and of aliphatic compounds containing oxygen or halogens. Variation of the impregnating liquid-to-active solid ratio causes the absolute and relative retentions of the sample components to vary, also. The higher permeability and lower capacity ratio of these columns (compared to conventional packed columns) result in shorter analysis times. A detailed description of the preparation of these columns is given.

Hamilton, L. H., TWO-LOOP SAMPLING VALVE FOR USE IN GAS CHROMATOGRAPHY, J. Gas Chromatog., 2, 302-303 (1964).

A gas sampling valve has been designed which will permit either one or two sampling loops to be introduced into the carrier gas stream by operation of a single valve. It permits analysis of either small or large samples in any desired sequence.

Huber, J.F.K., A.I.M. Keulemans, POSSIBILITIES AND THE LIMITATIONS OF COMPOUND IDENTIFICATION ACCORDING TO THEIR BEHAVIOR AT ELUTION IN ISOTHERMAL GAS CHROMATOGRAPHY, Z. Analyt. Chem., 205, 263-273 (1964).

It is recommended to use partition coefficients for the identification of compounds and to determine these by a simple gas-chromatographic procedure, which allows the control of the measuring conditions.

This recommendation combines a relative method of measurement with the determination of absolute quantities. The accuracy of the measurement, which is decisive for the identification, was investigated and it was found that the accuracy in most cases will be limited by the resolving power of the column. For the evaluation of the results obtained with columns with different stationary phases a method was tested in which the partition coefficients measured on two different columns were combined. A table of partition coefficients of 80 hydrocarbons at 50,0°C on squalane and dinonylphthalate as stationary phases was compiled. On the basis of this table the identification of the C_5 - C_7 hydrocarbons in a crack product was carried out.

Jackson, R. B., GAS-LIQUID CHROMATOGRAPHY OF VOLATILE FATTY ACIDS FROM FORMIC ACID TO VALERIC ACID. I. CARBOXYLIC ACIDS AS STATIONARY PHASES, J. Chromatog., 16, 306-310 (1964).

The use of behenic acid and sebacic acid as liquid phases for the gas-liquid chromatography of C_1 to C_5 fatty acids has been described. Complete resolution of all normal and iso-acids was obtained on 122 cm columns containing sebacic acid as the liquid phase at 135°. With behenic acid as the liquid phase the separations of formic from acetic acid and isobutyric from n-butyric acid were not quite complete at 135°, however, complete separation was obtained at 115°. Both the behenic and sebacic acid columns showed satisfactory stability at 135°.

Karr, C., Jr., E. E. Childers, W. C. Warner, P. E. Estep, ANALYSIS OF AROMATIC HYDROCARBONS FROM PITCH OILS BY LIQUID CHROMATOGRAPHY ON GAS CHROMATOGRAPHY ANALOG, Anal. Chem., 36, 2105-2108 (1964).

Liquid chromatography on the gas chromatography analog has been demonstrated for the first time to be an effective method of analyzing complex natural mixtures of high boiling aromatic hydrocarbons, including the identification of individual constituents. Pitch oil fractions boiling in the range 290° to 315° C. were analyzed by this method and shown to contain about 70 components. Of these 11 were readily identified by relative retentions and by infrared and ultraviolet spectra. Those identified were dibenzofuran, fluorene, their various methyl derivatives, and phenanthrene. Many additional compounds were partially or tentatively identified. The method also proved to be convenient for purifying samples of compounds and determining their impurities.

Kilner, A. A., G. A. Ratcliff, DETERMINATION OF PERMANENT GASES DISSOLVED IN WATER BY GAS CHROMATOGRAPHY, Anal. Chem., 36, 1615-1623 (1964).

The method employs the technique of gas solid chromatography coupled with a heated precolumn in which the gases are liberated and the water absorbed. Developed principally for hydrogen, quantities of the order of 0.001 ml. can be determined with an accuracy of ± 3% from liquid samples of volume 0.2-0.3 ml. Helium may be determined under the same operational conditions while modifications can readily be made for the analysis of CO_2 and other gases.

Landheer, C. A., GAS CHROMATOGRAPHIC SEPARATION OF BROMO- AND CHLOROPYRIDINES, J. Chromatog., 16, 293-297 (1964).

A method is described for quantitative analysis of mixtures of mono- and dibromopyridines or mono- and dichloropyridines by gas chromatography.

The procedure consists of two subsequent chromatographic separations. In the first one a column containing tritolyl phosphate on Chromosorb is used; it enables the separation of all components except the 3- and 4-halogenopyridines which have the same retention volume. A second separation is carried out with a column containing a filling developed on the basis of an extract of the commercial detergent Tide, which gives an excellent analysis of the monohalogeno pyridines.

Locke, D.C., C.E. Meloan, GRADIENT LOADED COLUMNS IN GAS CHROMATOGRAPHY, Anal. Chem., 36, 2234-2243 (1964).

The use of gradient loaded columns in gas chromatography is a new technique involving the systematic variation of the partition ratio, k, during the course of an analysis by varying the liquid loading from the beginning to the end of the column. The case of a continuous linear decrease in k down the column is considered theoretically and experimentally. Equations are derived describing solute retention behavior, column efficiency, and solute resolution on columns with a linear gradient in k. Good agreement is obtained between the theoretical predictions and the experimental results on a 16-stage step-wise approximation to a continuous linear gradient column. For linear gradient columns, the partition ratio is reduced to 50% of that which it would be on a regular column of liquid loading corresponding to the initial k on the gradient column. Column efficiency is improved for solutes of low or intermediate partition ratio on the gradient column. The combination of these effects results in resolution of solutes of low retention which is superior to that which could be obtained on a regular column.

Lovelock, J. E., G. R. Shoemake, A. Zlatkis, IMPROVED IONIZATION CROSS-SECTION DETECTORS, Anal. Chem., 36, 1410-1415 (1964).

The ionization cross-section detector is recognized as one of the few unequivocal detection devices available for use in gas chromatography. The use of an integral pair ionization cross-section detector makes it possible to utilize the desirable characteristics associated with this detection method at reduced pressures, for programmed temperature and pressure (or flow programmed operation) without the accompanying deficiencies often encountered with other detection systems. A micro cross-section detector has been developed with a total volume of 8 µl. This cell is used to provide cross-section responses for components emerging from 0.01 inch diameter capillary chromatographic columns, thus extending the range of application of ionization cross section. The foregoing detectors are readily adaptable to the constraints imposed on a flight model chromatograph for interplanetary exploration. The value Q, the cross section for ionization for elements, can be experimentally determined and calculations applied that allow the determination of the mass of component represented by any chromatographic peak.

Lowry, R.L., SOLID SAMPLE INJECTOR FOR GAS LIQUID CHROMATOGRAPHY, Anal. Chem., 36, 1407-1408 (1964).

The basic components and assembly of a solid sample injector for gas liquid chromatography are described.

Merritt, C., Jr., J.T. Walsh, D.A. Forss, P. Angelini, S.M. Swift, WIDE-RANGE PROGRAMMED TEMPERATURE GAS CHROMATOGRAPHY IN THE SEPARATION OF VERY COMPLEX MIXTURES, Anal. Chem., 36, 1502-1508 (1964).

The range of programmed cryogenic temperature gas chromatography has been widened to include temperatures from -196° to over + 200°C. Various and variable rates of temperature rise may be employed and automatic programming can be provided. The necessity for employing very low starting temperatures for mixtures containing very volatile components is demonstrated, and an example of a separation of a mixture of compounds having a boiling range from -161° to +200°C. is given. The technique has been applied to the total analysis of the carbon dioxide, center cut, and water fractions of the volatile compounds from irradiated beef. The efficacy of the separations enhances the use of a rapid scanning mass spectrometer for identification of the components in the eluate.

Neto, C. C., J.T. Köffer, J. W. De Alencar, PROGRAMMED FLOW GAS CHROMATOGRAPHY, PART I, J. Chromatog., 15, 301-313 (1964).

The results obtained on programmed flow gas chromatography of a mixture of hydrocarbons are presented. The following relationships between various parameters and flow rate are discussed:

(1) Peak migration and flow rate of the mobile phase.
(2) Effect of flow rate on peak width, height and area.
(3) Effect of flow rate on efficiency and resolution.

Nikelly, J. G., GAS CHROMATOGRAPHY OF FREE FATTY ACIDS, Anal. Chem., 36, 2244-2248 (1964).

Most free fatty acid homologs and isomers from C_2 through C_{18} can be completely separated with little or no peak tailing on columns made with a polar liquid phase and an acidic additive coated on acid-washed glass microbeads. Washing the glass microbeads with dilute acid and using isophthalic acid in the liquid phase reduces or eliminates the adsorption and dimerization of the fatty acids. The columns can be operated isothermally or with temperature programming up to 180° to 190°C.

Parcher, J.F., P. Urone, AN IMPROVED SOLUTION COATING TECHNIQUE FOR GAS CHROMATOGRAPHIC SUPPORTS, J. Gas Chromatog., 2, 184-185 (1964).

An improved method of coating support particles for gas chromatography columns has been developed. Among the advantages cited are a better assurance of a uniform coating of the substrate on the support, a distinct saving in time and less fragmentation of the particles.

Park, K., G.H. Kennedy, H.H. Dobson, COMPARISON OF GAS CHROMATOGRAPHIC METHOD AND pH-ALKALINITY METHOD FOR DETERMINATION OF THE TOTAL CARBON DIOXIDE IN SEA WATER, Anal. Chem., 36, 1686 (1964).

The chromatographic method offers a direct and rapid means of determining total carbon dioxide in sea water. Reproducibility of the method was good with a relative standard deviation of ± 0.7% for five replicate determinations. The chromatographic method should prove more useful than the pH-alkalinity method in routine oceanographic, immunological and water pollution works.

Parsons, J. S., BRACKET METHOD FOR MOLECULAR WEIGHT DETERMINATION OF PYROLYSIS PRODUCTS USING GAS CHROMATOGRAPHY WITH A GAS DENSITY DETECTOR, Anal. Chem., 36, 1849-1852 (1964).

The Gew-Mac gas density detector has been investigated for molecular weight determination of certain volatile pyrolysis products from polymers as an aid in identifcation of these substances. By using several carrier gases, and in particular a carrier gas of higher molecular weight than the unknown substance and one of lower molecular weight, the molecular weight of the unknown may be bracketed with good accuracy.

Purnell, J. H., PHYSICAL MEASUREMENT BY GAS CHROMATOGRAPHY, Endeavor, p. 142-147, Sept. 1964.

Although gas chromatography is very widely used for analysis, few are aware of its potential value for physical measurement. Studies of column performance can yield information about solubility, adsorption, thermodynamic quantities, and diffusion. Specialized techniques permit measurement of solid surface areas, boiling points and vapour pressures, and, with developing understanding, the assignment of molecular structure. One of the attractive features of this particular technique is its technical simplicity and the rapidity with which information is obtained. The field is only just beginning to be explored, but already it shows great promise.

Richey, J.M., H. G. Richey, Jr., R. Schraer, QUANTITATIVE ANALYSIS OF CARBOHYDRATES USING GAS-LIQUID CHROMATOGRAPHY, Anal. Biochem., 9, 272-280 (1964).

Sugars can be analyzed quantitatively as their trimethylsilyl derivatives using gas-liquid chromatography. Standardization of polyethylene glycol succinate columns with α-methylgalactopyranoside as the standard gave a quantitative correlation between GLC relative peak areas and relative molar compositions of sugar standard solutions for: the pentose, ribose; the deoxyhexose, fucose; and the hexoses, glucose, galactose, and mannose. Quantitative data were also obtained for N-acetylamino sugars. Mixtures of sugars were analyzed by using the standardization graphs, and the amounts determined were accurate within 10%. This use of GLC will make it easier for the biochemist to attack problems in carbohydrate chemistry be enabling quantitative work to be done readily on mixtures heretofore difficult to analyze.

Roesler, J.F., PRELIMINARY STUDY OF CHARACTERISTICS OF PHOTOIONIZATION DETECTOR FOR GAS CHROMATOGRAPHY, Anal. Chem., 36, 1900-1903 (1964).

A photoionization detector was constructed utilizing Kovar metal seals. The glow current was regulated achieving a noise level on the order of 70 μμa. The effects of carrier gas and argon flow rate were observed. Nitrogen and hydrogen were the primary carrier gases used. An extra electrode was incorporated into the detector in an effort to control the standing current. Polarities with respect to the glow discharge were important, affecting the sensitivity and linearity. Thermal effects of the glow discharge were also investigated. A 4.9-cc. sample of 2.8 p.p.m. propane in nitrogen gave a maximum response of 660 μμa.

Rooney, T.B., W. Aznavourian, MINIMIZING TIME FOR GAS CHROMATOGRAPHIC ANALYSIS OF COMPLEX MIXTURES, Anal. Chem. 36, 2112-2115 (1964).

Several authors have presented methods for minimizing the time required for the chromatographic separation of two components. In applying these methods to more complex mixtures, it has been assumed that the resolution of a particular pair of components will determine the length of column regardless of analysis conditions. In the situation where the pair of components that is most difficult to resolve depends on analysis conditions, these methods may be impossible to apply. The use of a digital computer search technique overcomes this basic problem. At the same time, it makes feasible the use of more complex refinements of chromatographic theory. This paper presents the theory behind the digital search method, along with an example of the application of this method to the analysis of complex mixtures.

Schneider, W., H. Bruderreck, I. Halász, GAS CHROMATOGRAPHIC SEPARATION OF HYDROCARBONS (C_1 to C_8) BY CARBON NUMBER USING PACKED CAPILLARY COLUMNS, Anal. Chem., 36, 1533-1540 (1964).

Capillary columns were packed with graphited carbon black and impregnated with about 0.4 wt.% of squalane. The order of the retention volumes of hydrocarbons in the C_1 to C_8 range corresponds, with a few exceptions only, to the number of carbon atoms in the molecules. Retentions relative to n-pentane on nonimpregnated and impregnated graphited carbon black are tabulated.

Sweeley, C.C., B. Walker, DETERMINATION OF CARBOHYDRATES IN GLYCOLIPIDES AND GANGLIOSIDES BY GAS CHROMATOGRAPHY, Anal. Chem., 36, 1461-1465 (1964).

Simultaneous gas chromatographic determinations were made of glucose, galactose, galactosamine, and sialic acid in neutral glycolipides and gangliosides. Methanolysis in dry, dilute methanolic HCl was used to convert the oligosaccharide portion of the glycolipides to monomeric carbohydrates. Hexoses were converted to methyl glycosides, N-acetylhexosamine was partially converted to hexosamine hydrochloride, and sialic acid gave the 2-O-methyl ketal of methyl neuraminate. Separate procedures were used to convert these products of methanolysis to trimethylsilyl derivatives for gas chromatography. Samples of sialolactose and ceramidetrihexoside were used to validate the procedures for determination of hexose and neuraminic acid. Reproducible determinations of these components were made with a relative error of ± 5%. Problems were encountered in the quantitative determination of hexosamine by gas chromatography. Several alternative methods are given, and possible explanations for the difficulties are discussed.

Tadmor, J., APPLICATIONS OF ISOTOPIC EXCHANGE IN GAS CHROMATOGRAPHY, Anal. Chem., 36, 1565-1573 (1964).

Isotopic exchange in gas chromatography was studied and applied to labelling of inorganic compounds, analytical determination of inorganic compounds separated by gas chromatography, and a study of the interaction between the solid stationary phase and the solute in gas liquid chromatography. By gas chromatography isotopic exchange, the use of a radioactivity detector is made possible, without the introduction of radioactive metal compounds as starting materials. $GeCl_4$, $SnCl_4$, $AsCl_3$, and $FeCl_3$ were labelled and determined by using Cl^{36} labelled Sil-O-Cel as the solid stationary phase. Gas liquid chromatography experiments showed that even after coating the radioisotope labelled solid stationary phase with a thin liquid layer, isotope exchange still occurs between the Cl^{36} sorbed on the solid phase and the gaseous inorganic compound sample, indicating that the solid support is not always inert. For a given surface area of the solid support both the isotopic exchange and the number of theoretical plates increase with the decrease of its specific porosity and tortuosity coefficient. More highly polar liquids reduced the isotopic exchange to a greater extent than liquids of low polarity.

Tamura, Z., T. Imanari, GAS CHROMATOGRAPHY OF O-GLUCURONIDES, Chem. Pharm. Bull., 12, 1386-1388 (1964).

This paper deals with microscale preparation and gas chromatographic examination of some volatile glucuronide derivatives.

Teranishi, R., R.G. Buttery, W. H. McFadden, T.R. Mon, J.Wasserman, CAPILLARY COLUMN EFFICIENCIES IN GAS CHROMATOGRAPHY-MASS SPECTRAL ANALYSES, Anal. Chem., 36, 1509-1512 (1964).

Column efficiencies have been calculated with n-hexanol, n-amyl acetate, n-octanal, and limonene, and results show no significant loss in efficiency by operating one end of the capillary column under mass spectrometer vacuum. Optimum efficiency for the compounds examined and for the columns used is achieved at a linear velocity of 15 cm. per second under vacuum or at atmospheric pressure. Operating temperature range and extent of stationary liquid phase bleed from several liquids coated on stainless steel capillary columns have been examined with hydrogen flame ionization detector and with a fast-scan mass spectrometer. Limitations of the various stationary phases for combined mass spectral-GLC analysis at 200°C. are discussed.

Teranishi, R., R.G. Buttery, T.R. Mon, DIRECT VAPOR ANALYSES WITH GAS CHROMATOGRAPHY, Ann. N.Y. Acad. Sci., July 30, 1964, 116, 583-589, Art. #2.

This report discusses some of the problems encountered in detecting and recording food volatiles, the parameters which must be considered in order to utilize the sensitivity possible with the ionization detectors and some examples of direct vapor sampling analyses.

Urbach, G., ION EXCHANGERS FOR GAS SOLID CHROMATOGRAPHY, Anal. Chem., 36, 2368 (1964).

The potential value of ion exchangers in gas solid chromatography was briefly investigated. By modifying the ion exchanger it was possible with this technique to separate compounds of higher bioling point than those hitherto susceptible to gas solid chromatography.

Vanden Heuvel, W.J.A., W. L. Gardner, E.C. Horning, CHARACTERIZATION AND SEPARATION OF AMINES BY GAS CHROMATOGRAPHY, Anal. Chem., 36, 1550-1559 (1964).

The separation, identification, and estimation of biologically important amines by gas chromatographic methods presents a number of unresolved problems. The use of appropriate derivatives and selective stationary phases permits a wide choice of conditions which may be used to increase or decrease volatility of the compounds under study, and to improve both separation patterns and the quantitative aspects of analytical separations. These experimental variables have been less thoroughly investigated for amines than for many other substances. Accordingly, a study was carried out of several groups of amines as model substances with different kinds of structure (long chain and alicyclic monoamines, aliphatic diamines, and aromatic amines) with the aim of obtaining basic information which might be used in biochemical separation problems. At the same time, observations were made with respect to relationships between gas chromatographic behavior and the structure of amines and their derivatives.

Wells, W.W., T. Chin, B. Weber, QUANTITATIVE ANALYSIS OF SERUM AND URINE SUGARS BY GAS CHROMATOGRAPHY, Clin. Chim. Acta, 10, 352-359 (1964).

A method for the quantitative determination of serum and urinary sugars by gas-liquid chromatography of their trimethylsilyl ethers is described. The method is fast, sensitive and like the glucose oxidase method emphasizes the absolute values since non-sugar reducing substances can be distinguished. Sugars other than glucose may be determined conveniently, e.g., galactose, mannitol, fructose, inositol, pentoses, etc. An example of a mannitol clearance test is presented illustrating the ease of analysis. Agreement between gas chromatography and a glucose oxidase method for 15 random serum samples was satisfactory. Average recovery of added glucose for 10 samples was 97.1%.

Wilson, R. H., BIOLOGIC APPLICATION OF GAS CHROMATOGRAPHY, J. Gas Chromatog. 2, 365-373 (1964).

A gas chromatographic method is presented for resolving mixtures of inert and chemically active biologic and experimental gases in solution in the body fluids of experimental animals and human beings. The technique is applicable to any chemically combined mixture of dissolved gases in blood and body fluids of animals, seawater or any other gas being in solution in sufficient quantities to be detected, and recorded by the gas chromatographic apparatus being used at the time of the analysis.

Yajima, S., K. Shiba, M. Handa, Y. Takahashi, THE DETERMINATION OF WATER BY GAS CHROMATOGRAPHY, Bull. Chem. Soc. Japan, 37, 800-804 (1964).

The authors used lithium aluminum hydride to reduce water to hydrogen and developed a method for determining the amount of water by gas chromatography. By this method they could determine water in amounts as small as 0.1 ug in 10 ml of a gas sample with a high degree of accuracy.

Yamakawa, T., N. Ueta, GAS-LIQUID CHROMATOGRAPHY OF CARBOHYDRATES, Japan J. Exptl. Med., 34, 37-51 (1964).

To get the most suitable condition for the gaschromatographic separation of carbohydrate derivatives, several fundamental experiments were carried out be various combinations of solid supports and liquid stationary phases. Polar stationary phases on celite-type supports were found to give generally good results. Clear separations could be obtained by capillary columns in some cases. Sweeley's trimethylsilylation procedure was slightly modified and applied to the determination of ratios of glucose and galactose in several glycolipids. Furthermore, using this technique, a minute amount of monosaccharide was accurately detected in several examples.

5.3 THIN LAYER CHROMATOGRAPHY

Bancher, E., H. Scherz, K. Kaindl, THIN LAYER CHROMATOGRAPHY OF CARBOHYDRATES, Mikrochim. Acta, 6, 1043-1051 (1964). (In German)

A description is given of the separation by means of thin layer chromatography of lower hydroxy-oxo compounds, which occur as degradation products of carbohydrates, from sugar acids and their lactones as well as sugar osazones. A new arrangement is given for improving the elution technique, and it also makes possible an increased sensitivity in the identification.

Crépy, O., O. Judas, B. Lachese, METHODS FOR THE DETECTION OF CONJUGATED STEROIDS IN THIN LAYER CHROMATOGRAMS, J. Chromatog., 16, 340-344, (1964). (In French)

Two procedures for the detection of conjugated steroids on thin-layer chromatograms are described. In the first, pyridyl-azonaphthol is used to reveal glucosiduronates, and in the second methylene blue reagent for sulphates. The application of these reagents to the chromatographic separation of the glucosiduronates of 5α- and 5β-pregnan-3α-yl-20α-ols and 5α- and 5β-pregnan-3α-yl-20-ones, as well as to that of five C_{19} sulphates, is discussed.

Frodyma, M.M., R. W. Frei, THE DETERMINATION BY REFLECTANCE SPECTROPHOTOMETRY OF AMINO ACIDS RESOLVED ON THIN LAYER PLATES, J. Chromatog. 15, 501-509 (1964).

A procedure was devised whereby amino acids resolved on chromatoplates can be determined by spectral reflectance. Direct examination of plates yielded a degree of precision comparable to that afforded by direct transmission methods applied to paper chromatography. Precision approaching that afforded by transmittance is attained if the reflectance measurements are carried out on spots removed from the plates and specified precautions are observed in the generation of the ninhydrin color.

Kaiser, R., DIRECT AND AUTOMATIC COUPLING OF THIN LAYER CHROMATOGRAPHY TO GAS CHROMATOGRAPHY, Z. Anal. Chem., 205, 284-297 (1964). (In German)

Direct coupling of gas chromatography (GC) with thin-layer chromatography (TLC) offers new possibilities in qualitative analysis of high boiling polar substances. Direct coupling of GC with TLC controls as separating method in preparative scale and for infrared, ultraviolet nmr or mass-spectrometric identification of gc-separated substances direct coupling seems to be a new analytical quality.

Koller, A., H. Neukom, DETECTION OF OLIGOGALACTURONIC ACIDS BY THIN-LAYER CHROMATOGRAPHY, Biochim. Biophys. Acta, 83, 366-367 (1964).

Thin-layer chromatography has been successfully applied for the detection and separation of galacturonic acid oligomers in enzyme digests of pectin.

Morris, C.J.O.R., THIN-LAYER CHROMATOGRAPHY OF PROTEINS ON SEPHADEX G-100 and G-200, J. Chromatog., 16, 167-175 (1964).

1. A detailed description is given of a technique for the thin-layer chromatography of 1-20 μg amounts of proteins on the cross-linked gel filtration media Sephadex G-100 and G-200.
2. A close correlation has been obtained between the results of the chromatography of twelve test proteins on chromatographic columns and on thin-layer plates.
3. The relation between the molecular weights of proteins and their behaviour on Sephadex gels is discussed and a method for the estimation of protein molecular weights from the results of thin-layer chromatography is derived.

Pollard, F. H., G. Nickless, T. J. Samuelson, R. G. Anderson, THIN FILM CHROMATOGRAPHY OF SOME AZO-DYESTUFFS, J. Chromatog., 16, 231-233, (1964).

Thin film chromatography was found to be the most useful method to check the purity of azo-dyestuffs used in an investigation of metal complexes of these compounds.

Rai, H., G. F. Lee, SEPARATION OF PLANKTONIC ALGAE PIGMENTS BY THIN LAYER CHROMATOGRAPHY, Anal. Chem. 36, 2208-2209 (1964).

This paper describes the separation of the chloroplast pigments of algae in thin layers of powdered cellulose.

Rouser, G., C. Galli, E. Lieber, M.L. Blank, O.S. Privett, ANALYTICAL FRACTIONATION OF COMPLEX LIPID MIXTURES: DEAE CELLULOSE COLUMN CHROMATOGRAPHY COMBINED WITH QUANTITATIVE THIN LAYER CHROMATOGRAPHY, J. Am. Oil Chem. Soc., 41, 836-840 (1964).

A quantitative chromatographic procedure for the fractionation of complex lipid mixtures is described. The method utilizes diethylaminoethyl (DEAE) cellulose column chromatography followed by thin layer chromatography (TLC). Spots produced in TLC are charred with sulfuric acid-potassium dichromate and heat and are then measured by quantitative densitometry. Results obtained with beef brain and beef heart mitochondrial lipids are presented, and the close correspondence between column isolation procedures and the new procedure is demonstrated. Methods utilizing only column chromatography, column chromatography and TLC, and one- and two-dimensional TLC without column chromatography are compared.

Russel, J.H., THIN LAYER CHROMATOGRAPHY, Rev. Pure Appl. Chem., 13, 15-29 (1963).

This paper discusses various aspects of thin layer chromatography including the historical development of this technique, selection of solvent and adsorbent, types of development used as well as the reproducibility of the method.

Samuel, D., I. Wasserman, THIN LAYER CHROMATOGRAPHIC SEPARATION AND ANALYSIS OF O^{18}-LABELED COMPOUNDS, Anal. Biochem., 9, 246-249 (1964).

It was found that mixtures of O^{18}-labeled compounds can be very satisfactorily separated in thin-layer chromatography using silica gel. The separation of mixtures of two amino acids and of two steroids are given as examples. The method can obviously be extended to many other system in which thin-layer chromatography can be used.

Simonianova, E., M. Rybak, THIN-LAYER CHROMATOGRAPHY OF PROTEINS ON PHOSPHOCELLULOSE, Biochim. Biophys. Acta, 93, 194-196 (1964).

Serum proteins were separated on a thin layer of phosphocellulose.

Snavely, M. K., J.G. Grasselli, THE USE OF THIN-LAYER CHROMATOGRAPHY WITH INFRARED SPECTROSCOPY, Developments in Applied Spectroscopy, ed. by J. E. Forrette and E. Lanterman, Plenum Press, N.Y. 3, 119-141 (1964)

Thin-layer chromatography is a fast and economical way of separating mixtures of non-volatile liquids or solids. It requires only a small amount of sample and is applicable to problems in diversified fields. It serves as a useful complement to column and paper chromatography, and, like these methods, it requires some other analytical tool for positive identification of the separated components. In this work infrared spectroscopy has been used with thin-layer chromatography to analyze synthetic mixtures, organic reaction products, and commercial samples. Several techniques for obtaining IR spectra from the thin-layer spots will be described, and special methods of preparing the thin-layer plates will be recommended. The combined use of these two tools holds unique advantages and is certain to be employed even more frequently in the analytical and research laboratories.

Snyder, F., RADIOASSAY OF THIN-LAYER CHROMATOGRAMS: A HIGH-RESOLUTION ZONAL SCRAPER FOR QUANTITATIVE C^{14} AND H^3 SCANNING OF THIN-LAYER CHROMATOGRAMS, Anal. Biochem., 9, 183-196 (1964).

1. Construction of a high-resolution zonal scraper for rapid and quantitative transfer of small zones (1-, 2-, and 5-mm) of adsorbent from narrow glass plates (2 cm wide) into counting vials for liquid scintillation radioassay has been described in detail. Zonal scans made with this scraper are shown for thin-layer chromatograms of an impure tripalmitin-C^{14}OOH sample and of a total lipid extract of C^{14}-lipids from rat bone marrow.

2. The scintillation solvent system described (dioxane-water-naphthalene) deactivates silica, thereby preventing adsorption on particles of silica and self-absorption loss of many polar radioactive compounds. It has been shown that silica, iodine, dichlorofluorescein, and rhodamine 6G have no quenching properties in this system, whereas elemental carbon (H_2SO_4 charring) causes severe quenching.

Stahl, E., GRADIENT AND LOW-TEMPERATURE THIN-LAYER CHROMATOGRAPHY, Angew. Chem. (Int. Ed.), 3, 784-790 (1964).

The preparation and the use of gradient layers for thin-layer chromatography are described. On a gradient layer there are three flow surfaces, all differing in their separation behavior. It is therefore possible to determine, for example, the basicity and/or activity which gives the optimum separation for a mixture of substances. Gradient thin-layer chromatography was also carried out at low temperatures, after the effect of temperature on the separation of various mixtures had been studied.

Wilde, P. F., THE DESAGA SCANNER: A NEW SCANNER FOR RADIOACTIVE SUBSTANCES ON THIN-LAYER CHROMATOGRAMS, Laboratory Practice, 13, 741-745 (1964).

The new Desaga Scanner for the detection of radioactive substances on thin layer chromatograms is discussed, together with some results obtained under laboratory conditions.

SECTION 6

COMPUTER APPLICATIONS

Abel, K., APPLICATION OF AN ANALOG COMPUTER IN ANALYTICAL CHROMATOGRAPHIC AND ELECTROPHORETIC SEPARATIONS, Anal. Chem., 36, 1855-1856 (1964).

When two or more components of a mixture can be separated sufficiently to provide indication that more than one component is present but the resolution is insufficient for accurate determinations of either retention times (or migration distances) or percentage composition, the system can be resolved by computer techniques. The use of a relatively simple and inexpensive analog computer developed for this application is discussed.

Bradley, D. F., C. R. Merril, M. B. Shapiro, RECONSTRUCTION OF PROTEIN AND NUCLEIC ACID SEQUENCES. I. SYSTEMATICS AND COMPUTER PROGRAM, Biopolymers, 2, 415-444 (1964).

The protein sequences now known have been reconstructed as a kind of intriguing logical-mathematical puzzle using information about fragments of the molecules. We wish to show that the reconstruction can be done systematically by repeating a series of elementary operations on these same data governed by a set of well-defined rules. The completely automatic reconstruction of polymer sequences by a high speed digital computer using these operations and rules is demonstrated.

Carroll, R. F., DIGITAL COMPUTER CONTROL OF A CHEMICAL PROCESS, The 4th National Pulp and Paper Instrumentation Symposium, Memphis, Tenn., May 8-10, 1963.

This paper describes in brief the B. F. Goodrich Chemical Company's computer controlled plant at Calvert City, Kentucky which produces vinyl chloride. It was found that computer control provided smoother and more efficient operation at considerable savings.

Ledley, R. S., HIGH-SPEED AUTOMATIC ANALYSIS OF BIOMEDICAL PICTURES, Science, 146, 216-223, (1964).

Outlines use of digital computer for the quantitative analysis of photomicrographs, electron micrographs and X-ray diffraction patterns.

Montigny, P., APPLICATION OF ELECTRONIC COMPUTERS TO THE DETERMINATION OF THE TRUE OPTICAL DENSITIES AND TRUE BAND WIDTHS IN INFRARED SPECTROMETRY, Spectrochim. Acta, 20, 1373-1386 (1964). (In French)

The aim of this paper is to study, with the help of electronic computers, the relations between maximum true optical densities $(D_o)_{vrai}$ and true widths B_{vrai} of infra-red absorption bands on one hand, maximum apparent optical densities $(D_o)_{app}$ and apparent widths B_{app} on the other hand, when some laws (Lorentz function; triangular slit function) are assumed to be valid.

They at first explain the mathematical methods used for this purpose. They then give the results obtained in the range $0 \leq s/B_{app} \leq 0{\cdot}95$ and $0 \leq (D_o)_{app} \leq 1$ (s = spectral slit width), paying particular attention to the slit range $s/B_{app} \leq 0{\cdot}65$ for which computations were previously hand-made by Ramsay and (independently from him) by Pirlot, and for which the present work makes a choice about divergences found between the results obtained by these two authors. Finally, from the results of this study, they suggest two simple graphical methods allowing, the former to compute integrated absorptions, the latter to determine B_{vrai} in case s is not known with sufficient accuracy.

Schoenfeld, R.L. and N. Milkman, DIGITAL COMPUTERS IN THE BIOLOGICAL LABORATORY, Science, 146, 190-198 (1964).

This article seeks to study the requirements for use of a digital computer as a valuable adjunct to analytical instruments used in the laboratory and also as an "on-line" instrument in biological experiments - that is, an instrument used in the course of the experiment.

Tunnicliff, D.D., J.R. Weaver, AUTOMATIC DATA PROCESSING, INTERPRETING, AND REPORTING OF RESULTS OF EMISSION SPECTROGRAPHIC ANALYSES, Anal. Chem., 36, 2318-2321 (1964).

A generalized Fortran computer program has been developed which calculates and reports the results for the common-matrix method of emission spectrographic analysis. If the input contains data for more than one line for an element, the program computes the proper value to report corrected for interference from other elements. The elements to be determined, the lines used for their determination, and the element to be used as the internal standard are left entirely to the option of the user. The computer calculation costs for an IBM 7090 at $500 per hours is only 27 cents per sample of 15 elements.

SECTION 7

FLUORESCENCE STUDIES

Bakalor, S., THE RELATIONSHIP BETWEEN UV FLUORESCENCE AND THE PROTEIN CONTENT OF MILK, Australian J. Dairy Tech., 19, 29 (1964).

The relationship between fluorescence values and the protein content of milk as determined by the Kjeldahl method was tested. A definite relationship was found between the two sets of variables. The use of an instrument and cells more adapted to this technique is being investigated.

Berlinguette, G.E., P.A. Tate, FLUOROMETER FOR CHEMICAL DOSIMETRY, Rev. Sci. Instr., 35, 1725-1726 (1964).

A filter fluorometer designed for chemical dosimetry which approaches a grating instrument in performance is described.

Carpenter, J.H., TRACER FOR CIRCULATION AND MIXING IN NATURAL WATERS, Public Works, 91, 110-112 (1960).

A sufficiently sensitive tracer material to allow direct experimental estimates of the time and space distribution of materials introduced into natural bodies of water has been developed. Rhodamine B, as assayed by its fluorescence, was found to be an excellent tracer for this purpose.

Connors, W.M., W.K. Boak, A PROCEDURE FOR THE DIRECT READING OF FLUORESCENT SPOTS ON THIN LAYER CHROMATOGRAPHY PLATES USING THE TURNER FLUOROMETER, J. Chromatog., 16, 243-245 (1964).

In conjunction with analytical studies, a rather novel use of the Turner Model III Fluorometer was developed. This involved the direct reading of fluorescent carbohydrate spots on TLC plates of special design. The unique point of this procedure involved the use of a flexible stainless steel plate as a support for the thin-layer medium. Both the steel plate and the thin-layer medium had the ability to bend to the configuration of the rotating drum in the chromatography door of the fluorometer. Fluorescent spots on the plates thus could be read directly; this technique coupled the advantages of separation by thin-layer chromatography with quantitative analyses by an instrument heretofore used almost exclusively with paper chromatograms. The technique should have application to substances other than carbohydrates.

Djuric, D., FLUORIMETRIC DETERMINATION OF PORPHYRINS, Arch. Environ. Health, 9, 742-744 (1964).

A new, sensitive method for determination of small amounts of porphyrins is described. The method is based on measurements of porphyrin fluorescence when adsorbed on magnesium hydroxide. The fluorescence of this adsorbate is much higher than the fluorescence of solution.

This method is recommended for very low concentrations of porphyrins because of very high sensitivity and accuracy.

Endo, M., STAINING OF A SINGLE MUSCLE FIBRE WITH FLUORESCENT DYES, J. Physiol., 172, 11P, (1964).

This report shows a method of detecting whether or not fluorescent dyes can quickly diffuse into and out of a certain part of a single muscle fibre.

Haugen, G.R., R.J. Marcus, A SPECTROFLUOROPHOSPHORIMETER, Appl. Optics, 3, 1049-1056 (1964).

An instrument is described which allows the determination of fluorescence and phosphorescence spectra, fluorescence and phosphorescence excitation spectra, and the decay of triplet states involved in phosphorescence. A variable chopping speed (0-6000 rpm) allows determination of lifetimes down to 0.1 msec. Fluctuations in the 450-W light source are compensated by a quantum counter and a ratio divider, which plots the ratio of signals from the light emitter and the quantum counter. The instrument has been calibrated so that wavelength variations in excitation intensity, bandwidth, monochromator transmission, and phototube sensitivity are corrected, and only the number of quanta emitted by a sample at each wave length is reported. Examples are given of the spectra of Rhodamine B and eosin.

Hooper, P.R., RAPID ANALYSIS OF ROCKS BY X-RAY FLUORESCENCE, Anal. Chem. 36, 1271-1276 (1964).

A series of rocks and refractories of diverse chemical composition has been analyzed for Mg, Al, Si, P, K, Ca, Ti, Mn, Fe, and Sr on a Philips all-vacuum x-ray spectrograph. In all cases the precision is better than that obtained by analysts for W_1 and G_1. An estimate of error indicates that matrix effects can be overcome if a borax dilution method is used with concentrations exceeding 2% of oxide in the rock and that analyses by x-ray fluorescence are much quicker and probably more accurate for most elements than routine gravimetric, rapid, and optical spectrograph analyses undertaken by the average geologist.

Karttunen, J.O., H.B. Evans, D.J. Henderson, P.J. Markovich, R.L. Niemann, A PORTABLE FLUORESCENT X-RAY INSTRUMENT UTILIZING RADIOISOTOPE SOURCES, Anal. Chem., 36, 1277-1282 (1964).

Tritium absorbed in zirconium furnishes an excellent excitation source for the generation of fluorescent x-rays in elements requiring 3 to 12 k.e.v. The bremsstrahlung radiation from this radioactive source is used to excite the characteristic fluorescent x-rays of elements in the range Z = 16 to 35. The quantitative analysis of binary, ternary, and quaternary mixtures is illustrated. The apparatus is miniaturized and can be contained in a volume of less than 1 cu. foot.

Karush, F., N.R. Klenman, R. Marks, AN ASSAY METHOD FOR DISULFIDE GROUPS BY FLUORESCENCE QUENCHING, Anal. Biochem., 9, 100-114 (1964).

The fluorescence of FMA is quenched by combination with a thiol group and by reaction with the disulfide group at high pH. This property of FMA has been used as the basis of a sensitive and specific method for the assay of S—S groups either on paper or in solution. When used as a spray an alkaline solution of FMA can detect about 10^{-10} mole of disulfide. In solution FMA can be employed at 10^{-7} M to measure disulfide concentrations in the same range. The solution procedure has been adapted to the continuous assay of column effluents for their content of cystine-containing peptides. With oxidized glutathione the FMA method is at least fifty times more sensitive than the ninhydrin assay.

Koziol, J., FLUOROMETRIC DETERMINATION OF FLAVINS IN WHEAT GRAINS, Collec. Czech. Chem. Comm., 29, 2865-2868 (1964).

The considerable differences of the values obtained by the determination of the flavin content in foodstuffs are due to the difficult choice of a suitable method of analysis. Since the flavins may occur in stable linkage to proteins their determination is possible only by the fluorometric method based on the natural fluorescence of the flavins. A modified method was used employing the cation exchanger K-28 which proved suitable for the isolation of riboflavin from biological material.

Losev, N., A.N. Smagunova, Y.I. Stakheev, CURRENT METHODS OF ANALYSIS BY X-RAY FLUORESCENCE, Ind. Lab., 30, 525-530 (1964).

Review article outlining some of the latest developments in fluorescence analysis as regards theory, methods and experimental techniques.

Maddy, A.H., A FLUORESCENT LABEL FOR THE OUTER COMPONENTS OF THE PLASMA MEMBRANE, Biochim. Biophys. Acta, 88, 390-399 (1964).

1. The synthesis of a new fluorescent reagent (4-acetamido, 4'-isothiocyanostilbene-2,2'-disulphonic acid) for the specific labelling of the outer components of the plasma membrane is described.

2. The reaction of the reagent with ox erythrocytes is examined. It is concluded that the reagent reacts with a fixed number of sites on the surface of the cell.

3. The problems of designing reagents of this type, and the nature of the reaction between the stilbene isothiocyanate and erythrocytes are discussed.

Parker, C.A., C.G. Hatchard, T.A. Joyce, SENSITISED DELAYED FLUORESCENCE AS AN ANALYTICAL METHOD. SOME PRELIMINARY EXPERIMENTS, The Analyst, 90, 24-28 (1965).

The results of recent investigations of the phenomenon of sensitised P-type delayed fluorescence are briefly reviewed, and their possible application to organic trace analysis is discussed. Experiments have shown that the delayed fluorescence from various compounds can be selectively sensitised by means of suitable sensitisers. Tests with some aromatic hydrocarbons indicate that, in favourable instances, impurity concentrations of less than 1 p.p.m. can be detected without prior separation. Further work is required before the full potentialities of the technique can be decided.

Schachter, M.M., E.O. Haenni, AUTOMATIC TRIPAROMETRIC RECORDING IN FLUOROMETRY OF POLYNUCLEAR HYDROCARBONS, Anal. Chem., 36, 2045-2047 (1964).

A new oscillographic technique is described in this report which permits simultaneous recording of any three variable inputs. The technique has been utilized to record excitation and emission wave lengths and emission intensity. Continuing development is directed toward increasing scanning speed, improving sensitivity and resolution and extending the technique to recording of phosphorescence phenomena.

Turner, G.K., AN ABSOLUTE SPECTROFLUOROMETER, Science, 146, 183-189 (1964).

A new instrument has been developed for simple determinations of absolute fluorescence spectra.

Winefordener, J.D., R. A. Staab, STUDY OF EXPERIMENTAL PARAMETERS IN ATOMIC FLUORESCENCE FLAME SPECTROMETRY, Anal. Chem., 36, 1367-1369 (1964).

The influence of flame type, excitation source, solvent, sheath gas surrounding the flame gases, and inert gas added to the fuel gas on the atomic fluorescence - particularly the limit of detection - of zinc, cadmium, mercury and thallium have been investigated.

Wyckoff, R.W.G., F.D. Davidson, WINDOWLESS X-RAY TUBE SPECTROMETER FOR LIGHT ELEMENT ANALYSIS, Rev. of Sci. Instr., 35, 381-383 (1964).

A windowless tube spectrometer is described for the x-ray "fluorescent" analysis of the light elements down through fluorine. The high efficiency of x-ray excitation makes possible the analysis of elements as light as sodium when present in less than 1% and of fluorine in larger amounts.

Zvyagintsev, D.G., USE OF QUENCHERS IN THE INVESTIGATION OF SOIL MICRO-ORGANISMS BY FLUORESCENCE MICROSCOPY, Microbiology (USSR), 32, 622-625 (1964).

1. Fourteen different substances were investigated for their effect on the definition and brightness of the microscopic picture obtained in an investigation of soil microflora by the fluorescence method with the soil suspension stained with acridine orange and reflected light used for exciting the fluorescence.

2. The best results were given by the addition of sodium pyrophosphate, Ziehl's carbol-fuchsin, or diazine green to the stained preparations. The use of these substances more distinctly revealed more of the soil bacteria, fungi, and actinomycetes on the surface of soil particles and core sample, and on the surface of root hairs and plant roots. The application of quenchers allows the use of weaker light sources, and this greatly facilitates the work.

SECTION 8

GAS ANALYSIS

Barbato, L., I.M. Barbato, A MICROMETHOD FOR THE SIMULTANEOUS DETERMINATION OF CO_2 AND ITS RADIOACTIVITY APPLIED TO NERVOUS TISSUES, J. Neurochem., 11, 745-755 (1964).

A micromethod is described which permits the simultaneous quantitative determination of CO_2 produced during incubation of small samples of nervous tissue in $[U\text{-}^{14}C]$ glucose, and its radioactivity. The sensitivity of the method is $7{\cdot}5 \times 10^{-10}$ moles of CO_2.

The percentage relative specific radioactivities (S.RA.) of CO_2 from grey matter, corpus callosum and spinal ganglia were determined and the values found to be in agreement with those obtained by Geiger et al.(1960) during the in vivo perfusion of cat brain. Values for sympathetic ganglia and retina were higher, indicating a different glucose metabolism/endogenous substrates metabolism ratio during the respiration of these two tissues.

The S.RA. of CO_2 from grey matter and corpus callosum incubated in $[U\text{-}^{14}C]$-glucose with and without $0{\cdot}1$ m-K Cl did not differ. This is interpreted as representing similarity in the behaviour of glial cells and neurons in the utilization of endogenous substrates during rest and stimulation.

The effects of iodoacetate and tranylcypromine (an inhibitor of monoamineoxidase) on the S.RA. of CO_2 from grey matter were studied and found not to be significant.

The significance of these findings is discussed.

Ebeling, M., D. Marcenkus, A NEW AUTOMATED APPARATUS FOR THE DETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS, Microchem. J., 8, 213-221 (1964).

An automated instrument has been developed for the direct determination of oxygen in organic compounds dissociable below 900°. The sample is pyrolyzed at 900° in an alumina reaction tube in the presence of a carbon-platinized carbon packing at 940° with all the oxygen from the sample being converted to carbon monoxide. The gas stream is scrubbed to remove halogens and sulfur, passed through an oxidizing furnace to convert the carbon monoxide to carbon dioxide, and then gravimetrically determined. Eighteen to twenty sample analyses can be performed in an 8-hour workday with an accuracy of ± 0.30%.

Frazer, J.W., A MANOMETRIC METHOD FOR THE DETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS, Mikrochim. Acta, 5, 679-686 (1964).

A vacuum apparatus is described for the determination of oxygen in 3 to 5 mg of organic substance. The oxygen of the substance is converted to carbon monoxide by ignition in a bomb at 1050 to 1055°C. Corrections are calculated from thermodynamic data for the amounts of water and carbon dioxide not reacting at the ignition temperature.

Fuhrmann, H., MEASURING TRACES OF GASES WITH AUTOMATIC ANALYSERS, Glas-Instr. Tech., 8, 340-347 (1964). (In German)

(Measuring emission or immission in the range 0.001-1000 p.p.m.) Two types of equipment are described in this comprehensive review - an analyzer for the continuous measurement of emission with photometric evaluation and an analyzer working discontinuously measuring immission. The former is suitable for the range 0.5 to 1000 p.p.m. - the latter type for 0.001 to 0.1 p.p.m.

Halpert, G., A.C. Madsen, R.T. Foley, ANALYSIS FOR OXYGEN BY GAS-PHASE POLAROGRAPHY AT LOW TEMPERATURES AND LOW PRESSURES: A PROTOTYPE ASSEMBLY, Rev. Sci. Instr., 35, 950-952 (1964).

The design of a prototype model of an oxygen analyzer is presented. This unit utilizes the gas polarographic principle and is capable of analysis for oxygen over the temperature range of from -20 to 80°C and at pressures to as low as 10 mm Hg absolute. The unit can operate for two months unattended. It has a range of 0.001 to 100% oxygen with an accuracy of 1%. The design parameters are discussed and a critique of the unit is made. Temperature dependence is discussed, as are the other pertinent characteristics of the analyzer.

Johnson, M.J., J. Borkowski, C. Engblom, STEAM STERILIZABLE PROBES FOR DISSOLVED OXYGEN MEASUREMENT, Biotech. Bioeng., VI, 457-468 (1964).

Steam-sterilizable membrane probes for monitoring the dissolved oxygen level in fermentors, or the oxygen content of gas streams, are described. The probes have a silver cathode, a lead anode, and an acetate buffer as an electrolyte. The membrane is Teflon. The current output of the probes in the absence of oxygen is negligible.

Pavelka, F., NEW ABSORPTION APPARATUS FOR THE DETERMINATION OF GASEOUS IMPURITIES IN THE ATMOSPHERE, Mikrochim. Acta, No. 6, 1121-1125 (1964). (In German)

A description is given of an absorption vessel for gaseous materials that has been found especially good for the absorption of air pollutants. However, it has general applicability.

Robinson, J.R., W. Chefurka, CONTINUOUS MEASUREMENT OF $C^{14}O_2$ RESPIRED BY INSECTS. AN IONIZATION CHAMBER METHOD, Anal. Biochem., 9, 197-203 (1964).

Details of a method and apparatus for continuous assay and recording of $C^{14}O_2$ respired by insects treated with C^{14}-labeled materials are described. The technique, based upon an ionization flow chamber and vibrating reed electrometer, is sensitive to less than 10^{-3} μc of carbon-14 as $C^{14}O_2$ in the system and allows very economical use of labeled materials in the study of normal and poisoned metabolic pathways *in vivo*.

Schittko, F.J., MEASUREMENT OF GAS EMISSION FROM SOLID SURFACES, Vacuum, 13, 525-537 (1963).

Considerable difficulties from a physical point of view and as regards apparatus arise in the investigation of processes of gas emission. A large number of discrepancies result from the measuring procedures themselves, as well as from the equipment required for them. It is difficult to correlate measured values of the gas quantities (pressure) and of the time with the physical processes of gas emission. It is therefore necessary to find an accessible method of measuring further variables directly. Characteristic dependence of the processes of gas emission on temperature and energy can be determined by heating the experimental specimen in stages. This paper gives a report on methods of measuring gas emission and on the systematic sources of discrepancies. An exact method is given for determining the suction capacity for the measuring equipment used. The results of experiments at room temperature are summarized. Heating in stages gives a value of 10 Kcal/mol for the activation energy in the case of materials where the gas given off consists mainly of H_2O.

SECTION 9

INSTRUMENTS AND DEVICES

Botan, E. A., J. Phaneuf, and J. Lambert, STUDY OF AN INSTRUMENTED ANALYTICAL SYSTEM FOR EXTRATERRESTRIAL STUDY OF ATMOSPHERES, POSSIBLE LIFE FORMS AND SOILS, Aerospace Med 36, No. 1, 21-25 (1965).

A compact, lightweight analytical instrument package is proposed which can be landed on an extraterrestrial body. This system will sample and then analyze the environment by means of ultraviolet, visible, and infrared microspectrometry, microscopy and emission spectrometry. The data thus obtained will be converted to telemetry signals for transmission to earth.

The advantage of absorption spectroscopy, emission spectroscopy, and microscopy are manifold. For example, the samples examined can be visually presented through television techniques. This would yield information concerning size, shape, and possible cellular or morphological characteristics. Also information concerning the chemical composition of the visualized particles can be obtained. The presence of hydroxyls, methyls, amidos, carbonyls, and double bonds are just a few of the structural features that can be determined by absorption spectrometry. Proteins and nucleic acids are structures which can also be determined by these methods. Emission spectroscopy will determine the presence of virtually all the elements in the periodic table of the samples examined. Thus a comprehensive analysis (inorganic, organic, and biological) can be made of the particles visualized.

Doering, C. H. and H. Tarver, A SIMPLE LIQUID-LIQUID EXTRACTION APPARATUS, Anal. Biochem. 9, No. 4, 498-500, (1964).

An apparatus for the extraction of fatty acids from cellular hydrolyzates is described.

Frank, M., G. Guidarelli, and G. Serlupi Crescenzi, MICROFLUORIMETER RECORDER OF HIGH SENSITIVITY AND LOW NOISE FOR MEASUREMENTS IN LIVING TISSUES, Ann. Chim. Rome 54, No. 8-9, 788-794, (1964). (In Italian)

A recording microfluorimeter is described, based on a selective circuit completely transistorised. The apparatus is suitable to study the oxidation-reduction kinetics of pyridin nucleotides in biological systems, like tissues or animal organs, both *in vivo* and *in vitro*. The measure can be carried out on a few μ area. By this technique several measurements can be made simultaneously on the same tissue.

Gold, N. I., AN ADAPTABLE AIR STREAM EVAPORATOR FOR MULTIPLE SAMPLES, J. Chromatog. 15, No. 3, 431-432, (1964).

A versatile apparatus, designed from simple components, for the evaporation of solvent from multiple samples is described.

Goldstone, L., SIMPLE PARTIAL PRESSURE GAUGE, Rev. Sci. Instr. 35, No. 10, 1265-67, (1964).

A gauge based on the 180° mass spectrometer is described which is simple to make and to operate. It can be used to analyze the constituent gases in a vacuum system at partial pressures as low as 2×10^{-11} Torr. Several of these instruments have been tested and the sensitivity and resolution have been constant to within 10%. The gauge has a resolution of about 50, which is adequate for separating the common residual gases in a high vacuum system, and it is small so that it can easily be outgassed. Constructional details are given, and its operating characteristics are discussed.

Keimakh, R. Ya. and V. I. Kudryavtsev, THEORY AND DESIGN: AUTOMATIC SPECTROPOLARIMETER, Priborostroyeniye (Instrument Construction), No. 5, 3-5, (1964).

An automatic spectropolarimeter to measure and record rotational dispersion of optically active matter over a wide band of the UV and visible spectrum is described. A block diagram and general view of the instrument are included.

King, D. M. and A. J. Bard, COULOMETRIC ANALYSIS WITH GAS VOLUME MEASUREMENT, Anal. Chem. 36, No. 12, 2351-2352, (1964).

A coulometric cell was designed and built which allows the measurement of volumes of gaseous electrolysis products. The cell is air-tight, and the gas volume is determined by measuring the amount of water displaced in a graduated pipet by a technique similar to that used in gas coulometers. The most promising use of this cell is in the study of electrode reactions which occur at potentials sufficiently cathodic or anodic to cause concurrent oxidation or reduction of the solvent.

King, W. H., Jr., PIEZOELECTRIC SORPTION DETECTOR, Anal. Chem. 36, No. 9, 1735-1739, (1964).

Piezoelectric quartz crystals have long been used as frequency and time standards accurate to 1 part in 10^8 or better. These stable elements become selective gas detectors when coated with various materials. Crystals coated with gas chromatographic substrates produce gas chromatographic detectors which have several advantages: Sensitivity increases with solute boiling point, detectors can be made selective to compound type and respond in 0.05 second, and the output signal is a frequency which simplifies integration of peak areas and digital presentation of the data. The crystals used in this work were quartz plates 1/2 inch in diameter, 7.3 mils thick, that vibrate at 9 Mc. A readily measured signal of 1 c.p.s. corresponds to a weight increase of about 10^{-9} gram. Coated-crystal moisture detectors sensitive to 0.1 p.p.m. are now commercially available. Hydrocarbon detectors sensing as little as 1 p.p.m. of xylene have been tested.

LeCroissette, D. H., SYSTEMS CONSTRAINTS ON THE SEARCH FOR EXTRATERRESTRIAL LIFE, Proc. First Annual Rocky Mt. Bioeng. Symp., U.S. Air Force Academy, 84-87, May 4-5, 1964).

The systems constraints imposed on the life detection instrumentation at present are severe. The three most limiting factors are (1) the limitation in data rate to below 10 bits per second, (2) the relatively low scientific payload weights, and (3) the severe impact which the capsule will suffer in reaching the Martian surface which will require the instrumentation to be extremely rugged to survive.

Licht, S., B & L 505 SPECTROPHOTOMETER MODIFICATIONS FOR MEASURING SPECTRAL RESPONSE OF PHOTODETECTORS, Rev. Sci. Instr. 35, No. 8, 1027-1031, (1964).

Modifications to the Bausch and Lomb model 505 recording spectrophotometer, to allow the instrument to measure the spectral response of photodetectors, are described. Although originally performed for silicon photoconductors, the techniques are applicable for any type of photosensitive device.

Masterson, Jr., T. S., A. D. Mason, Jr., and W. L. Brown, INSTRUMENT FOR THE QUANTITATION OF ATP UTILIZING FIREFLY BIOLUMINESCENCE, Am. J. Med. Electron, 3, No. 4, 283-285 (1964).

A translucent spiral attached to the face of a photomultiplier has been encased in a light tight box together with accompanying preamplifier circuitry. An external high voltage power supply, an amplified RMS voltmeter and an oscilloscope comprise the instrumentation for measuring bioluminescence.

Millikan, D. F. and L. B. Thomas, AN APPARATUS FOR LARGE-SCALE LYOPHILIZATION OF BIOLOGICAL MATERIAL, Anal. Biochem., 9, No. 3, 386-388 (1964).

An all glass lyophilizing apparatus based on a high vacuum system is described. Inclusion of two mercury condensation pumps insures a more complete removal of permanent gas molecules by a factor of a thousand or more than with mechanical pumps alone.

Mulay, L. N. and L. K. Keys, A SPRING MICROBALANCE FOR MAGNETIC SUSCEPTIBILITY, ADSORPTION AND THERMOGRAVIMETRIC STUDIES, Anal. Chem., 36, No. 12, 2383-2384, (1964).

Some unique constructional and operational details of a microbalance are described for studies on magnetic susceptibility, adsorption and thermogravimetry and for measuring small changes in susceptibility occurring during these processes.

Pietrokowsky, P., THE ELECTRON MICROPROBE, Ind. Res., 6, No. 9, 56-57, (1964).

The principle of operation and the various applications of the electron microprobe as an analytical tool are reviewed.

Reker, H., A UNIVERSAL TIMER, Nucl. Instr. Methods, 29, 299-305, (1964). (In German)

A timer is described which gives time-intervals between one and 999 seconds in setps of one second. The relative accuracy of these intervals is in the range 6 x 10^{-5} and the deviations from an official time-signal with a higher relative accuracy (in the range of 10^{-8}) will be measured. Besides the timer gives time signals with frequencies of 10,000, 1000, 100, 10 of 1 Hz for coupling other time interval-units. A special set gives the possibility for calibrating feather-clocks.

Slevogt, K., and H. Wirth, THE CHEMOMETER, A NEW TYPE OF MULTI-PURPOSE INSTRUMENT FOR THE CHEMICAL LABORATORY, Z. Instrum. Kde., 72, No. 3, 72-75 (1964). (In German)

This report concerns a new instrument usable for different purposes for the execution of electrochemical measurements. This instrument, which is named "Chemometer", allows conductometric and potentiometric determinations and titrations in a wide range. Furthermore, tregohm measurements are possible by using this unit.

Stuart, J. L., INSTRUMENTATION REQUIREMENTS FOR LIFE DETECTION SYSTEMS, Proc. First Annual Rocky Mt. Bioeng. Symp., U.S. Air Force Academy, 88-97, May 4-5, 1964.

The approaches taken in performing biological and chemical analyses on a planetary surface must differ from conventional techniques. Analytical and functional experiments should be performed in which both simple and highly specialized organic compounds are sought. Well-understood fundamental measuring techniques should be adapted and combined to give the instrumentation a wide, versatile performance capability. Each class of instruments (e.g., wet chemistry, dry chemistry, morphological analyses, etc.) should be unified into an experimental instrument in order to economize the spacecraft systems constraints. A review of the sample collection problem is presented along with a brief discussion of several of the life detection instruments being developed at the present time.

Tal, E., S. Dikstein and F. G. Sulman, ATP DETERMINATION WITH THE TRICARB SCINTILLATION COUNTER, Experientia, 20, 652, (1964).

A liquid scintillation counter has been adopted to measure light output in the presence of luciferin-luciferase for ATP determination.

Thomason, P. F., PYROLYTIC GRAPHITE CUP AS BOTH VESSEL AND ELECTRODE FOR MICRO REDOX AND ACID - BASE POTENTIOMETRIC TITRATIONS, Microchem. J., 8, No. 3, 234-240, (1964).

A potentiometric titration vessel of pyrolytic graphite described for use in microtitrations, which are usually performed with colored indicators. The vessel also serves simultaneously as the indicator electrode, the reference electrode being an in-burette platinum wire. Thus, the need for internal electrodes is eliminated. The vessel has been used satisfactorily in both manual and automatic titrations.

Tuzzolino, A. J., SILICON PHOTODIODE VACUUM ULTRAVIOLET DETECTOR, Rev. Sci. Instr., 35, No. 10, 1332-1335 (1964).

The photosensitivity of silicon surface-barrier photodiodes has been measured over the photon energy range from 4.9 to 21.2 eV (2537 to 584Å). The photodiodes are operated in the reverse bias mode at room temperature. The sensitivity of a typical photodiode with approximately 100Å of gold on the sensitive surface is 0.16 electron per photon at 2537Å and 1.1 electrons per photon at 584A. Photosensitivity did not vary more than a few percent over the sensitive area. The operating characteristics of these devices are reported and the use of the silicon photodiode directly, or in combination with sodium salicylate, as a vacuum ultraviolet detector is discussed.

Weston, Charles R., PRINCIPLES OF OPTICAL MEASUREMENTS APPLIED TO BIOLOGICAL GROWTH IN THE WOLF TRAP, Proc. First Annual Rocky Mt. Bioeng. Symp , U.S. Air Force Academy, 99-111, May 4-5, 1964.

The search for life on Mars will initially be directed toward detection of microorganisms. The relative concentration of microorganisms in a suspension can be estimated by measuring either the attenuation of a beam of light which passes through the suspension or the intensity of the light scattered by the organisms. The measurement of the scattered light, nephelometry, has been selected to measure the growth of organisms in the Wolf Trap because of its inherently greater sensitivity. With the present optics in the two chambers of the engineering breadboard, the Wolf Trap gives a reliable signal at approximately 10^5 bacteria per milliliter. The breadboard is controlled from a battery-operated portable console which supplies power, simulates spacecraft interface functions, and provides a convenient method of monitoring the data. The entire breadboard can be heat sterilized at 145°C for 24 hours in line with the sterilization requirement for Martian landers.

SECTION 10

LIFE

Bieri, R., HUMINOIDS ON OTHER PLANETS? Am. Scientist, 52, 452-458 (1964).

This paper presents the view that intelligent life on other planets will bear a strong resemblance to homo sapiens. The argument is based on the premise that the physical properties of the elements, the forms of energy available and the environmental conditions which would allow life to arise and evolve are such that severe limitations are imposed on the number of routes available to evolving forms.

Corliss, W. R., DETECTING LIFE IN SPACE, Int. Sci. & Tech., 28-34, Jan. 1965.

Life may exist elsewhere, or it may not. The only way we'll ever know for sure is to go and look, and that's what NASA proposes to do as soon as possible. The "possible", however, includes the availability of dependable instrumentation for detecting life, and so far we don't have it. Enough programs are now underway that a wide variety of experimental questions may be asked. These should narrow the ambiguity that will result from possible single discoveries such as the existence of amino acids, organized elements, or artifacts, which at best are indications of life rather than proofs. The big problem, and one which may never be resolved, is what will happen if any existing life is so unlike our own that it doesn't eat, transpire, or excrete the same things ours does. As in all other fields, we can only detect what we can define, and our abilities here are woefully weak.

Landsberg, P. T., DOES QUANTUM MECHANICS EXCLUDE LIFE?, Nature, 203, No. 4948, 928-930, Aug. 1964.

This paper attempts to discover if spontaneous generation and self-reproduction are compatible with quantum mechanics.

Montgomery, P. O'B., E. Rosenblum and B. Stapp, GRAVITY, RADIATION AND GROWTH, Aerospace Med., 35, 731-733 (1964).

Phage free E. coli B cells were exposed to continuous ionizing radiation from cobalt 60 source which delivered 55.8R per hour. Cells so treated show a depression of their growth curves when compared to unirradiated control cells. Ultrastructural observations indicate that these irradiated cells continue to enlarge despite their failure to divide. This enlargement involves the entire cell and its intracellular ultrastructural components. A comparison of these effects of X-radiation and the effects of increased gravity on these cells was made. It is apparent that increased gravity and increased X-radiation produce similar disturbances in the growth curves and in ultrastructural characteristics of E. coli B cells. The possibility that these alterations may be of a genetic nature is considered.

O'Parin, A. I., THE ORIGIN OF LIFE IN SPACE, Space Sci. Rev., Netherlands, 3, 5-26, (1964).

Discussion of how life evolved on earth and how this is applicable to the evolution of life in other parts of the universe.

Palade, G. E., THE ORGANIZATION OF LIVING MATTER, Proc. Nat. Acad. Sci, 52, 613-634, (1964).

The author discusses cellular organization.

Pay, R., BOOSTERS PACE MARS LIFE DETECTION, Missiles and Rockets, 16, No. 3, 32-33, (1965).

This article discusses the suggestions of R. Young of Ames Research Center for life detection experiments to be included in a Mars landing package.

Ponnamperuma, C., CHEMICAL EVOLUTION AND THE ORIGIN OF LIFE, Nature, 201, No. 4917, 337-340 (1964).

Some theories about the origin of life are reviewed. The author discusses chemical evolution and the likelihood of life in other parts of the universe.

Ruzic, N. P., THE CASE FOR LIFE BEYOND THE EARTH, Ind. Res., 7, No. 1, 64-80 (1965).

The author speculates on the possibility of life in other parts of the universe and what characteristics this life might possess.

Siegel, S. M., IS THERE LIFE BEYOND THE BLUE?, SAE J., 72, No. 10, 66-67 (1964).

Experiments involving subjection of earth organisms to simulated Martian conditions are described.

Sneath, P. H. A., THE LIMITS OF LIFE, Discovery, 25, 20-24 (1964).

The ability of living things to adapt to a variety of conditions is discussed.

Sylvester-Bradley, P., THE ORIGIN OF OIL - AND LIFE, Discovery, 25, 37-42 (1964).

The author cites reasons why he believes oil is both biogenic and abiogenic in origin. He suggests that it is likely that the first living forms arose at the interface of globules of crude oil (produced abiogenically) and the clay deposits left on river estuaries.

SECTION 11

MACROMOLECULE STUDIES

Anonymous, PROTEIN OFFERS CLUE TO EVOLUTION, Chem. & Eng. News, 42, No. 33, 52-54 (1964).

Studies of the structure and function of the protein cytochrome C from 13 species ranging from yeast to man indicate that life on earth may have originated as the result of a single occurrence.

Baxter, J. H., DIFFERENCES IN SERUM ALBUMINS REFLECTED IN ABSORPTION SPECTRA OF A BOUND DYE, Arch. Biochem. Biophys., 108, No. 3, 375-383 (1964).

Binding of the anionic dye 2-(4'-hydroxphenylazo)-benzoic acid (HABA) by human and other serum albumins in phosphate buffer, p.H. 6.2, was studied by using equilibrium dialysis. Absorption spectra of the bound dye were determined. Free HABA has an absorption maximum at 348 mμ. When the dye is bound by albumin, its 348 mμ absorption band alters, and an impressive new band develops at about 480 mμ. The changes vary in a characteristic manner depending on the type of albumin employed. The new absorption band of albumin-bound HABA is pH dependent, reaching maximum intensity at about pH6. The band does not develop if dyes differing slightly from HABA are used, indicating that the structural requirements of the dye are highly specific. The changes in absorption of HABA induced by albumin-binding may be closely simulated by dissolving HABA, but not related dyes, in certain organic solvents or detergent solutions. Thus it appears that the changes depend on certain environmental conditions not uniquely associated with albumins. Differences in absorption of HABA that is bound to different albumins are attributed to differences in binding-site structure of the albumins.

Botre, C., F. DeMartiis and M. Solinas, ON THE INTERACTION BETWEEN MACROMOLECULES AND COLLOIDAL ELECTROLYTES, J. Phys. Chem., 68, No. 12, 3624-3628, (1964).

The interaction in aqueous solution between sodium lauryl sulfate either with water insoluble (such as polyvinyl acetate) or water-soluble (such as bovine serum albumin) macromolecules was studied. Potentiometric determinations with permselective membrane electrodes or cationic glass electrodes and specific conductivity were employed in the investigation. Several evidences clearly confirm the formation of a "complex" between macromolecule and colloidal electrolyte. Data are also reported about the shift observed in the c.m.c. values, as well as the binding of sodium and calcium ions in solution of these complexes. In spite of the poor solubility of the calcium salt of a detergent in aqueous solution, it is shown that the solution of the "complex" before precipitation may sequester significant amounts of calcium. The behavior of the complex was studied both as a function of the molar detergent-polymer ratio and as a function of the concentration of the complex in solution. On the basis of these experiments, a theoretical approach is proposed to treat the complex as a polyelectrolyte.

Commoner, B., DEOXYRIBONUCLEIC ACID AND THE MOLECULAR BASIS OF SELF-DUPLICATION, Nature, 203, No. 4944, 486-491 (1964).

The author attempts to determine what criteria are required to establish that a molecule such as DNA is capable of self-duplication and control of inheritance and to examine the degree to which the available evidence meets such criteria.

Fong, P., THE REPLICATION OF THE DNA MOLECULE, Proc. Nat. Acad. Sci., 52, 641-647 (1964).

This paper considers the kinetics of replication and the dynamics of unwinding and rewinding.

Freifelder, D., A. K. Kleinschmidt and R. L. Sinsheimer, ELECTRON MICROSCOPY OF SINGLE-STRANDED DNA: CIRCULARITY OF DNA OF BACTERIOPHAGE ϕ X174, Science, 146, 254-255 (1964).

The single-stranded DNA of coliphage ϕ X174 has been examined with the electron microscope by a modification of the protein-monolayer-adsorption technique. The molecules were found to be circular with a total length of 1.77 ± 0.13 microns.

Frisman, E. V., V. I. Vorob'yev, L. V. Shchagina and N. K. Yanovskaya, FLOW BIREFRINGENCE IN DNA SOLUTIONS - II. EFFECT OF THERMAL DENATURATION AND THE IONIC STRENGTH OF THE SOLUTION ON THE STRUCTURE OF DNA MACROMOLECULES, Polymer Sci. USSR, 4, No. 5, 1301-1307 (1963).

(1) The flow birefringence, viscosity and absorption in the ultraviolet range $\lambda = 260$ mμ have been studies for DNA solutions previously heated at different temperatures and cooled at $t = 0^{\circ}$. (2) Below the melting point heating has a marked effect on the birefringence value Δn, but does not change $E(p)_{260}$, the relative viscosity or the birefringence orientation. It is suggested that this change in Δn is due to the breaking of a small number of hydrogen bonds in the DNA molecule. (3) It has been found that the characteristic birefringence of native DNA increases as the ionic strength of the solution falls. The latter does not change the birefringence orientation, nor the characteristic viscosity or $E(p)_{260}$.

Goldstein, A., D. B. Goldstein and L. I. Lowney, PROTEIN SYNTHESIS AT 0°C IN ESCHERICHIA COLI, J. Mol. Biol., 9, No. 1, 213-235 (1964).

Leucine-starved cells of an *Escherichia coli* auxotroph will incorporate radioactive leucine into protein at 0°C. The incorporation is linear for the first 10 to 15 min. It appears that all the essential steps in protein synthesis go on at 0°C, and a wide variety of proteins is synthesized. The rate of synthesis is about 350 times slower than at 37°C. In this system the polarity of assembly of polypeptide chains, from N-terminal to C-terminal, can be demonstrated by treating the proteins with carboxypeptidase. A quantitative analysis of the release of incorporated leucine by carboxypeptidase permits estimation of the average time required to add a single amino acid residue to a nascent protein chain at 0°C, whence the number of nascent chains can be derived. This number has also been estimated by direct measurement of nascent protein in sucrose density-gradient centrifugation. A cell contains about 5000 chains of nascent protein, and 18,000 70 s ribosomes. The assembly time of a protein of 400 residues is 5 sec at 37°C.

Goodman, M., and Y. Masuda, DETECTION OF POLYPEPTIDE HELIX-COIL TRANSITIONS BY NUCLEAR MAGNETIC RESONANCE, Biopolymers, 2, No. 2, 107-112 (1964).

We have studies the helix coil transition for poly-γ-ethyl-L-glutamate (PELG) in the mixed solvent system: trifluoracetic acid-trifluoroethanol by high resolution nuclear magnetic resonance spectroscopy. At 25°, the transition occurs over a range of solvent compositions between 62-64% trifluoroacetic acid. In addition, we have assigned τ -values to the various types of protons in PELG.

Itzhaka, R. F. and D. M. Gill, A MICRO-BIURET METHOD FOR ESTIMATING PROTEINS, Anal. Biochem., 9, No. 4, 401-410 (1964).

A rapid and sensitive method for estimating proteins using an alkaline copper sulfate reagent is described. The method is reasonably nonspecific for type of protein and can be used for solutions containing DNA even at concentrations of the latter as high as 0.7 mg/ml in the final reaction mixture. In the presence of DNA, 0.15 to 3.0 mg of protein can be estimated and in the absence of DNA, as little as 0.075 mg. The effects are described of various salts, of perchloric acid, and of urea on the estimation. Measurements on several dipeptides showed that proline peptides do not form ultraviolet-absorbing complexes with copper whereas prolyl peptides do form such complexes. This explains the finding that gelatin (which has a high proportion of proline and of hydroxyproline residues) is less reactive with copper than are the other proteins studied here.

Karyakin, A. V., and L. A. Chmutina, SPECTRAL INVESTIGATION OF DYE SALT SOLUTIONS IN THE PRESENCE OF BIOPOLYMERS, Biofizika, 9, No. 4, 515-518 (1964). (In Russian)

The purpose of this work is to study the optical properties of luminescent dyes in the presence of glysine. The change in the color of glycine was observed only for sodium fluorescein and acridine orange. Biopolymers cause the association of fluorescein molecules, but destroy dimers of acridine orange.

Kay, R. E., E. R. Walwick and C. K. Gifford, SPECTRAL CHANGES IN A CATIONIC DYE DUE TO INTERACTION WITH MACROMOLECULES. I. BEHAVIOR OF DYE ALONE IN SOLUTION AND THE EFFECT OF ADDED MACROMOLECULES, J. Phys. Chem., 68, No. 7, 1896-1906 (1964).

In the course of examining the use of carbocyanine dyes as agents for the detection of trace amounts of protein and other macromolecules, the spectral changes resulting from interaction of various macromolecules with the dye 4,5,4',5'-dibenzo-3,3'-diethyl-9-methyl-thiacarbocyanine bromide were observed, and the effects of environmental factors on the absorption spectrum of the free dye were determined. The aqueous dye solution was stable over the pH range 3.8-9.6 and unaffected by storage at temperatures below 60°, but it was unstable when exposed to light. The effects of pH, solvent, dye concentration, temperature, and inorganic ions on the wave length of the dye absorption maximum were ascertained. The pH had no effect on the position of the absorption maximum, but other variables such as the composition of the solvent system or changes in the dye concentration produced changes in the wave length of the maximum. Maxima were observed at 575, 555, 535, 510, 450, or 650 mμ (J-band) and these maxima are believed to represent increasing degrees of aggregation of the dye in the order: 575, 535, 510, 450, and 650 mμ The 555 mμ band appears to be associated with the J-band maximum and probably does not represent the first increase in aggregation from the monomer. The interactions of the dye with inorganic salts, polypeptides, simple proteins, conjugated proteins, synthetic polypeptides, nucleic acids, carbohydrates, amino acids, pyrimidine and purine bases, nucleosides, and nucleotides were all investigated. In trace amounts (less than 0.002%) only proteins, synthetic polypeptides, nucleic acids, and substituted polysaccharides caused changes in the absorption spectrum of the dye. Mono-, di-, and trisaccharides, purine and pyrimidine bases, amino acids, and nucleosides had no effect. Polypeptides and nucleotides were usually effective only at higher concentrations, and the action of the inorganic salts was found to depend upon the nature of the anion. Divalent anions were very effective, and small amounts induced the formation of J-bands. On the other hand, monovalent anions were much less effective, and relatively large amounts were required to induce the formation of a J-band.

Kay, R. E., E. R. Walwick, and C. K. Gifford, SPECTRAL CHANGES IN A CATIONIC DYE DUE TO INTERACTION WITH MACROMOLECULES. II. EFFECTS OF ENVIRONMENT AND MACROMOLECULE STRUCTURE, J. Phys. Chem., 68, No. 7, 1907-1916 (1964).

Studies were conducted to determine the influence of pH, temperature, and dye-macromolecule ratio on the spectral changes induced by macromolecules in the dye 4,5,4',5'-dibenzo-3,3'-diethyl-9-methylthiacarbocyanine bromide. Adjustment of the pH to values considerably below the isoionic point prevented interaction of the dye with proteins, whereas a pH above the isoionic point was conducive to the formation of dye-protein complexes. On the other hand, interaction of the dye with DNA was virtually unaffected by pH changes, but important alterations in the wave length of the adsorption maximum occurred due to denaturation of the DNA. Dye aggregation induced by inorganic salts was favored by temperatures of less than 20°, and at higher temperatures the aggregate was dispersed. On the other hand, the aggregation of the dye when adsorbed on a protein was favored by higher temperatures and the interaction of the dye with DNA was not significantly altered by changes in temperature. The stoichiometry of the dye-macromolecule reaction was investigated in the case of DNA and oxidized ribonuclease. The limiting ratio of dye to phosphate groups was 1:1 for both native and denatured DNA. For oxidized ribonuclease, a ratio of 5.7:1 dye molecules to protein molecules was found. When the ratio was greater than 5.7:1, new peaks formed at shorter wave lengths. Completely denatured DNA reacted with the dye to produce an absorption peak at 535 mμ, whereas native DNA inducedan absorption peak at 575 mμ. It was found that the ratio of the absorbance at 535 mμ to the absorbance at 570 mμ could serve as an accurate and sensitive measure of the degree of denaturation. Native ribonuclease solutions did not interact with the dye to produce new absorption peaks. On the other hand, oxidized ribonuclease reacted with the dye to form a number of new maxima.

Kenner, G., and A. Jackson, PORPHYRINS - KEY MOLECULES OF LIFE, Discovery, 24, 24-29 (1963).

General description of the structure and function of the porphyrins.

Laurent, T. C., INTERACTION BETWEEN POLYSACCHARIDES AND OTHER MACROMOLECULES. 9. THE EXCLUSION OF MOLECULES FROM HYALURONIC ACID GELS AND SOLUTIONS, J. Biochem, 93, No. 1, 106-112 (1964).

1. A number of substances have been chromatographed on a cross-linked hyaluronic acid gel with a concentration of 1.45 x 10^{-2} g./ml. at high ionic strength and at high pH. 2. The results are interpreted on the basis of a steric exclusion of the substances from the gel. Calculations show that the results are compatible with the hypothesis that hyaluronic acid forms a continuous network of extended rigid linear polysaccharide chains in the gel. 3. The excluded volumes obtained by equilibrium dialysis of proteins between a hyaluronic acid phase and a buffer phase at polysaccharide concentrations of 1 x 10^{-3} - 8 x 10^{-3} g./ml. were somewhat lower than those obtained in the gel experiments, indicating that the network model breaks down at lower concentrations. The results are in good agreement with previous osmotic results. 4. Gel filtration should be a useful tool for the structural analysis of gels.

May, P., THE INFLUENCE OF TEMPERATURE ON THE DISSOCIATION AND FORMATION OF AGGREGATES OF THERMALLY DENATURED DNA. COMPARISON OF THIS INFLUENCE OF TEMPERATURE WITH THE PHENOMENA OF DENATURATION AND RENATURATION OF DNA, J. Mol. Biol., 9, No. 1, 263-265 (1964).

The author has found that a rheological treatment of denatured DNA does not provoke aggregation at either low (T = .3°C) or high (T = 70°C) temperatures, the most favorable temperature for aggregation being about 40°C.

Mayr, E., FROM MOLECULES TO ORGANIC DIVERSITY, Federation Proc., 23, No. 6, Part I, 1231-1235 (1964).

The evolution of organic diversity is to a large extent due to the elaboration of even more complex, more diverse systems. During much of this evolution the same basic chemical constituents have been used. However there has been a great deal of modification of macromolecules which presumably is correlated with the interaction of various proteins and with the regulation of enzyme activity. Evolution of higher organisms must be studied both as an elaboration of systems and through the analysis of elementary units.

Seliger, H. H., and W. D. McElroy, THE COLORS OF FIREFLY BIOLUMINESCENCE: ENZYME CONFIGURATION AND SPECIES SPECIFICITY, Proc. Nat. Acad. Sci., 52, No. 1, 75-81 (1964).

Studies with twenty species of firefly lead the authors to conclude that probably all natural firefly luciferins have the same structure. The color of the emitted light is due only to the species enzyme.

Semmel, M., and J. Huppert, THE INTERACTION OF BASIC DYES WITH RIBONUCLEIC ACID, Arch. Biochem. Biophys., 108, 158-168 (1964).

Ribonucleic acid reacts *in vitro* with basic dyes such as toluidine blue, acridine orange, and pyronine to provoke a shift in the absorption maximum of the dye, either toward a longer (negative metachromasy) or shorter wavelength (positive metachromasy). The direction of the metachromatic shift is dependent on both the relative concentration of the polymer to the dye and on the secondary structure and the chainlength of the polymer. In studies with synthetic polymers, RNA, and RNA-fractions, at known polymer-dye ratios, it was found that the length of the polymer chain determined the extent of positive metachromasy. On the other hand, negative metachromasy appears dependent on density of double-stranded regions in RNA molecules.

Den Tonkelaar, E. M., and P. Van Duijn, PHOTOGRAPHIC COLORIMETRY AS A QUANTITATIVE CYTOCHEMICAL METHOD. III. DETERMINATION OF THE ABSOLUTE AMOUNT OF DNA IN CELL NUCLEI, Histochemie, 4, No. 1, 16-19 (1964).

The determination of absolute amounts of DNA per cell nucleus by means of photographic colorimetry is described. A cytochemical model-system consisting of DNA containing cellulose films was used as an internal standard in the procedure. The films were stained together with the microscopic object and pieces of the films were placed in front of the photographic plate during photography. The DNA content of these pieces of film was determined by phosphorus analysis at the end of the procedure. The DNA content of cell nuclei was calculated by comparing the blue extinction values of the pictures of the nuclei with those of the punches in the blue print, taking into account the magnification factor of the microscope. Good agreement between the DNA content of nuclei determined in this way and by biochemical and ultraviolet microspectrophotometrical methods was found.

Torten, J., and J. R. Whitaker, EVALUATION OF THE BIURET AND DYE-BINDING METHODS FOR PROTEIN DETERMINATION IN MEATS, J. Food Sci., 29, No. 2, 168-174 (1964).

The biuret method of protein estimation was compared with the Kjeldahl method. Highly significant positive correlations with Kjeldahl protein of 0.99, 0.99, 0.98, and 0.99 were obtained for ground beef, pork, chicken breast, and cod, respectively. The high correlations between the two methods and the small standard deviations for the biuret values point out the reliability and the accuracy of the biuret method. The same substances were analyzed by the Orange G dye-binding method with highly significant positive correlations with Kjeldahl protein of 0.90, 0.80, 0.94, and 0.95 for ground beef, pork, chicken breast, and cod, respectively. However, the amount of dye bound per g protein varies with the protein content of the sample, and the precision is poor. Orange G dye binding has possibilities for use in analyzing meat proteins only if the preparations and procedures are carefully standardized and the protein content does not vary much more than a few percent. With Amido Black 10B, the amount of dye bound was too strongly dependent upon sample size to justify further investigation of this dye for estimation of the protein content of comminuted meats.

Weygand, F., AMINO ACIDS AND PEPTIDES, Z. Anal. Chem., 205, 406-416 (1964). (In German)

A survey is given of the analytical methods available for amino-acids and peptides and it is shown that several new procedures have been developed which can be successfully employed for solving various problems.

SECTION 12

MARS

Anonymous, MARINER MARS 1964, NASA press release No. 64-266. October 29, 1964, 73 pages.

This report describes in detail the various aspects of the Mariner Missions for Mars. The Mariner spacecraft, the scientific experiments to be performed, the launch vehicle used as well as the mission itself are discussed.

Danielson, R. E., J. E. Gaustad, M. Schwarzschild, H. F. Weaver, and N. J. Woolf, MARS OBSERVATIONS FROM STRATOSCOPE II, Astron. J., 69, No. 5, 344-352 (1964).

On 1 March 1963 Stratoscope II, a balloon-borne telescope, was flown for the first time with the aim of investigating the infrared spectrum of Mars. A series of technical difficulties arose during the flight and severely restricted the number and quality of the spectrometer scans that were obtained. Nevertheless, the following results could be deduced from these scans: (1) It is improbable that the water vapor content of Mars is greater than 40 μ ; (2) If the total pressure at the surface of Mars is assumed to be 87 mbar, the amount of CO_2 in the atmosphere of Mars amounts to about 6000 cm-atm rather than 3000 cm-atm as previously estimated.

Harrison, F. B., and W. Bernstein, A DETECTOR FOR THE ARGON ABUNDANCE IN THE MARTIAN ATMOSPHERE, Planetary Space Sci., 12, 726-727 (1964).

This paper describes a simple instrument of low weight and small power consumption suitable for inclusion in an early Mars package, which would determine the argon abundance provided the total atmospheric density were independently measured.

Kaplan, L. D., G. Münch, and H. Spinrad, AN ANALYSIS OF THE SPECTRUM OF MARS, The Astrophys. J., 139, No. 1, 1-15 (1964).

On a high-dispersion spectrogram of Mars taken at Mount Wilson rotational lines of H_2O near λ 8300 and CO_2 near λ 8700 have been detected. Recent laboratory measurements of line strengths by D. Rank have been used to determine the amounts of H_2O and CO_2 in the atmosphere of Mars: 14 ± 7 μ precipitable water and 55 ± 20 m atm CO_2. From the absence of O_2 in the Martian spectra, we set an upper limit of 70 cm atm for the O_2 content. By suitably combining the CO_2 amount with observations by Kuiper and Sinton of the strongly saturated bands in the 2-μ region, a surface pressure of 25 ± 15 mb has been derived. The implications of the results on the composition of the Martian atmosphere are discussed.

Musman, S., AN UPPER LIMIT TO A RAYLEIGH SCATTERING ATMOSPHERE ON MARS, Planetary Space Sci., 12, 799-800 (1964).

Based on Rayleigh scattering calculations the author finds the surface pressure values for N_2 and CO_2 for Mars consistent with the 25 ± 15 millibars obtained by Kaplan, Münch and Spinrad.

Myers, O. E., OPTICAL PHENOMENA IN PLANETARY METEOROLOGY, Report: Visibility Lab., Univ. Calif., Scripps Inst. Oceanography, San Diego, California. August 1963, SIO Ref. 63-4, 46 pgs.

This report is a compilation in the form of an annotated bibliography of available information concerning what is now known of planetary atmospheres, pertinent optical phenomena in terrestrial meteorology and the means for acquisition of further data concerning terrestrial and extraterrestrial atmospheres.

Salisbury, F. B., THE PARADOX OF MARS, A preprint obtained from the author at Colorado State Univ., Fort Collins, Colorado, 1964, 24 pgs.

The author outlines various conditions in Mars that would make life as we know it impossible. He then discusses the observations of Mars that indicate a flourishing life on this planet. He feels that the strength of the paradox will not permit a moderate position between the two extremes.

Salisbury, F. B., EXOBIOLOGY, Proc. 1st Annual Rocky Mt. Bioeng. Symp., U.S. Air Force Academy, 75-83, May 4-5, 1964.

The case for extraterrestrial life cannot be proven. But theories on the origin of life and organic materials in meteorites suggest that it might exist. Although the environment on Mars appears to be so harsh that we can scarcely imagine life existing there, the markings on Mars provide a fairly direct, reproducible evidence for life. The Martian "canal" system, the satellites, and the flares could even indicate intelligence on Mars. There are witnesses who describe visitations by extraterrestrial beings and vehicles. Such accounts should be studied carefully. We should make every effort to study the markings on Mars more closely, using our space flight capabilities. If the markings represent "vegetation", it may well be quite different from our own, and its detection might be very difficult, but the chances of success are high enough to merit a great deal of effort.

Seiff, A., and D. E. Reese, Jr., DEFINING MARS' ATMOSPHERE - A GOAL FOR THE EARLY MISSIONS, Astronautics & Aeronautics, 3, No. 2, 16-21 (1965).

Carefully designed measurements of the response during entry of a small probe can define the Mars atmosphere for more complicated landing vehicles to follow.

Shirk, J. S., W. A. Haseltine and G. C. Pimentel, SINTON BANDS: EVIDENCE FOR DEUTERATED WATER ON MARS, Science, 147, 48-49 (1965).

The infrared absorption bands observed by Sinton at 2710, 2793, and 2898 cm^{-1}, in the spectrum of Mars, may be due to gaseous D_2O and HDO in the Martian atmosphere. The implication would be that the deuterium: hydrogen ratio exceeds that on Earth, presumably because of escape of the lighter gases from Mars, with accompanying gravitational fractionation of the hydrogen isotopes.

Tilson, S., PLANET MARS, Space-Aeronautics, 42, No. 1, 46-53 (1964).

Life may exist on Mars, and then again it may not. The answer to one of man's most persistent questions is not likely to come until late in this decade. But whether or not they contain life, the seemingly arid wastes of our neighbor planet may hold answers to other equally important questions about the origin of all the planets.

SECTION 13

MASS SPECTROMETRY

Averina, A. P., G. N. Levina, V. T. Lepekhina, and A. E. Rafal'son, OMEGATRON MASS-SPECTROMETER FOR ANALYSIS OF THE COMPOSITION OF RESIDUAL GASES IN HIGH-VACUUM SYSTEMS, Instr. Exper. Tech., 384-389, March/April 1964.

The authors describe the MKh4301 omegatron mass-spectrometer for investigation of the composition of residual gases in vacuum studies and for study of phenomena occurring during evacuation, outgassing, and gettering of electrovacuum instruments. The resolution of the mass spectrometer is 25 for mass 25; the duration of mass-spectrum recording on the screen of an oscilloscope is 2, 5, or 10 sec; on the chart of an ÉPP-09 recording potentiometer it is 3 or 10 min. The sensitivity relative to the partial pressure of argon with ÉPP-09 recordings is $5 \cdot 10^{-11}$ torr; with an oscilloscope recording it is $5 \cdot 10^{-10}$ torr.

Biemann, K., HIGH RESOLUTION MASS SPECTROMETRY OF NATURAL PRODUCTS, Pure & Applied Chem., 9, No. 1, 95-118 (1964).

A new and different way of interpreting mass spectra has been found. Making use of the elemental composition of all the ions formed in the spectrometer rather than a selected few as hitherto done and representation in the form of an element map makes it possible to exploit the tremendous amount of information that can be obtained with a double focusing mass spectrometer.

Biemann, K., P. Bommer, and D. M. Desiderio, ELEMENT-MAPPING, A NEW APPROACH TO THE INTERPRETATION OF HIGH RESOLUTION MASS SPECTRA, Tetrahedron Letters, No. 26, 1725-1731 (1964).

The authors used a spectrometer that permits simultaneous recording of the entire mass spectrum with high resolution on a photographic plate. They developed a semi-automatic technique to measure the distances of all lines and to convert these with the aid of an IBM 7094 computer via their accurate masses to the elemental composition of all the ions produced from organic compounds presently up to mol. wt. 900.

Blosser, E. R., SPARK SOURCE MASS SPECTROGRAPH - NEW TOOL FOR IMPURITY DETECTION, Chem. in Canada, 16, 14-15 (1964).

The advantages of using a spark source mass spectrograph for detecting trace amounts of impurities in a variety of materials are discussed.

Djerassi, C., ISOTOPE LABELLING AND MASS SPECTROMETRY OF NATURAL PRODUCTS, Pure and Applied Chem., 9, No. 1, 159-178 (1964).

Isotope labelling with deuterium is a powerful and frequently indispensable tool for the structure elucidation of mass spectrometric fragment ions and for gaining insight into the bond fission mechanisms which occur after electron bombardment.

Farrar, E., R. M. Macintyre, D. York, and W. J. Kenyon, A SIMPLE MASS SPECTROMETER FOR THE ANALYSIS OF ARGON AT ULTRA-HIGH VACUUM, Nature, 204, No. 4958, 531-533 (1964).

The authors conclude that the MS10 mass analyser is useful for isotopic dilution determination of the minute amounts of Argon-40 generated in rocks by the radioactive decay of potassium-40. Isotope ratios can be measured with an accuracy of ± 0.5 per cent after calibration of the amplifier and recorder system.

Happ, G. P., and D. P. Maier, IDENTIFICATION OF POLYMERS BY MASS SPECTROMETRIC EXAMINATION OF BOTH VOLATILE AND NONVOLATILE PYROLYSIS PRODUCTS, Anal. Chem., 36, 1678-1679 (1964).

This method of pyrolysis, in which the volatiles and nonvolatiles are separated and collected simultaneously, permits rapid examination of each in a mass spectrometer equipped with a heated inlet system. The method has been successfully applied to the identification of many cellulose esters and ethers. It has also been used for studying thermal decomposition reactions.

Hedin, A. E., C. P. Avery, and C. D. Tschetter, AN ANALYSIS OF SPIN MODULATION EFFECTS ON DATA OBTAINED WITH A ROCKET-BORNE MASS SPECTROMETER, J. Geophys. Res., 69, No. 21, 4637-4648 (1964).

Peak heights obtained with a neutral gas magnetic mass spectrometer flown on an Aerobee rocket were compared with a theoretical expression based on a model for the spectrometer source used. By use of a least squares analysis, number densities of the major neutral atmospheric constituents are found. Because temperature is a factor in determining the variation of mass spectrometer output with rocket orientation, it was found possible to estimate the ambient temperature independent of the density gradient.

Henneberg, D., APPLICATION OF HIGH RESOLUTION MASS SPECTROMETERS FOR ORGANIC ANALYSIS, Z. Anal. Chem., 205, Nos. 1-6, 124-133 (1964). (In German)

A report is given on the application of a mass spectrometer with high resolving power for the determination of the molecular formula and structure of organic compounds. Three different examples are described.

Kearns, G. L. SYSTEM FOR VAPORIZING SAMPLES DIRECTLY IN ION SOURCE OF A MASS SPECTROMETER, Anal. Chem., 36, No. 7, 1402-1403 (1964).

A system for vaporizing samples directly in the ion source of a mass spectrometer is described. The system which has been developed utilizes (a) a linear-motion high vacuum feed through; (b) a high conductance isolation valve; (c) a vacuum lock pumped by an external vacuum system and (d) a vacuum-tight sample holder (probe).

Kleipool, R. J. C., J. Th. Heins, MASS SPECTROMETRIC IDENTIFICATION OF ORGANIC DERIVATIVES, Nature, 203, No. 4951, 1280 (1964).

This report describes some features of the mass spectra obtained from the 2,4 dinitrophenylhydrazones of unbranched aliphatic aldehydes and methyl- and ethyl- ketones up to ± 10 carbon atoms.

Narcisi, R. S., H. I. Schiff, J. E. Morgan and H. A. Cohen, CALIBRATION OF A FLYABLE MASS SPECTROMETER FOR N AND O ATOM SENSITIVITY, Space Research, V. III, ed. by W. Priester, North-Holland Publ. Co-Amsterdam (1963).

Active gas atoms of N and O were produced in a flow system by subjecting N_2 to a microwave discharge. The amount of N atoms produced was accurately measured by titration with NO. The O atoms were generated by the titration reaction $N+NO \rightarrow N_2+O$. The gas in the flow system was sampled through a leak by a time-of-flight mass spectrometer which was developed for upper atmosphere sampling. Various experiments were conducted to find the optimum conditions for the detection of these atoms. It was found that the O atom response of the mass spectrometer was most affected by the entrance geometry into the ion source, while the N atom response was hardly changed. The most sensitive mass spectrometer variable for atom determination in the presence of air gases was found to be the energy of the ionizing electron; the optimum electron energy range was found to be 16 eV to 24 eV.

Narcisi, R. S., AFCRL MASS SPECTROMETER OBTAINS HIGH PRECISION IONOSPHERIC DATA, OAR Oct. 1964, Research Reviews, p. 10.

A quadrupole AF CRL mass spectrometer was flown to an altitude of 112 km. The most surprising feature of the measurements obtained by the spectrometer was the high concentration of metallic ions in the nighttime E region. This concentration represented some 20 to 30 per cent of the total ion content of the ionosphere at about 95 km.

Poklunkov, A. A., MASS SPECTROMETER RESEARCH OF STRUCTURAL PARAMETER OF THE EARTH'S ATMOSPHERE AT ALTITUDES FROM 100 TO 210 KM, J. Astronaut. Sci., 11, No. 4, 118-124, (1964).

The basic characteristics of and the results obtained with a mass spectrometer for study of the earth's atmosphere are discussed.

Rohwedder, W. K., E. Selke, and E. D. Bitner, SOURCE AND MULTIPLIER MODIFICATIONS OF A TIME-OF-FLIGHT MASS SPECTROMETER TO INCREASE SENSITIVITY, Appl. Spectr., 18, No. 5, 134-136 (1964).

The usefulness of a gas chromatograph and a mass spectrometer in tandem to analyze odor constituents is limited by the sensitivity of the mass spectrometer and by the large amount of helium carrier gas compared with the amount of sample. A time-of-flight mass spectrometer was fitted with a tightly enclosed source and operated in a continuous ionization mode to increase instrument sensitivity. A gate pulse was applied to the front end of the magnetic electron multiplier to eliminate the electrons due to the helium pulse before they reached the multiplier dynode strips. This procedure prevented saturation of the multiplier by the helium carrier gas.

Ryhage, R., USE OF A MASS SPECTROMETER AS A DETECTOR AND ANALYZER FOR EFFLUENTS EMERGING FROM HIGH TEMPERATURE GAS LIQUID CHROMATOGRAPHY COLUMNS, Anal. Chem., 36, No. 4, 759-764 (1964).

A modified Atlas CH4 mass spectrometer has been coupled to a gas liquid chromatography (GLC) column. As the compounds emerge from the column they are ionized in the ion source of the mass spectrometer and about 10% of the total ion current is used for continuous registration of the effluent. The temperature of the column can be regulated from

50^{o} to 350^{o}C. by using the temperature programmer. Two molecule separators are coupled in series between the column and the gas inlet line of the mass spectrometer. With this technique the sample-to-helium ratio is increased at least 100 times. Less than 1μ g. of material introduced onto the column suffices for a good mass spectrum. The mass range m/e 12 to 500 can be scanned and recorded in 1 or 2 seconds. Examples are given of the separation and mass spectrometric identification of 27 components from 200 μg. of methylated fatty acids from butter fat and the separation of a mixture of C_{19} to C_{30} hydrocarbons.

Schaeffer, E. J., and M. H. Nichols, UPPER AIR NEUTRAL COMPOSITION MEASUREMENTS BY A MASS SPECTROMETER, J. Geophys. Res., 69, No. 21, 4649-4660 (1964).

A quadrupole mass spectrometer with an ion source designed to minimize recombination effects was flown on a Nike-Cajun rocket, NASA 10.91 UA, from Wallops Island (latitude 37°50'N, longitude 75°29'W) at 1302 EST, May 18, 1962, to an altitude of 134.5 km. The results indicate a ratio of O/O_2 number densities of 3.1 at apogee with a rms error estimated at 0.3. At apogee, the ratio of N/N_2 number densities was less than 0.05, and the ratio of ion currents due to constituents of mass greater than 40 was less than 0.04 of the total ion current. The mean molecular weight computed from the data at 133 km is 25.5 with a rms error estimated at 0.4. These data are uncorrected for effects of the motion of the instrument package. On the basis of a simplified geometrical model, bounds on the dynamic effects are established.

Steinhagen, E., PRESENT STATE OF MASS SPECTROSCOPY FOR ORGANIC ANALYSIS, Z. Anal. Chem., 205, Nos. 1-6, 109-123 (1964). (In German)

The application of mass spectrometry to organic structure analysis is discussed. The following problems are dealt with: the apparatus, especially the use of a mass spectrometer as detector in gas chromatography; the interpretation, identification and comparison of the mass spectra.

Wolstenholme, W. A., ANALYSIS OF DRIED BLOOD PLASMA BY SPARK SOURCE MASS SPECTROMETRY, Nature, 203, No. 4951, 1284-1285 (1964).

Work has been carried out on the application of spark source mass spectrometry to the determination of trace elements in dried blood plasma. The results of this preliminary work appear to be very encouraging.

SECTION 14

MICROBIOLOGICAL STUDIES

Boyd, W. L., and J. W. Boyd, THE PRESENCE OF BACTERIA IN PERMAFROST OF THE ALASKAN ARCTIC, Can. J. Microbiol., 10, No. 6, 917-919 (1964).

Throughout the depth of the permafrost soil section examined the number of thermophilic bacteria was more or less constant; markedly fewer misophilic forms were observed in the permafrost than in the active layer. During this work many colonies of the thermophilic bacteria were isolated and examined and almost all were able to produce spores.

Brown, A. D., ASPECTS OF BACTERIAL RESPONSE TO THE IONIC ENVIRONMENT, Bacterial Rev., 28, No. 3, 296-329 (1964).

Because it contains a barrier to the diffusion of ions, the cell envelope is of outstanding importance in determining the response of bacteria to their ionic environments. In gram-positive bacteria, this barrier includes the cytoplasmic membrane, but the contribution of the cell wall is uncertain. In gram-negative bacteria, the barrier very probably comprises both membranous components of the envelope, namely, the cytoplasmic membrane and the external membrane or "cell wall".

Gram-positive bacteria become less plentiful in bacterial populations as the salt requirement (as distinct from tolerance) of these populations increases. No gram-positive extreme halophiles have been reported. In gram-negative bacteria, mucopeptide seems to become less important as salt requirement is increased; the only two extreme halophiles so far examined do not contain detectable quantities of mucopeptide, and are bounded by a single membranous structure rather than by two distinct structures such as occur in other types of bacteria. Halophilic, as well as other bacteria, have the ability to accumulate K^+ and exclude Na^+ against concentration gradients. The extent of K^+ accumulation has been correlated with the salt tolerance of some organisms. Intracellular enzymes from halophilic bacteria generally have higher salt optima than corresponding enzymes from nonhalophiles and are frequently more active in the presence of K^+ than of Na^+.

The roles of water activity and osmotic pressure in ionic phenomena are uncertain, but are probably of minor importance in many situations. An exception is during the dilution of a suspending salt solution, when transient increases in osmotic pressure occur. There are no reliable measurements to date of the magnitude of an osmotic pressure within a bacterial cell. The principal mode of action of salts on bacteria is evidently through the ions themselves by a mechanism which is largely electrostatic. In organisms with high salt requirements, cations are involved in an association with -COO- groups on membrane proteins. The halophile, *H. halobium*, contains a greater excess of aspartic and glutamic acids (excess over lysine and arginine) in its membrane than does the marine pseudomonad NCMB 845, which needs a much lower concentration of salt for membrane stability. The isolated membranes of this latter organism acquire halophilic properties (i.e., they disaggregate rather than autolyze at low ionic strengths and need higher salt concentrations for stability) when lysine- ϵ-NH_3^+ groups are substituted by -COO- groups on succinylation. A mechanism is available by which environmental cations not only stabilize a membrane against dissolution, but also contribute to its mechanical rigidity. It is likely that all bacteria which have a high salt requirement do so at least partly because of acidic proteins in their cell envelopes.

Godding, R. M., and V. H. Lynch, VIABILITY OF *BACILLUS SUBTILIS* SPORES IN ROCKET PROPELLANTS, Appl. Microbiol., *13*, 10-14 (1965).

The sporicidal activity of components used in liquid and solid rocket propellants was tested by use of spores of *Bacillus subtilis* dried on powdered glass. Liquid propellant ingredients tested were N_2O_4, monomethylhydrazine and 1,1-dimethylhydrazine. N_2O_4 was immediately sporicidal; the hydrazines were effective within several days. Solid propellants consisted of ammonium perchlorate in combination with epoxy resin (EPON 828), tris-1-(2-methyl) aziridinyl phosphine oxide, bis-1-(2-methyl) aziridinyl phenylphosphine oxide, and three modified polybutadiene polymers. There was no indication of appreciable sporicidal activity of these components.

Hagen, C. A., E. J. Hawrylewicz, and R. Ehrlich, SURVIVAL OF MICROORGANISMS IN A SIMULATED MARTIAN ENVIRONMENT, I. *BACILLUS SUBTILIS* VAR. *GLOBIGII*, Appl. Microbiol., 12, No. 3, 215-218 (1964).

Survival of *Bacillus subtilis* var. *globigii* in a simulated Martian environment was demonstrated. Previous contact with the simulated Martian soil or atmosphere reduced germination or outgrowth of unheated spores, or both. Inoculation into simulated Martian soil and then flushing with a simulated Martian atmosphere were lethal to both vegetative cells and spores. After one diurnal temperature cycle (26 to -60 C), the majority of cells present were spores. No further effect of the diurnal cycle on survival was noted in any of the experimental samples.

Hall, E., and J. Bedford, SOME NEGATIVE RESULTS IN THE SEARCH FOR A LETHAL EFFECT OF MAGNETIC FIELDS IN BIOLOGICAL MATERIALS, Nature, 203, No. 4949, 1086-1087 (1964).

Results indicate that gross lethal effects on mammalian cells are not produced either by powerful magnetic fields applied for short periods or by lower field strengths extending over many cell generation times.

Hannan, P. J., PRESSURE AS A FACTOR IN ALGAL GROWTH, Progress Report of NRL No. CS-60, 11-17 (1964).

Photosynthesis by algae is being considered as a possible source of oxygen on board submarines. Pressure is one of many variables being studied in an effort to obtain the maximum production of oxygen from a system in which algal cultures are employed. It was found that pressure is either an advantage or a detriment, depending on the flow rate and the amount of carbon dioxide fed into the system. Some of the results may have application in the fields of marine ecology and oceanography.

Ishikura, T., T. Sakamoto, I. Kawasaki, T. Tsunoda, and K. Narui, TURBIDIMETRIC MICROBIOLOGICAL ASSAY OF AMINO ACIDS, Agr. Biol. Chem., 28, No. 10, 700-709 (1964).

To shorten the time necessary for the determination of L-glutamic acid a turbidimetric microbiological assay method with *Lactobacillus arabinosus* 17-5 has been studied. It was found that the assay can be completed within 30 hours including the incubation period for the inoculum, the assay and the time for medium preparation. Turbidimetric assay methods of other amino acids such as DL-alanine with *Leuconostoc citrovorum* 8081, L-aspartic acid and L-lysine with *Leuc. mesenteroides* P-60 have also been studied.

Johnson, M. J., UTILISATION OF HYDROCARBONS BY MICROORGANISMS, Chem. & Ind., No. 36, 1532-1537, (1964).

This paper deals with a few aspects of substrate specificity in microbial growth on aliphatic hydrocarbons, with the production of microbial cells from hydrocarbons, and with the mechanism of the initial attack of hydrocarbons by microorganisms.

Ley, F. J., and A. Tallentire, STERILIZATION BY RADIATION OR HEAT - SOME MICROBIOLOGICAL CONSIDERATIONS, Pharmaceutical J., 193, No. 5255, 59-61 (1964).

The evidence is that with both heat and radiation the inactivation of bacterial spores follows an exponential law and therefore the definition of a sterilization process must be based on the probability of the existence of survivors.

Lovett, S., EFFECT OF DEUTERIUM ON STARVING BACTERIA, Nature, 203, No. 4943, 429-430 (1964).

Experiments designed to study the effect of deuterium oxide on bacteria starving in buffer solutions showed that deuterium oxide was not toxic under these conditions and that the longivity of the bacteria was increased. Aerobacter aerogenes N.C.T.C. 418 was used as the test organism.

Packer, E., S. Scher, and C. Sagan, BIOLOGICAL CONTAMINATION OF MARS II. COLD AND ARIDITY AS CONSTRAINTS ON THE SURVIVIVAL OF TERRESTRIAL MICROORGANISMS IN SIMULATED MARTIAN ENVIRONMENTS, Icarus 2, No. 4, 293-316 (1963).

It has been postulated that the accidental introduction of terrestrial microorganisms to other planets during the course of space exploration may impede or bias the detection or organic matter and possible indigenous organisms, and thereby obscure subsequent studies of extraterrestrial life. To assess the likelihood of biological contamination of Mars, we have applied the principle of natural selection on a laboratory scale. Terrestrial microorganisms were collected from a variety of environments, including regions of high alkalinity, low mean daily temperature, and low annual rainfall. The air-dried soils were then subjected in the presence of a dessicant to a simulated Martian environment involving 12-hour freeze-thaw cycles from about -60°C to about $+ 20^{\circ}$C; atmospheres of 95% nitrogen, 5% carbon dioxide, and low moisture content; ≤ 0.1 atm. pressure; and a total ultraviolet dose at 2537 Å at 10^9 erg cm^{-2}. Survivors were scored on supplemented agar. Preliminary results indicate a wide variety of survivors including obligate and facultative anaerobic spore-formers and non-spore-forming faculative anaerobic bacteria. Diurnal freezing and thawing were continued for 6 months. There was no significant loss of viability after the first freeze-thaw cycle. An extensive survey of the literature shows that survival of terrestrial microorganisms under individual simulated Martian conditions has been known for decades. Survival varies greatly with such parameters as the rate of freezing and thawing, the physics and chemistry of the medium, and the individual species studied. A primary deleterious effect of low temperatures is the unavailability of liquid water. The present investigation shows the absence of pronounced synergistic effects inhibiting survival. The probable existence of organic matter and moisture on Mars, at least in restricted locales and times, makes it possible that terrestrial microorganisms can also reproduce on Mars. The demonstration that all samples of terrestrial soil tested contain a population of microorganisms which survive in simulated Martian environments strongly underscores the need for scrupulous sterilization of all spacecraft intended for Mars landing.

Rouf, M. A., SPECTROCHEMICAL ANALYSIS OF INORGANIC ELEMENTS IN BACTERIA, J. Bacteriol, 88, No. 6, 1545-1549 (1964).

Quantiative spectrochemical analyses of inorganic elements in the vegetative cells of Escherichia coli, Sphaerotilus natans, Micrococcus roseus, Bacillus cereus, and the spores of B. cereus were made. The following elements were found to be present in the ash samples: B, Na, Mg, Al, Si, P, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sr, S, Ag, Sn, Ba, Pb, V, and Mo. These could be divided into major, minor, and trace elements, depending on the relative amounts in the cells. Mg, P, K, and S were considered as the major elements; Ca, Fe, Zn, and, perhaps, Cu and Mn as the minor elements, and the rest as trace elements. Mg concentrations were higher in the cells of the gram-positive M. roseus and B. cereus than in the gram-negative E. coli and S. natans. The latter organism contained 2.6% Fe_2O_3 (dry weight basis). The vegetative cells of B. cereus were higher in Mg, P, K, Na, Ag, and lower in Si, Ca, Zn, Mn, and Cu than were its spores.

Sweeney, E. E., STUDY OF MARBAC EXTRATERRESTRIAL LIFE DETECTION CONCEPT, Seventh Monthly Letter Report on Contract NASw-810, NASA Report No. X64-17515, May 1964.

A new digital voltmeter provided sensitivity and reliability sufficient to advance research significantly concerning microbial oxidation-reduction potential changes. The voltmeter's high impedance (1000 megohms) and short sample periods (0.01, 0.1, and 1 second) have given readings precise to within ± 1 millivolt. Four microbes were tested in six standard media and some distinctive differences were noted. Differences in total potential change produced or time required to reach a given potential change, in one medium, indicate the usefulness of redox in differentiating microorganisms. For example, Escherichia coli and Aerobacter aerogenes both produce nitrite from nitrate (a classical bacteriological test), but the potential changes from their growth in nitrate broth are distinctive. Although Pseudomonas fluorescens grew well in trypticase soy broth, its potential change in 20 hours was only about one-half that of E. coli in the same medium in 7 hours.

Bacterial counts were shown to be reproducible to about 3 to 8% (deviations from the median) for Coulter (electronic) counts and to about 6 to 11% for plate (viable) counts.

Woolfolk, C. A., and H. R. Whiteley, REDUCTION OF INORGANIC COMPOUNDS WITH MOLECULAR HYDROGEN BY MICROCOCCUS LACTILYTICUS, I. STOICHIOMETRY WITH COMPOUNDS OF ARSENIC, SELENIUM, TELLURIUM, TRANSITION AND OTHER ELEMENTS, J. Bacteriol., 84, 647-658 (1962).

Extracts of Micrococcus lactilyticus (Veillonella alcalescens) oxidize molecular hydrogen at the expense of certain compounds of arsenic, bismuth, selenium, tellurium, lead, thallium, vanadium, manganese, iron, copper, molybdenum, tungsten, osmium, ruthenium, gold, silver, and uranium, as well as molecular oxygen. Chemical and manometric data indicate that the following reductions are essentially quantitative: arsenate to arsenite, pentavalent and trivalent bismuth to the free element, selenite via elemental selenium to selenide, tellurate and tellurite to tellurium, lead dioxide and manganese dioxide to the divalent state, ferric to ferrous iron, osmium tetroxide to osmate ion, osmium dioxide and trivalent osmium to the metal, uranyl uranium to the tetravalent state, vanadate to the level of vanadyl, and poly-molybdate ions to molybdenum blues with an average valence for molybdenum of +5. The results of a study of certain other hydrogenase-containing bacteria with respect to their ability to carry out some of the same reactions are also presented.

Yu-Sun, C. C. C., BIOCHEMICAL AND MORPHOLOGICAL MUTANTS OF ASCOBOLUS IMMERSUS, Genetics, 50, No. 5, 987-998 (1964).

Eight biochemical mutants and 16 morphological mutants have been obtained in the heterothallic ascomycete Ascobolus immersus after X-ray or ultraviolet irradiation of ascospores from wild strains. Six of the biochemical mutants require amino acids and one requires a nucleic acid component. There was a preponderance of colonial mutants among the morphologicals. Both the biochemical and morphological mutants are due to mutations of single genes. Genetic data indicate three linkage groups, with two loci in each of groups I and II and four loci in group III. Mating type and w-1 are closely linked to their respective centromeres.

Vishniac, W., BACTERIAL ECOLOGIES IN LIMONITE, Presented at the COSPAR Meeting, May 1964, Florence, Italy.

In conclusion it can be said that an environment of limonite may provide a suitable ecological basis for respiratory and photosynthetic organisms, while the extent to which water of crystallization is retained in limonite may function as a water reservoir for growing microorganisms.

SECTION 15

OPTICAL ROTATION STUDIES

Craig, J. C., S. K. Roy, OPTICAL ROTATORY DISPERSION AND ABSOLUTE CONFIGURATION - I. α-AMINO ACIDS, Tetrahedron Letters, 21, 391-394 (1965).

Optical rotatory dispersion measurements of six enanitiomeric pairs of α-amino acids, both in neutral and in acidic solution, have shown that the direction and slope of the ORD curve between 200 and 225 mμ will indicate the absolute configuration of the α-asymmetric center.

Dirkx, I. P., P. J. Van der Haak, F. L. J. Sixma, EVALUATION OF A SIMPLE METHOD FOR OPTICAL ROTATORY DISPERSION MEASUREMENTS IN THE VISIBLE AND ULTRAVIOLET REGIONS, Anal. Chem., 36, 1988-1991 (1964).

A method for measuring optical rotations based on the laws governing the transmittance of polarized light by a polarizing prism can be extended to optical rotatory dispersion measurements by constructing an ORD attachment for a standard spectrophotometer. Expressions for sensitivity and maximal sensitivity are derived. The effects of these relationships on constructional possibilities, precision, reproducibility, etc., are discussed. This indirect method can introduce a number of systematic errors. The causes of these errors together with the precautions to be taken for their elimination are discussed. The rather complex expressions can be reduced to more simple formulas to be used in practice. The instrument described has a sensitivity of about 0.002° and a standard deviation of 0.004°, and measurements can be carried out down to about 215 mμ.

Fasman, G. D., E. Bodenheimer, C. Lindblow, OPTICAL ROTATORY DISPERSION STUDIES OF POLY-L-TYROSINE AND COPOLYMERS OF L-GLUTAMIC ACID AND L-TYROSINE. SIGNIFICANCE OF THE TYROSYL COTTON EFFECTS WITH RESPECT TO PROTEIN CONFORMATION, Biochem., 3, 1665-1674 (1964).

The synthesis of high-molecular-weight (60,000-125,000) poly-L-tyrosine and copolymers of L-tyrosine and L-glutamic acid (random and block) is reported. Poly-L-tyrosine can exist in either a helical or a random-chain conformation in the un-ionized form. The optical rotatory dispersion (ORD) of helical poly-L-tyrosine (in 0.2 M NaCl, pH 11.2) over the wavelength range 500-227 mμ is recorded. Multiple Cotton effects are observed with peaks at 286 mμ $[m']_{286} = 2650^{\circ}$, and 254 mμ $[m']_{254} = 4240^{\circ}$, and a trough at 238 mμ $[m']_{238} = -6410^{\circ}$. Upon ionization of the phenolic hydroxyls of poly-L-tyrosine the positive peak of the Cotton effect at 286 mμ vanishes, the peak at 254 mμ diminishes, and simultaneously the trough at 238 mμ decreases. This probably represents a helix → random-coil transition. The b_o changes from + 570 to + 413 during this structural change. Ultraviolet-absorption spectra of the helical polypeptide indicate that the pK_a of the tyrosyl hydroxyl is much higher than that of the monomer, and a red shift of 2 mμ (λ_{max} = 277 mμ) is observed. The ORD and ultraviolet spectra suggest that tyrosyl-tyrosyl interactions occur in the helical conformation. ORD and ultraviolet spectra are also reported for films of poly-L-tyrosine. The negative Cotton effect (trough, 238 mμ) further suggests that poly-L-tyrosine is a right-handed helix. The tyrosyl Cotton effect (peak, 286 mμ) is not observed in copolymers of L-tyrosine and L-glutamic acid until 20 mole % tyrosine is present. Although this Cotton effect is therefore unlikely to be observed in proteins, the b_o and $[m']_{233}$ values can be significantly altered and the interpretation of such values, for proteins with high tyrosine contents, may be complex.

Gill, S. J., R. L. Glogovsky, APPARATUS FOR THE MEASUREMENT OF OPTICAL ROTATION OF SOLUTIONS AT HIGH PRESSURE, Rev. Sci. Instr., 35, 1281-1283 (1964).

A polarimeter was constructed so that the sensitive optical components could be subjected to the same pressure within a high pressure optical bomb, thereby avoiding the problem of large double refraction effects from two windows under a large difference of pressure. One of two Polaroids within the high pressure bomb is rotated through a fixed angle by a mechanical coupling with a solenoid driven magnet. The transmission of light for a given wavelength setting is measured in both Polaroid positions by means of a Beckman DU spectrophotometer. The sensitivity of the apparatus is ± 0.01° in the range of 0-5° rotation. The apparatus has been specifically designed for pressure studies to 2000 atm, although the method is inherently capable of even higher pressures.

Izuka, E., and J. T. Yang, OPTICAL ROTATORY DISPERSION OF L-AMINO ACIDS IN ACID SOLUTION, Biochem., 3, No. 10, 1519-1524 (1964)

Optical rotatory dispersion of twenty L-amino acids in aqueous solution (pH 1) was measured between 190 and 600 mμ at 27°. All exhibited a positive Cotton effect near 210 mμ , which is perhaps attributable to the carboxyl chromophore attached to the asymmetrical α -carbon. Tyrosine and tryptophan (but not phenylalanine) showed an additional Cotton effect near 275 mμ in the absorption band of the aromatic group. Cystine had an unusually high levorotation, an order of magnitude higher than the other amino acids studied. The molar rotations, [M] , above 270 mμ can be fitted with a two-term Drude equation: $[M] = k_1/(\lambda^2 - \lambda_1^2) + K_2/(\lambda^2 - \lambda_2^2)$, one accounting for the 210 mμ Cotton effect and the other for the remaining partial rotations. The equation was solved graphically by plotting [M] $(\lambda^2 - \lambda_2^2)$ for λ_1 = 210 mμ and trial values of λ_2 until a straight line was obtained. In all cases (except tyrosine, tryptophan, and cystine) k_1 was positive and k_2 was negative, although the total rotations in the visible region differed widely in both sign and magnitude.

Jirgensons, B., STUDY OF THE OPTICAL ROTATORY DISPERSION OF PROTEINS WITH IMPROVED SPECTROPOLARIMETRIC TECHNIQUES, Makrolmol. Chem., 72, 119-130 (1964).

The optical rotatory dispersion of a series of proteins was studied and compared by using two improved instrumentations. The measurements were made in the wave length range of 200-400 mμ . The earlier with less perfect instruments obtained results were corrected. It was found that regarding the rotatory dispersion in far ultraviolet, all native globular proteins can be classified into two groups: 1) those showing a negative COTTON effect with a sharp minimum in the dispersion curves at 233 mμ , and 2) those having in their curves a flat minimum at 220-233 m μ. To the first group belong the proteins which have a strongly negative MOFFITT-YANG constant (b_o) and whose polypeptide chains probably have the α-helical conformation to a large extent. The native proteins of the second group (b_o - 0) probably are devoid of the α-helix or have it only in relatively insignificant amount. The amplitude and position of the negative COTTON effect can be applied as an independent criterion for the study of conformation. The COTTON effect study is especially useful for substances which are available in very small quantities, since the specific rotation measured with the wave length of 233 mμ ranges between -1600 and -12,000°.

Keston, A. S., A SENSITIVE POLARIMETRIC ASSAY OF MUTAROTASE UTILIZING RACEMIC MIXTURES OF SUGARS, Anal. Biochem., 9, No. 2, 228-242 (1964)

A sensitive method is described for assays of mutarotase that involves following the optical rotation of a racemic mixture containing one enantiomer which is a substrate of the enzyme. Changes in optical rotation are produced only when a specific catalyst is present. The method is quite insensitive to nonspecific catalysts and to variations of pH, substrate concentration, and temperature. It is also insensitive to the presence of substantial amounts of extraneous proteins. The peak value of optical rotation produced constitutes the sole observation required for calculation of mutarotase content. Enantiomers of five substrates of mutarotase were found to be inhibitors of kidney and intestinal mutarotase.

Lin, C. Y., D. W. Urry, and H. Eyring, ULTRAVIOLET ROTATORY DISPERSION OF ADENOSINE, INOSINE AND THEIR MONOPHOSPHATES, Biochem. & Biophys., Res. Comm. 17, No. 6, 642-647 (1964).

This paper reports the rotatory dispersion of adenosine and AMP in the ultraviolet region from 200 mμ to 320 mμ and of inosine and IMP in the range 210 mμ to 280 mμ . No anomolous dispersion is found at wavelengths greater than 320 mμ , whereas three Cotton effects may be noted at shorter wavelengths, centering approximately at 260 mμ , 210 mμ and 190mμ. The effect of pH, temperature and solvent on these three Cotton effects is treated here.

Mason, S. F., OPTICAL ROTATORY POWER: SOME RECENT DEVELOPMENTS, Chem. & Ind., No. 29, 1286-1290 (1964).

The author discusses the theoretical aspects and the various applications of optical rotatory power.

Rao, V. W. R., ROTATORY DISPERSION BEHAVIOR OF CARBOHYDRATES: A COTTON EFFECT IN D-GLUCOSE, D-XYLOSE AND VARIOUS RELATED SACCHARIDES, Nature, 200, No. 4906, 570-571 (1963).

During an examination of the rotatory dispersion behavior of amylose, we observed suggestive evidence for a COTTON effect near or above 200 m μ . Studies of various model compounds now indicate that this behavior is general for carbohydrates.

Samejima, T., and J. T. Yang, OPTICAL ROTATORY DISPERSION OF DNA AND RNA, OPTICAL ROTATORY DISPERSION OF DNA AND RNA, Biochem., 3, No. 5, 613-616 (1964).

Optical rotatory dispersion (ORD) of salmon sperm DNA was measured over a wavelength range of 190-600 mμ. The dispersion curve obeyed a one-term Drude equation at wavelengths above 350 mμ. Strong Cotton effects occurred in the ultraviolet region with three peaks at 290, 228, and 200 mμ, two troughs at 257 and 215 mμ, and cross-overs (zero rotations) at about 274 and 248 mμ. Heat (90°) or alkaline (pH 12.3) denaturation of DNA depressed the Cotton effects; the profile below 250 mμ appeared to be particularly sensitive to the breaking up of the secondary structure. The ORD or rat liver RNA, which followed a simple Drude equation down to about 310 mμ wavelength, showed a strong peak and trough at 280 and 252 mμ, with a cross-over at 265 mμ. A weak peak and trough occurred at 228 and 218 mμ, followed by another very strong peak at 195 mμ. In alkaline solution or at high temperatures the 280 mμ peak and 252 mμ trough shifted to 290 and 260 mμ.

Shechter, E., and E. R. Blout, AN ANALYSIS OF THE OPTICAL ROTATORY DISPERSION OF POLYPEPTIDES AND PROTEINS, Proc. Nat. Acad. Sci., 51, No. 4, 695-702, (1964).

In this communication the authors present a new analysis of the visible and near-ultraviolet rotatory dispersions of synthetic polypeptides and proteins in aqueous solutions. The analysis not only allows the determination of α-helix content of proteins in solution, but also provides a basis for the differentiation of α-helix containing proteins from proteins containing other structures.

Shechter, E., and E. R. Blout, AN ANALYSIS OF THE OPTICAL ROTATORY DISPERSION OF POLYPEPTIDES AND PROTEINS, II, Proc. Nat. Acad. Sci., 51, No. 5, 794-800 (1964).

In this report the authors extend their system of analysis to the optical rotatory dispersions of polypeptides and proteins in a variety of organic solvents, and compare the results so obtained with the ones obtained in aqueous solutions.

Shashoua, V. E., MAGNETS - OPTICAL ROTATION SPECTRA OF CYTOCHROME C, Nature, 203, No. 4948, 972-973 (1964).

The authors have investigated the application of a new technique of magneto-optical rotation spectroscopy to the examination of different oxidation states of the cytochrome C molecule. The results for cytochrome C are quite pronounced and show large changes with the oxidation state of the molecule.

SECTION 16

SOIL CONSTITUENT ANALYSIS

Alexander, M., BIOCHEMICAL ECOLOGY OF SOIL MICROORGANISMS, Annual Rev. Microbiol., 18, 217-252 (1964).

Considerable progress has been made in the last few years in the application of biochemical concepts and techniques to ecological problems. Nevertheless, no more than the merest outer films surrounding the entire discipline of microbial ecology has been removed, a surface scratching which still has demonstrated that the field of microbial ecology is now ripe for biochemical exploration and interpretation. Only a few of the fruitful areas have been examined, even in the most cursory fashion, but the preliminary steps reveal a broad vista for future investigation. The physiological basis of microbial distribution, the geochemical functions of the population, the biochemical relationships between species and communities, the phenotypic and genotypic modifications of microorganisms in response to environment change and population pressure, the ecological and biochemical significance of the primary ecological determinants, and the metabolic basis for dominance of individual genera in specific ecosystems are but a few of the problems awaiting careful and perceptive inquiry by experimental rather than descriptive approaches and by means of an _in vivo_ rather than an _in vitro_ view of microbial biochemistry and ecology.

Aleksandrova, L.N., I.M. Andreyeva, TRANSFORMATION OF HUMIC SUBSTANCES IN THE SOIL, Soviet Soil Sci., No. 7, 634-638 (1963).

It has been established that when humic acids interact for a long period with moist non-carbonate clay loam, a fraction not precipitable by acid is split from the humic acid of sod-podzolic soil and chernozem. This fraction we have conditionally called fulvic acid. The process appears to be chemical and to be classifiable as some sort of hydrolytic splitting of the humic acid. Fulvic acids split from humic acids show a narrower C:N ratio and differ from the humic acids in the nature of their paper chromatograms.

Ball, D.F., LOSS-ON-IGNITION AS AN ESTIMATE OF ORGANIC MATTER AND ORGANIC CARBON IN NON-CALCAREOUS SOILS, J. Soil Sci., <u>15</u>, 84-92 (1964).

Examination of data on North Wales soils shows that a good correlation exists between loss-on-ignition and organic C values, determined by Tinsley's method. Ignition for half an hour at 850°C, and for 16 hours at 375 ± 5°C have both been employed. The latter has advantages over the former procedure. Regression lines and prediction limits for organic C from loss-on-ignition are given from the data obtained. Although these regressions are not necessarily expected to be generally applicable, examination of some published data suggests that closely similar expressions may be. The method, because of its simplicity, can be usefully applied in a wide range of survey, analytical, and ecological studies, in spite of the known sources of error.

Bowen, H.J.M., P.A. Cawse, SOME EFFECTS OF GAMMA RADIATION ON THE COMPOSITION OF THE SOIL SOLUTION AND SOIL ORGANIC MATTER, Soil Sci., <u>98</u>, 358-361 (1964).

The composition of the solutions extracted from two soils were altered by treatment with 5 megarads of gamma radiation. The bulk of the carbon, nitrogen, and inorganic elements set free by irradiation are thought to have arisen from the lysis of microbial cells. Manganese is increased by other processes, probably involving reduction of insoluble oxides. Much of the magnesium, nitrogen, and phosphorus present in the soil solutions after irradiation is organically bound. The composition of the soil solution is a more sensitive index of radiation damage than the changes in exchangeable nutrients.

Burges, N.A., H.M. Hurst, B. Walkden, THE PHENOLIC CONSTITUENTS OF HUMIC ACID AND THEIR RELATION TO THE LIGNIN OF THE PLANT COVER, Geochim. et Cosmochim. Acta, 28, 1547-1554 (1964).

Studies on the structure of humic acids have been retarded by the lack of suitable degradation procedures that yield aromatic monomers with some side chains intact. A relatively mild degradation under reducing conditions is described which liberates up to 30 per cent of ether-soluble material from soil humic acids and native lignin preparations. The ether-soluble fraction consists of a rich complex of phenolic and phenolic acid monomers, including C_6-C_1 and C_6-C_3 units, which have been identified by thin-layer chromatography. Two-way chromatography patterns differ for humic acids of different origins and provide a "fingerprint" technique that may remove some of the current confusion arising from lack of criteria for the characterization of this class of compounds.

The contribution of lignin from the overlying vegetation to the formation of humic acid was demonstrated by the presence of relatively unchanged lignin residues. Vanillic, syringic p-hydroxyl benzoic, guaiacyl and syringyl propionic acids have been identified. Syringyl residues occur in humic acids formed under deciduous hardwood vegetation (oak), but are absent under coniferous softwoods (pine) where vanillic acid predominates. The assumption that these are lignin-derived components was supported by the complete absence of such residues in humic acid developing in a lignin-free environment below Antarctic clumps of the moss Bryum argenteum.

Other degradation products that may be used to distinguish between different humic acids include phloroglucinol, methylphloroglucinol, protocatechuic acid, resorcinol, 3,5-dihydroxybenzoic acid, pyrogallol and orcinol. Several of these can be obtained by degradation of model substances of the C_6-C_3-C_6 type. They may represent a flavonoid contribution of the parent vegetation or, alternatively, could be derived from soil microbial syntheses where 1-3-5 substitution patterns are quite common.

Native spruce lignin yielded a mixture of 34 compounds. The presence of p-hydroxbenzoic acid confirmed the probable existence of non-methoxylated phenyl residues in soft-wood lignin.

Coulson, C.B., R.I. Davies, E.J.A. Khan, HUMIC-ACID INVESTIGATIONS. II. STUDIES IN THE FRACTIONATION OF HUMIC ACIDS, J. Soil Sci., 10, 271-283 (1959).

Paper and column chromatography using partition and ion-exchange conditions, high- and low-voltage paper electrophoresis, and gelatine-gel diffusion have all been used in an attempt to fractionate humic acids, but only limited success is recorded.

Dormaar, J.F., FRACTIONATION OF THE HUMUS OF SOME CHERNOZEMIC SOILS OF SOUTHERN ALBERTA, Can. J. Soil Sci., 44, 232-236 (1964).

Two orthic profiles, widely separated geographically, of each of four parent materials - lacustrine, alluvial-lacustrine, glacial till, and aeolian - were selected at undisturbed sites within each of the Brown, Dark Brown, and Thin Black soil zones. Material from the Ah and Bm horizons was subjected to solvent extraction, and for each sample the total organic carbon of seven different fractions was determined.

The efficiency of the procedure in extracting humus carbon decreased as the total carbon content of the soil increased. Total organic matter, the first humic acid fraction, and the combined total of the three humic acid fractions showed significant differences between soil zones. The only significant separation between all four parent materials was made by the alcohol-benzene fraction. Other parent material separations were possible only following the summation of data of several fractions, such as the three humic acid fractions or the two fulvic acid fractions. A simplification of the procedure in case of soils of one Order and a modification to overcome the impeding effect of increased carbon content are requisite.

Dormaar, J.F., D.L. Lynch, AMENDMENTS TO THE DETERMINATION OF "URONIC ACIDS" IN SOILS WITH CARBAZOLE, Soil Sci. Soc. Amer. Proc., 26, 251-254 (1962).

The release of soil "uronic acids" from four soil profiles was determined using 0.5N NaOH extracting solutions at 22° and 70°C. with an intermediate treatment using N HF-HCl. The amounts of "uronic acids" released by alkali extractions were compared with the amounts released by either an HCl or H_2SO_4 hydrolyses of these soils. An exchange resin Amberlite IR-120 (hydrogen form) and other means were investigated as to their efficiency in removing excessive amounts of iron from these soil solutions. A comparison of recoveries of pure galacturonic acid after hydrolysis with HCl and H_2SO_4 solutions was also made.

Both the extraction and the hydrolytic procedures released large amounts of soil "uronic acids" from the four soils. However, in terms of time and simplicity the hydrolytic methods are to be preferred. Iron was most effectively removed from these soil solutions by an ion-exchange resin (Amberlite IR-120). A more rapid rate of decarboxylation of pure galacturonic acid occurred with HCl hydrolyses than similar hydrolyses with equivalent solutions of H_2SO_4. The content of "uronic acids" ranged from 1.2 to 3.9% of the organic matter in the four soil profiles.

Eno, C.F., H. Popenoe, GAMMA RADIATION COMPARED WITH STEAM AND METHYL BROMIDE AS A SOIL STERILIZING AGENT, Soil Sci. Amer. Proc., 28, 533-535 (1964).

Red Bay loamy fine sand and Everglades muck were sterilized with gamma radiation, steam, and methyl bromide. Exchangeable NH_4^+; extractable N, P, S; moisture equivalent; cation-exchange capacity; and organic matter were measured. None of the sterilization treatments significantly altered cation-exchange capacity. Steam significantly increased the amounts of N, P, and S extracted and the organic matter content values, compared to the check and the other two soil treatments; it also significantly decreased the moisture equivalent percentage. Gamma ray and methyl bromide sterilization generally increased the release of N, P, and S above the check. There was also a strong indication, based on the N data, that sterilization by gamma rays disrupted the soil organic materials more than methyl bromide. Finally, the intensity of all these factors is most closely associated with the organic matter content of the soil. Therefore, a sand, for example, would not be altered nearly as much as a loam or an organic soil.

Flaig, W., EFFECTS OF MICRO-ORGANISMS IN THE TRANSFORMATION OF LIGNIN TO HUMIC SUBSTANCES, Geochim. Cosmochim. Acta 28, 1523-1535 (1964).

Conditions important in the formation of humic substances are mentioned briefly. Because of the relatively fast decomposition of cellulose and the slower rate of decompositon of lignin, the latter can be considered to be the essential parent material of humic substances.

Transformation of the lignin fraction isolated from rotted plant material, with respect to time, are discussed. During the decomposition of plant material, the lignin fractions are oxidatively decomposed. The most remarkable alteration are the increase in nitrogen content and the decrease in methoxyl content. Infrared spectroscopic investigations of lignin fractions isolated at different rotting times illustrate that these are progressively transformed into humic substances. During the decomposition of plant materials, different lignin decomposition products, such as guaiacyl- and p-hydroxyphenyl derivatives, could be identified in the aqueous extracts together with a number of unknown phenolic compounds. Syringyl derivatives have not yet been found.

During oxidation of different lignin decomposition products, the essential reactions are decomposition of the side chain, demethylation, oxidation to quinones, dimerization and polymerization, and cleavage of the ring. Examples of these oxidation reactions of the lignin decomposition products and the resultant products are discussed.

The transformation of lignin decomposition products by means of lignin-rotting fungi was also studied. The lignin decomposition products were added to the cultures of fungi as well as submitted to oxidation catalyzed by purified phenoloxidases. For this purpose, phenylacrylic derivatives were labelled at different positions in the carbon atoms of the side chain. Polymerizates are formed through intermediate radical-like or quinoid steps during oxidation catalyzed by the phenoloxidases.

Cleavage of methyl ethers is also an important reaction during oxidation of lignin decomposition products. Lignin decomposition products labelled at the methyl group of the methyl ethers, when added to the cultures of fungi, split off labeled carbon dioxide. Part of the activity can also be found in protein synthesized by the fungi. Most of the activity of the protein is found in the methionine and serine. The methyl group of the methyl ethers of the lignin decomposition products can, therefore, serve for methylation of the precursors of these two amino acids.

In the presence of phenyloxidases, polymerizates are formed from the compounds labeled at the methyl ether group total activity remains in the polymerizates. If these polymerizates are added to cultures of fungi, a slow cleavage of the methyl ether takes place. Cleavage of the ring also takes place during the enzymatic oxidation of lignin decomposition products. The mechanism of this cleavage was elucidated using carboxyl-labelled protocatechuic acid.

According to the experimental results, the formation of humic acids from lignin, that is, the decomposition products formed by the action of micro-organisms, can be described as follows: polymerizates are formed simultaneously with degradation of the side chain. Cross-linking of the polymers through the side chains decreases with continued decomposition, and linkage of the rings takes place to an increasing degree. Increasing demethylation enables increasing condensation with nitrogen-containing compounds.

Griffin, D.M., SOIL MOISTURE AND THE ECOLOGY OF SOIL FUNGI, Bio. Rev., 38, 141-166 (1963).

Some basic concepts concerning soil physical factors have been briefly discussed. The importance of evaluation of the total soil moisture stress, as indicative of the energy which must be used by an organism to gain water from the soil, is shown. This total stress can be divided into tensiometric and osmotic components, of which the latter is important only in saline or heavily fertilized soils and is but briefly mentioned. Tensiometric suction is discussed and shown to be best described along with a measure of the texture and structure of the soil by means of the moisture characteristic. From such a characteristic, additional information concerning porosity and aeration can be obtained.

Although there are few published experiments in which suction has been measured, none suggests a limitation of fungal growth directly due to suction factors in the soils between saturation and the permanent wilting point of mesophytic higher plants. Evidence derived from controlled humidity experiments reveals that most fungi can exert sufficient force to absorb water from atmospheres at a lower relative humidity than those in equilibrium with soil at the permanent wilting point. It is then suggested that absorption of soil water per unit area of absorptive surface will need to occur much less rapidly in the case of soil fungi than of higher plants, so that the growth of the former will not be limited to the same extent by reduction in the hydraulic conductivity of the soil. The conclusion is drawn that the majority of fungi will probably be able to grow in soils somewhat, or even considerably, drier than the permanent wilting point of higher plants.

From an examination of the evidence it is concluded that in a compact soil spores are dispersed by the soil water only when that water is moving through a nearly saturated soil. In natural soils, however, where cracks, root channels, etc., are present, rapid movement of water, and thus of spores, may take place to a considerable depth even when the general soil mass is far from saturated.

The literature reveals that such factors as moisture content, texture and structure, which affect soil aeration, have a profound influence on fungal activity and it is postulated that aeration is, in fact, the effective agent. Although the evidence is far from adequate, it appears that both excess of carbon dioxide and an insufficiency of oxygen are implicated as inhibitors.

Ivarson, K.C., I.L. Stevenson, THE DECOMPOSITION OF RADIOACTIVE ACETATE IN SOILS. II. THE DISTRIBUTION OF RADIOACTIVITY IN SOIL ORGANIC FRACTIONS, Can. J. Microbiol., 10, 677-682 (1964).

Soils incubated with C^{14}-labelled acetate for 6 to 9 hours showed that 22-30% of the acetate was oxidized to CO_2. Fractionation of the soil revealed that the radioactivity of the remaining substrate was widely distributed in various fractions. Greatest activity was noted in the acid hydrolyzable humin fraction (50%) with lesser amounts (5-10%) being recovered in the fulvic acid and alcohol extract. Hymatomelanic acid, α-humus, and β-humus contained only traces of activity.

Ion-exchange separation of the acid hydrolysate of the humin fraction indicated that a considerable portion of the activity was associated with an unidentified compound which had certain characteristics of itaconic acid. Radioactivity was also found to be present in the 15 amino acids identified.

Ivarson, K.C., F.J. Sowden, METHODS FOR THE ANALYSIS OF CARBOHYDRATE MATERIAL IN SOIL: I. COLORIMETRIC DETERMINATION OF URONIC ACIDS, HEXOSES AND PENTOSES, Soil Sci., 94, 245-250 (1962).

A method is described for the colorimetric determination of uronic acids, hexoses, and pentoses in soil and leaf litter. Samples are treated with 72 percent H_2SO_4 for 2 hours, then diluted to N H_2SO_4 and refluxed for 16 hours. The crude hydrolyzates thus obtained are neutralized and then clarified and separated into sugars and uronic acids by passage through an ion-exchange column. The hexoses and pentoses are determined with anthrone and aniline acetate, respectively. Determining hexoses with chromotropic acid gives higher results than with anthrone. The uronic acids are estimated with the carbazole procedure. These methods give data for the pentose and hexose sugars that are comparable to those obtained by the determination of the sugars after cellulose column and paper chromatography. Furfural determinations also indicated that the values obtained for pentoses and uronic acids were in the correct range. The proposed method should give, therefore, a satisfactory estimation of the amount and composition of the soil carbohydrate.

Johnston, H. H., SOIL ORGANIC MATTER: II. STUDIES OF THE ORIGIN AND CHEMICAL STRUCTURE OF SOIL HUMIC ACIDS, Soil Sci. Soc. Amer. Proc., 25, 32-35 (1961).

Small quantities of soil humic acids were supplied to cultures of Nostoc muscorum, resulting in stimulation of growth and nitrogen fixation. Various organic compounds were added to compare stimulations and structural relationships. Of all the compounds tested, catechol and humic acids were found to give the greatest increases of nitrogen fixed. Part of the increase in nitrogen fixation was thought to be due to boron contained by the humic acids. Lignin oxidized by H_2O_2 and microorganisms was analyzed by infrared spectroscopy. The product formed by microorganisms gave a material with similar paper electrophoretic mobility as natural humic acids. Controlled degradation of humic acids and lignin gave various phenols. Humic acid chromatograms showed four phenols present: catechol, phenol, guaiacol, and o-cresol. One spot found in the humic acid chromatograms has not yet been identified. Bean root lignin when subjected to the same degradation gave a spot in the same position and with the same color. Guaiacol and phenol were also identified from bean root lignin.

Jones, D., E. Griffiths, THE USE OF THIN SOIL SECTIONS FOR THE STUDY OF SOIL MICRO-ORGANISMS, Plant & Soil, *20*, 232-240 (1964).

Modifications of Alexander and Jackson's technique for the preparation of thin soil sections are described.

The distribution of bacterial colonies within soil aggregates has been examined using this technique and it has been demonstrated that distinct distribution patterns may occur.

Mayaudon, J., P. Simonart, ASSIMILATION OF ^{32}P ORTHOPHOSPHATE BY SOIL MICROORGANISMS, Annales del'Institut Pasteur N° d'orde 4124, *107*, 188-196 (1964). (In French)

In a meadow soil the authors study the take up of ^{32}P orthophosphate by the soil microflora.

The findings show that ^{32}P RNA appears first: after 10 minutes incubation; then after 2 days, ^{32}P DNA appear. This latency period seems to correspond to the mean time of cell division of the soil microflora. The rate of ^{32}P RNA formation varies according to the time: it is maximal during the first 30 minutes following inoculation; then it suddenly drops and remains constant for a few hours, during which the ^{32}P RNA formed corresponds to an actual RNA synthesis. This value is proportional to the microflora development.

Immobilization of ^{32}P in nucleic acids allows an *in situ* study of the soil microflora physiology.

Mayaudon, J., P. Simonart, HUMIFICATION OF SOIL MICROORGANISMS LABELLED WITH ^{14}C, Annoles de l'Institut Pasteur, N° d'orde 4067, *105*, 257-266 (1963). (In French)

Live ^{14}C *Azotobacter* inoculated into a pasture soil contributes to make radioactive humic and fulvic acids. Under the same conditions, ^{14}C *Aspergillus* yields an important radioactive residue in humine. The joint action of these two types of microbial flora might explain the distribution of nitrogen in the various humic fractions of the soil.

The ^{14}C residue formed by the decay of ^{14}C *Azotobacter* in soil constitutes a neoformation aggregate, whose resistance to physical agents is weaker than that of the organic matter which preexists in soil.

After stabilization of this aggregate by addition of calcium chloride, the ^{14}C microbiological flora constitutes about 4 p. 100 of the ^{14}C of the soil.

McLaren, A.D., R.A. Luse, J.J. Skujins, STERILIZATION OF SOIL BY IRRADIATION AND SOME FURTHER OBSERVATIONS ON SOIL ENZYME ACTIVITY, Soil Sci. Soc. Amer. Proc., 26, 371-377 (1962).

As an introduction to the study of radiation-sterilized soil as a medium for microbial and plant growth, survival curves for microorganisms have been obtained with 5 and 1 Mev. electrons, hard X-ray and gamma radiation. For a given soil, bacterial survival curves with these radiations are almost superimposable, but they differ among soils. Bacterial numbers in soils approach zero at 2 Mrep. doses, but 4Mrep. doses are necessary to insure complete sterility for larger soil volumes.

Soil sterilized by radiation still manifests enzyme activity (phosphatase, urease) in the presence of suitable substrates. If this is a general situation, studies of the uptake of some organic nutrients from sterile soil by sterile root systems will not be free from the problem of hydrolysis *in situ*. Sterilized soil is not toxic toward tomato plants nor does it provide extra nutrient to the plants as a result of radiation. It does, therefore, provide the plant physiologist with a medium for the study of uptake of inorganic nutrients by sterile plants which possesses all the purely chemical and structural features of natural soil.

Mortensen, J.L., F.L. Himes, SOIL ORGANIC MATTER, Chemistry of the Soil, 2nd Edition, ed. by F.E. Bear, Am. Chem. Soc. Monographic Series, Reinhold Pub. Co., N.Y., pp. 206-241 (1964).

The studies on a few components of soil organic matter have been reviewed. Many components have been studied in less detail because of many reasons. These constituents of soil organic matter include the aromatic compounds, sulfur compounds, free radicals, and coordination compounds. So far, no universal solvent has been found for dissolving soil organic matter. Similarly, no solvent has been found that is capable of dissolving all organic-nitrogen compounds or phosphorus compounds or other broad groups of compounds. Since the commonly used solvents dissolve a variety of organic and inorganic compounds from the soil, the separation, purification, and identification of one or more of the constituents in the extract is often tedious and complex. Yet, since the soil probably contains most types of organic compounds synthesized by biological organisms, the identification and characterization of these compounds will require the ingenuity and time of many chemists.

Nord, F.F., THE FORMATION OF LIGNIN AND ITS BIOCHEMICAL DEGRADATION, Geochim. et Cosmochim. Acta, 28, 1507-1521 (1964).

The mechanism of the biogenesis of lignin has intrigued lignin chemists ever since the discovery of this complex material. The process of lignification is the transformation in certain plants whereby the aromatic lignin polymer is synthesized, ultimately from CO_2, probably by way of intermediates related to carbohydrates. Lignification is but one illustration of the more general phenomenon of aromatization, i.e. the conversion by living cells of non-aromatic precursors into compounds containing benzenoid-type rings.

Fundamentally, an understanding of the biogenesis of lignin centers on knowing the enzymic pathway by which this highly polymeric aromatic compound is formed from substances pre-existing in the plant. A comprehensive solution to this problem requires consideration of two basic assumptions: First, the complex material must have its ultimate origin in certain relatively simpler units; and second, the biogenesis of lignin must involve the functioning of not one enzyme system but, rather, of several different systems, each exerting its influence in its substrate in an organized and integrated sequence, with the sum total of the reactions giving rise to a product, lignin, which is required for the existence of the mature plant. Thus, in such a biosynthetic study, both the precursors of the final product and the energetics of the reactions involved must be considered.

To elucidate the mechanism of the enzymic degradation of softwood lignin by white-rot fungi, studies were conducted of the chemical properties of isolated pine and spruce lignins after decay by Polyporus versicolor, Polyporus hirsutus, Poria subacida J247 and N199, Fomes fomentarius, Fomes annosus, and Trametes pini. Determinations of the intermediate products formed from these lignins by the action of the fungi were also carried out. Products thus derived from lignin were coniferaldehyde, p-hydroxycinnamic acid, guaiacylglycerol and guaiacylglycerol-β-coniferyl ether. The results indicate the presence of the guaiacylglycerol-β-coniferyl ether unit in the lignins of pine and spruce woods.

To understand the metabolism of lignin degradation products by white-rot fungi, investigations were carried out on the enzymic conversion by Polyporus versicolor and Fomes fomentarius of certain aromatic compounds structurally related to softwood lignin. Products derived in this way were vanillic acid, vanillian and dehydrodivanillin from ferulic acid and 4-hydroxy-3-methoxyphenylpyruvic acid; vanillic acid, vanillin, dehydrodivanillin and ferulic acid from coniferaldehyde and coniferyl alcohol; vanillic acid, vanillin, dehydrodivanillin and 4-hydroxy-3-methoxyphenylpyruvic acid from guaiacylglycerol and its β-guaiacyl ether. It is therefore suggested that the 4-hydroxy-

3-methoxyphenylpyruvic acid is an intermediate in the fugal decomposition of the guaiacylglycerol-β-coniferyl ether units present in softwood lignin, and that the enol form of this acid is converted to vanillic acid and vanillin. Coniferaldehyde and ferulic acid, obtained from lignin, were also converted to vanillic acid via vanillin.

Quinn, J.G., CHLORIDE INTERFERENCE IN THE DICHROMATE OXIDATION OF SOIL HYDROLYSATES, Soil Sci. Soc. Amer. Proc., 28, 456 (1964).

The addition of HgO to the dichromate-acid digestion mixture in the carbon determination of soil hydrolysates effectively eliminates the error due to the presence of chloride.

Savage, S.M., F.J. Stevenson, BEHAVIOR OF SOIL HUMIC ACIDS TOWARDS OXIDATION WITH HYDROGEN PEROXIDE, Soil Sci. Soc. Amer. Proc., 25, 35-39 (1961).

Humic acids from two Brunizem soils were oxidized with a view to obtaining and detecting intermediate products which would provide clues to their structures. A comparison of optimum conditions for the production of intermediate products showed that humic acid extracted from soil with 0.1M sodium pyrophosphate (pH 9.0) was more susceptible to oxidation than humic acid extracted with 0.5N NaOH. Intermediate products obtained from pyrophosphate humic acid by oxidation were different chemically from those derived from alkali humic acid.

Paper partition chromatography of the low molecular weight acids obtained by oxidation, as well as column chromatography on silic acid, failed to reveal the presence of the common aliphatic and benzenoid acids. In one preparation, phthalic and trimesic acids were identified tentatively by paper chromatography. Evidence obtained indicated that the intermediate products were polycarboxylic.

The intermediate products formed by H_2O_2 oxidation of humic acids contained N, suggesting that humic acids contain N as part of their molecular structures. Ultraviolet analyses of the intermediate products failed to reveal the presence of azo- or diazo-N compounds, or of constituents which contain heterocyclic 6-membered ring N.

Schnitzer, M., J.G. Desjardins, FURTHER INVESTIGATIONS ON THE ALKALINE PERMANGANATE OXIDATION OF ORGANIC MATTER EXTRACTED FROM A PODZOL Bh HORIZON, Canadian J. of Soil Sci., 44, 272-279 (1964).

Organic matter extracted from a Podzol Bh horizon was oxidized with alkaline permanganate. The oxidation product was extracted with organic solvents. The material soluble in the organic solvents was methylated and then distilled under vacuum. By means of gas chromatography the methyl esters of the following benzene carboxylic acids were identified in the distillate and estimated quantitatively: 0.03% o-phthalic acid, 0.05% trimellitic acid, 0.05% pyromellitic acid, 0.05% prehnitic acid, 0.06% mellophanic acid, 0.08% benzene pentacarboxylic acid, and 0.06% mellitic acid. These yields are expressed on the basis of the original dry ash-free organic matter.

The compounds identified are discussed in relation to the probable chemical structure of the organic matter and to previous investigations on the same organic matter.

Schnitzer, M., S.I.M. Skinner, ORGANO-METALLIC INTERACTIONS IN SOILS: 3. **PROPERTIES OF IRON- AND ALUMINUM-ORGANIC-MATTER COMPLEXES, PREPARED IN THE LABORATORY AND EXTRACTED FROM A SOIL**, Soil Sci., 98, 197-203 (1964).

Methods for the preparation of iron- and aluminum-O.M. complexes containing three different molar ratios of metal to O.M. are described. A number of analytical characteristics for each of the laboratory-prepared complexes were determined, from which it appeared that iron in the lower complexes occurred as $Fe(OH)^{++}$ and in the high complex as $Fe(OH)_2^+$. Aluminum appeared to be present in the low complex as $Al(OH)^{++}$ and as $Al(OH)_2^+$ in the higher complexes.

In studies on the relative stabilities of the organo-metallic complexes, it was found that, whereas large proportions of the metals could be extracted by a number of acids from the lower complexes, considerably less could be removed from the high complexes.

Infrared spectra indicated the occurrence of iron- and aluminum-carboxylate bonds in the complexes. In the DTG curves of the iron complexes, the peak of the main decomposition reaction was lowered from 430° in the original O.M. to 280°C. as more iron was complexed. The lowering of the main decomposition temperature was interpreted as being due mainly to the complexing of iron in such a manner as to exert a strain on the O.M. molecule rather than to the exertion of a catalytic effect.

An organo-metallic complex extracted from the soil exhibited chemical, spectroscopic, and thermogravimetric characteristics which were similar to those shown by the prepared lower metal-O.M. complexes. X-ray diffraction analysis failed to provide evidence of crystallinity in the complexes.

Schnitzer, M., U.C. Gupta, SOME CHEMICAL CHARACTERISTICS OF THE ORGANIC MATTER EXTRACTED FROM THE O AND B2 HORIZONS OF A GRAY WOODED SOIL, Soil Sci. Soc. Amer. Proc., 28, 374-377 (1964).

Organic matter extracted from the O and B2 horizons of a Gray Wooded soil was characterized by ultimate and functional group analyses and by infrared spectroscopy. The analytical data were compared with those obtained by the use of the same methods on Podzol O and Bh organic matter.

The experimental data indicated that Gray Wooded humic and fulvic acids were chemically similar to Podzol humic and fulvic acids except that Gray Wooded organic matter contained more phenolic hydroxyl groups. In analogy with Podzols, approximately 70% of the organic matter extracted from the Gray Wooded O horizon was humic acid, while 90% of the extract from the B2 horizon consisted of fulvic acid.

Gray Wooded organic matter was difficult to extract and purify because of intimate association with clay and possibly other inorganic constituents.

Schnitzer, M., I. Hoffman, PYROLYSIS OF SOIL ORGANIC MATTER, Soil Sci. Soc. Amer. Proc., 28, 520-525 (1964).

Organic matter extracted from O2 and Bh horizons of a Podzol soil was pyrolyzed between room temperature and 540°C. Samples were withdrawn at regular temperature intervals and analyzed by chemical and spectroscopic methods.

The carbon content of the chars increased with temperature accompanied by a simultaneous decrease in oxygen. The chars of both organic matter preparations heated to 540°C. contained identical percentages of carbon and hydrogen but no oxygen. Some of the nitrogen and sulfur in the original organic matter was very stable and was recovered in the chars heated to the highest temperature.

Schnitzer, M., R.C. Turner, I. Hoffman, A THERMOGRAVIMETRIC STUDY OF ORGANIC MATTER OF REPRESENTATIVE CANADIAN PODZOL SOILS, Can. J. Soil Sci., 44, 7-13 (1964).

Differential thermogravimetric (DTG) curves of untreated peat, muck, and 10 different Podzol L-H materials showed peaks at approximately 100°C (moisture), 280° (low-temperature band), and 370 to 390° C (high-temperature band). The maxima at 280°C were sharp and characteristic of all surface materials investigated. The DTG curves were essentially the same for all of the Podzol L-H materials investigated.

The DTG curves for 12 organic matter preparations extracted from Podzol Bh, Bfh, Bhf, Bfl, and Btf horizons showed maxima at 100°C and in the 420 to 520°C region (high-temperature band). The peaks at 280°C were virtually absent in these materials. This suggested differences in composition between L-H and B horizon organic matter of the Podzols studied. The variations in the positions of the high-temperature bands of the B materials were related to the morphological characteristics of these soils in the field. From this it appeared that thermogravimetry might be a useful aid in soil classification.

Addition of inorganic materials did not affect the position of the low-temperature bands but had a pronounced effect on the high-temperature bands of both L-H and B organic matter. Addition of Na caused the peaks of the latter to shift to higher temperatures while addition of Al and Fe caused shifts to lower temperatures.

Schnitizer, M., J.G. Desjardins, MOLECULAR AND EQUIVALENT WEIGHTS OF THE ORGANIC MATTER OF A PODZOL, Soil Sci. Soc. Amer. Proc., <u>26</u>, 362-365 (1962).

The number-average molecular weights of the organic matter of the A_o and B_h horizons of a Podzol, determined by freezing point depression in sulfolane, were 1684 and 669, respectively. From the molecular weights, in conjunction with ultimate and functional group analyses, molecular formulae were calculated. These were $C_{75}H_{33}O_{17}N_3(COOH)_3(OH)_{12}(CO)_2$ for the A_o and $C_{21}H_{12}(COOH)_6(OH)_5(CO)_2$ for the B_h organic matter. The presence of relatively large numbers of functional groups in the B_h molecule offers interesting possibilities for metallo-organic interactions.

The equivalent weights of the same organic matter preparations, measured by discontinuous potentiometric titrations, were 165 for the A_o and 76 for the B_h organic matter. The ratio of molecular to equivalent weight was 10 for the A_o and 9 for the B_h material. These ratios were in both cases equal to the sum of carboxyl plus phenolic hydroxyl groups in the two molecules.

Schnitzer, M., S.I.M. Skinner, ORGANO-METALLIC INTERACTIONS IN SOILS: 1. REACTIONS BETWEEN A NUMBER OF METAL IONS AND THE ORGANIC MATTER OF A PODZOL B_h HORIZON, Soil Science, <u>96</u>, 86-93 (1963).

Reactions between O.M., extracted from a podzol B_h horizon, and the metal ions Fe^{+++}, Al^{+++}, Ca^{++}, Mg^{++}, Cu^{++}, and Ni^{++} have been investigated by potentiometric and conductometric titrations, absorption, and infrared spectroscopy and flocculation experiments.

The O.M. formed stable water-soluble complexes with all of the metals over the pH range usually encountered in podzol soils. With the aid of the known molecular weight of the O.M., the weight ratios at which metals and O.M. combined were expressed in terms of molar ratios. While ferric iron, aluminum, and copper formed water-soluble 1:1 molar complexes with O.M. at approximately pH 3, 2:1 molar water-soluble complexes were formed at pH 5 between ferric iron, copper, calcium, and O.M. Indications were also obtained of the formation of water-insoluble 6:1 molar complexes between ferric iron, aluminum, and O.M., involving in each instance one COOH group per atom of metal. These experiments suggest the formation of a range of molar complexes, varying from 1:1 to 6:1 and becoming increasingly water-insoluble as more metal is complexed.

Evidence was procured for the formation of electrovalent bonds between negatively charged carboxyl groups of the O.M. and positively charged partially hydroxylated iron and aluminum compounds. No clear indication concerning the participation of phenolic hydroxyl groups in the organo-metallic reactions was obtained.

Schnitzer, M., S.I.M. Skinner, ORGANO-METALLIC INTERACTIONS IN SOILS: 2. **REACTIONS BETWEEN DIFFERENT FORMS OF IRON AND ALUMINUM AND THE ORGANIC MATTER OF A PODZOL Bh HORIZON**, Soil Sci., 96, 181-186 (1963).

The uptake by O.M. of iron and aluminum from hydrous oxides and metal-enriched exchange resins, and from a soil material under a variety of conditions such as might be encountered in podzol profiles, was investigated.

On continuous wetting and leaching in a perfusion apparatus, in 1 week 1.0 mole of O.M. mobilized 1.0 mole of iron from goethite and an iron-saturated exchange resin, and 1.1 mole of aluminum from aluminum-saturated exchange resin. Metal uptake on standing and shaking, and on intermittent leaching, was considerably lower.

The effect of pH was difficult to estimate. In the perfusion experiments it had no effect. In reactions with goethite and gibbsite, metal uptake decreased with increase in pH, whereas the opposite was essentially true when O.M. reacted with soil material.

Atmosphere (air vs. nitrogen) had no apparent effect on iron uptake by O.M.

Methylation of most of the active acid groups reduced iron uptake to very low values, thus demonstrating the important role of carboxyl groups in the organo-metallic reactions.

Schnitzer, M., J.R. Wright, STUDIES ON THE OXIDATION OF THE ORGANIC MATTER OF THE Aa AND Bh HORIZONS OF A PODZOL, 7th Intern. Congress of Soil Sci., Madison, Wis., 2, 112-119 (1960).

Studies on the oxidative degradation of the organic matter of a podzol soil with alkaline potassium permanganate and nitric acid showed that the organic matter of the Ao horizon contained appreciable amounts of aliphatic and/or alicyclic in addition to aromatic structures, while the organic matter of the Bh horizon consisted predominantly of aromatic structures. There were indications that the benzene rings contained hydroxyl groups as substituents.

Simonart, P., J. Mayaudon, HUMIFICATION OF THE C^{14} PROTEINS IN THE SOIL, Pédologie. Symp. intern. 2, Appl. sc. nucl. péd., pp. 91-103 (1961). (In French)

When the C^{14} globulin fraction from leaves extract of Tetragonia expansa is added to the soil, 45% of the radioactive carbon is found back as $C^{14}O_2$ after thirty days; 55% of the radioactive carbon remains in the soil as organic matter, of which 18% in cell material of microorganisms and 37% in C^{14} globulin fixed without decomposition to the clay-humic complex.

When C^{14} globulin hydrolysate is used instead of globulin, 29% of the radioactive carbon is found in soil microorganisms after thirty days.

The addition of C^{14} proteins to the soil, in the applied experimental conditions, leads to the formation of radioactive humic acid, the radioactivity being due to the hydrolisable nitrogen fraction of these acids.

Smith, D.G., J.W. Lorimer, AN EXAMINATION OF THE HUMIC ACIDS OF SPHAGNUM PEAT, Can. J. Soil Sci., 44, 76-87 (1964).

Humic acid fractions were prepared by repeated extraction of Sphagnum peat with dilute sodium hydroxide. The infrared spectra of the initial fractions were typical of humic acids. Spectra of the later fractions were indications of an aromatic structure similar to that of lignin. The amount of methoxyl groups, which had remained constant through the earlier fractions, increased rapidly in later fractions. The results show that humic acids of similar composition and increasing molecular weight were extracted initially, and that low molecular weight material resembling lignin predominated towards the end of the extraction.

Soukup, M., SEPARATION OF HUMIC SUBSTANCES BY GEL FILTRATION ON SEPHADEX, Collec. Czech. Chem. Comm., 29, 3182-3184 (1964).

The results of the experiments show that Sephadex can be used for separating humic substances. This technique has several advantages for studies of humic substances as compared to the previous methods. Humic substances can be separated by this method in a comparatively simple way, making use of their different particle size, which according to present opinions is one of the most reliable criteria for their differentiation. Elution with distilled water excludes the possibility of a change of their original character to a considerable extent.

Sowden, F.J., K. C. Ivarson, METHODS FOR THE ANALYSIS OF CARBOHYDRATE MATERIAL IN SOIL: 2. USE OF CELLULOSE COLUMN AND PAPER CHROMATOGRAPHY FOR DETERMINATION OF THE CONSTITUENT SUGARS, Soil Sci., 94, 340-344 (1962).

Methods of determining sugars in soil hydrolyzates by cellulose column and paper chromatography were studied. The sugars in the hydrolyzate are first separated by chromatography on a cellulose column by elution with n-butanol-acetone-water. Fractions thus obtained are further purified by paper chromatography. A reasonably satisfactory separation of the sugars present in largest amounts in the crude hydrolyzate--xylose, arabinose, mannose, glucose, galactose--can also be made by multiple development of chromatograms on 0.1 M, pH 5 phosphate buffered paper with butanol-acetone-water. The separated sugars are determined by the colorimetric method of Dubois et al.

The method was applied to four different kinds of soil. These were hydrolyzed by a two-stage method--a primary hydrolysis by 72 percent H_2SO_4 at room temperature for 2 hours, followed by a secondary hydrolysis with boiling N H_2SO_4 for 16 hours. After removal of the acid with Ba^{++} the hydrolyzates were added to the paper or to the columns. Besides the major sugars mentioned above, ribose, fucose, rhamnose, and a number of unidentified "high R_f" sugars were found. Glucose was two to three times as abundant as any other sugar, indicating, perhaps, the presence in soil of some residual cellulose. The sugars accounted for 7 to 10 percent of the total carbon; if the amounts of uronic acid and hexosamine are added, 12 to 14 percent of the carbon can be accounted for.

Stotzky, G., A.G. Norman, FACTORS LIMITING MICROBIAL ACTIVITIES IN SOIL, III. SUPPLEMENTARY SUBSTRATE ADDITIONS, Can. J. Microbiol., 10, 143-149 (1964).

Studies were conducted to examine further the circumstances prevailing during the phase of rapid decline in the respiration rate of soil after the addition of a soluble carbon substrate, and to investigate the potential metabolic activity of the microbial population at different stages in its sequential development. When the supply of required inorganic nutrients was adequate, the rapid decline in the rate of respiration following attainment of the respiratory peak resulted primarily from depletion of available carbon substrates, even though by this time only 30 to 50% of the carbon in the substrate (glucose) added had been recovered as CO_2. Supplementary additions of the same substrate, regardless of the concentration and time of addition, however, did not elicit secondary peaks comparable in height to the primary peaks, nor was the recovery as CO_2 from the supplements as high as from the initial substrate addition. This attenuation of the metabolic activity was attributed to limiting factors introduced by the initial growth of a large and active microbial population which restricted the development of sequential populations. The nature of these limiting factors and their implication in maintaining the ecological balance of microorganisms in soil are discussed.

Thomas, D.W., M. Blumer, THE ORGANIC CHEMISTRY OF A FOSSIL. III. THE HYDROCARBONS AND THEIR GEOCHEMISTRY, Geochim. Cosmochim. Acta, 28, 1467-1477 (1964).

The following aromatic hydrocarbons were isolated from a fossil crinoid of Jurassic age: anthracene, phenanthrene, fluoranthene, pyrene and alkyl derivatives, 1,2-benzpyrene, 3,4-benzpyrene, perylene, anthanthrene, 1,12-benzperylene, hexahydro-meso-naphthodianthrene, hexahydro-meso-anthrodianthrene and alkyl derivatives, and substituted meso-anthrodianthrenes. Several compounds, presumably aromatic hydrocarbons, of undetermined structure were also found. The eight- and nine-ring hydrocarbons are structurally and genetically linked to the fringelite pigments of the same fossil. A proposed sequence of consecutive irreversible and reversible redox reactions can explain the presence or absence of certain compounds in this complex assemblage of geochemical products.

Thompson, S.O., G. Chesters, L.E. Engelbert, COMPARATIVE PROPERTIES OF PLANT LIGNINS AND HUMIC MATERIALS OF SOILS. 1. YIELDS AND CATION EXCHANGE PROPERTIES OF PLANT LIGNINS ISOLATED BY DIFFERENT TECHNIQUES, Soil Sci. Soc. Amer. Proc., 28, 65-68 (1964).

Yields and cation-exchange capacities for Ca and Cu were determined for lignin samples isolated with 72% H_2SO_4, HCl-H_3PO_4 mixture, 5% aqueous NaOH, and 1,4-dioxane. Yields varied with extractant in the order: acid- > dioxane- >NaOH-extracted lignins. For equal time, a higher yield of dioxane pine lignin was obtained by fractional than by a one-step extraction. In most cases cation-exchange capacities varied with lignin source and with method of extraction as follows: (a) Straw lignins > wood lignins; (b) alkali- > dioxane- > acid-extracted lignins.

Lignins isolated by fractional extraction with dioxane showed the later fractions to have higher exchange capacities. Values for the one-step extracted isolates were intermediate with respect to the high and low values of the fractionally isolated samples. Lignin, like soil organic matter, had higher adsorptive capacity for Cu than for Ca, and the adsorptive capacity was pH dependent. All samples examined for the effect of pH on Cu adsorption showed the same relative change in adsorption for a given change in solution acidity.

Tsyplenkov, V.P., A RAPID COLORIMETRIC METHOD FOR DETERMINING HUMUS IN SOILS AND SOIL SOLUTIONS, Soviet Soil Sci., No. 10, pp. 986-990 (1964).

A colorimetric method for determining humus that is suitable for large scale analyses was developed. It is fairly accurate and requires much less time and costs less per analysis than the Tyurin method.

Turner, R.C., M. Schnitzer, THERMOGRAVIMETRY OF THE ORGANIC MATTER OF A PODZOL, Soil Sci., 93, 225-232 (1962).

An extension of the kinetic treatment of the thermal decomposition of coal and related substances published by Van Krevelen et al. has been presented. The extended theory has been applied to determine activation energies, specific rate constants, and weights of reacting substances for the main decomposition reactions of organic matter from the A_0 and B_h horizons of a podzol.

The kinetic data for the two organic matter preparations were compared with each other and with those published for similar substances. The data were related to information obtained from oxidative degradation experiments made with the same materials.

Visser, S.A., A PHYSICO-CHEMICAL STUDY OF THE PROPERTIES OF HUMIC ACIDS AND THEIR CHANGES DURING HUMIFICATION, J. Soil Sci., 15, 202-219 (1964).

Humic acids extracted from decomposing plant and peat core samples and changes in them during the process of humification were investigated in terms of their elementary composition, the acidity and the equivalent weight, the infra-red, visible and ultra-violet spectra and the shape and size of the molecules and their weight. With progressive humification in peat and decomposing plant samples, increases were noted for the carbon content and the aromatic character of the humic-acid molecules and in the number of their alcohol and ether groups, aliphatic side chains and double bonds, while decreases were observed for the hydrogen content, the molecular weight, the equivalent weight, and the hydrophilic character of the humic acids and possibly to a minor extent also for the ionization constant and the alkoxyl and alkimide groups. It was noticed that the presence of charcoal and, to a minor extent also, of clays in decomposing plant material promoted the formation of humic acids which were very similar to those found in older peat deposits, while the presence of ash did not seem to have much effect. Humic acids derived from different peat materials were found to be very similar in structure and composition, but when different types of plant material were mixed, the humic acids formed during the first stages of decomposition were very similar to those from more decomposed samples containing only the separate components.

Wright, J.R., M. Schnitzer, OXYGEN CONTAINING FUNCTIONAL GROUPS IN THE ORGANIC MATTER OF THE Ao AND Bh HORIZONS OF A PODZOL, 7th Intern. Congress of Soil Sci., Madison, Wisc., pp. 120-127 (1960).

The fulvic to humic acid ratios of the alkali-extracted organic matter of the Ao and Bh horizons of a podzol were 0.4 and 5.6 respectively. While practically all of the oxygen of the fulvic acid fractions was present in the functional groups only 50 to 70 per cent of the humic acid oxygen was similarly distributed. The fulvic acids were considerably more acidic than the humic acids due entirely to the presence of more carboxyl groups. From the findings, suggestions are made concerning the role of organic matter in podzolization.

Wright, J.R., M. Schnitzer, R. Levick, SOME CHARACTERISTICS OF THE ORGANIC MATTER EXTRACTED BY DILUTE INORGANIC ACIDS FROM A PODZOLIC B HORIZON, Can. J. Soil Sci., 38, 14-22 (1958).

Organic matter was extracted from the B_{21} horizon of a podzol soil by both 0.5 percent HF and 0.5 percent HCl. Dialysis of the extracts against distilled water reduced the halogen content to less than 0.1 percent and the iron plus aluminium to between two and three millimoles per gram of organic matter. Further treatment of this water-dialysed material with EDTA and 8-hydroxyquinoline removed almost all of the iron and about two-thirds of the aluminium.

The number average molecular weight of the organic matter, as determined by osmometry, ranged between 47,000 and 53,800. Paper electrophoresis studies showed that this organic matter consisted chiefly of one component, negatively charged, dark-brown in colour and mobile over the pH range investigated (1.8 - 9.0). Only traces to small amounts of glucose, galactose, arabinose and xylose were detected by paper chromatography in both the HF and HCl extracts even after hydrolysis. In addition traces of rhamnose were found in the hydrolyzed HF extract.

Yuan, T.L., COMPARISON OF REAGENTS FOR SOIL ORGANIC MATTER EXTRACTION AND EFFECT OF pH ON SUBSEQUENT SEPARATION OF HUMIC AND FULVIC ACIDS, Soil Sci., 97, 133-141 (1964).

Four reagents, 0.5 M NaOH, 0.1 M $Na_4P_2O_7$, 0.5 M NaF, and a cation-exchange resin, Dowex A-1, were used to extract organic matter from a Leon fine sand, using both the surface and organic pan layers. The amount of organic fraction extracted by the alkali was the largest both from the surface and from the subsoil layer. Dowex A-1 was effective for the surface soil but extracted only a small percentage of organic matter from the organic pan layer. The reverse was true when NaF was used as an extractant. Fairly large amounts of organic matter were extracted by $Na_4P_2O_7$ from both layers.

The C/N ratios, the C distribution in humic and fulvic acid fractions, and the optical properties suggested that the nature of the organic constituents extracted from two soil layers by different reagents are different.

The pH had considerable effect on organic matter precipitation. The effect varied with the reagents used and with the layers of the soil from which the organic fraction was extracted. The humic materials from the surface soil of Leon fine sand started to precipitate in the extracts using NaOH, $Na_4P_2O_7$, NaF, and Dowex A-1 resins at a pH below 5.5, 4.0, 4.0 and 2.5, respectively, and those from the organic pan layer below 8.5, 4.0, 4.0, and 4.0.

In general, the amount of organic matter precipitated increased when the pH of the extract was lowered. An exception was the NaOH extracts of the organic pan layer, in which case the maximum amount of precipitation occurred between pH 5.5 and 4.0. Further lowering of pH caused a portion of the precipitated material to redissolve. This was found to be related to the aluminum content in the soil extract.

Ziechmann, W., SPECTROSCOPIC INVESTIGATIONS OF LIGNIN, HUMIC SUBSTANCES AND PEAT, Geochim. Cosmochim. Acta, 28, 1555-1566 (1964).

The close structural and genetic relationships between lignin, humic substances and further products of the coalification process, often supported by strong arguments and well-based considerations, is generally accepted. Such relationships can be particularly well demonstrated by absorption of light by these substances in the ultraviolet and visible regions (250-700 mμ), in the near infrared (0·7-2·5 μ), and finally in the infrared region of the NaCl-prism (2-14 μ). In fact, the similarity among these substances also became apparent in the general gradation of these spectra; such gradation may take on particular significance if interpretation of the spectra is to be used for genetic, chemical, or even physical studies. In any case, if it is recognized that the spectra have different sources in different regions, then the spectra of individual regions must be very different.

In some cases, special atomic groups are associated with characteristic bands, and in many instances additional use of the near infrared region (harmonics) can be useful. Ultraviolet spectra are usually completely uncharacteristic, with absorption intensity dropping in going from shorter to longer wave lengths. Nevertheless, the general impression of the ultraviolet spectrum, along with other prominent maxima and minima from other spectra, and additional analytical data permit a certain delineation in the lignification-humification-coalification sequence. Therefore, it is obvious that it is necessary to study the materials in question over the entire accessible region of light absorption. As a further point, it should be noted that a spectrum is frequently difficult to interpret and become useful only when a reference material can be used.

The intermediate position of humic substances is not surprising inasmuch as they certainly arise from lignin, judging from the decomposition products of lignin, and, moreover, its natural conversion in the coalification process leads first to peat and the usual related substances. The particularly uncharacteristic ultraviolet spectrum of humic substances should be noted. If reactive acidic complexes (humic acid precursors) can be separated from the true, essentially unreactive humic acids, then it should be possible to determine their differences experimentally by absorption techniques using suitable preparations. If this study could then be generalized, it might illustrate that the further advanced a material is in the course of this natural process, the more uncharacteristic its ultraviolet spectrum becomes.

A number of maxima in the ultraviolet spectrum were taken as being characteristic for lignin, and in this way the substance could be differentiated from humic acid; the humic acid precursors gave the same general impression. It should be noted that for many lignins there is a displacement of certain maxima dependent upon pH, an effect that is not generally noted for humic acid precursors. The spectrum for lignin also shows a general decrease in the intensity of light absorption with increasing wave length.

As already stated, infrared spectra are particularly informative. For the materials in question, characteristic groups can be identified in spite of a more or less marked background absorption. Thus, the fewer the number of bands in the infrared spectrum or the further along the material is in the coalification process, the more intense the background absorption becomes.

Attempts are being made to define most low molecular weight constituents that do not at the outset enter into the lignification or humification process and to compare their absorptions with those for lignin or humic substances. These materials may play a special key role in the alteration of lignin or humic substances and there is also the possibility that something may be learned about the nature of their bonding with lignin or humic substances. It is felt that if these questions are answerable by the application of spectroscopic techniques, that later a solution to the overall picture may be attainable.

SECTION 17

SPACE PROBES AND STUDIES

Calvin, M., S.K. Vaughn, EXTRATERRESTRIAL LIFE: SOME ORGANIC CONSTITUENTS OF METEORITES AND THEIR SIGNIFICANCE FOR POSSIBLE EXTRATERRESTRIAL BIOLOGICAL EVOLUTION, Space Research, ed. by Kallmann, North-Holland Publ. Co. - Amsterdam, p. 1171-1191 (1960).

In order to decide the value and type of information to be obtained from outer space with regard to its pertinence for the evolution of life, a brief review is presented of the current status of our thinking on the origin of life on earth. This points up the particular kinds of chemicals whose presence, or absence, on other astral bodies might be significant.

Heretofore, the only data available are the result of telescopic spectroscopy. We report here information indicating the presence in meteorites of complex organic materials, some of them apparently uniquely pertinent to life processes.

Dayhoff, M.O., E.R. Lippincott, R.V. Eck, THERMODYNAMIC EQUILIBRIA IN PREBIOLOGICAL ATMOSPHERES, Science, 146, 1461-1464 (1964).

The concentration of a large number of compounds of biological interest which would be present in the atmosphere at thermodynamic equilibrium were computed under many combinations of temperature, pressure, and elemental composition. These computations revealed a possible mechanism for the abiological formation of asphaltic tar and an oxidative threshold at which all but the simplest compounds disappear.

Degens, E.T., GENETIC RELATIONSHIPS BETWEEN THE ORGANIC MATTER IN METEORITES AND SEDIMENTS, Nature, 202, 1092-1095 (1964).

This article presents further information in support of the abiotic nature of the finely disseminated organic matter in the carbonaceous chondrites.

Gillespie, R.W., R.V. Rogsac, S.E. Ross, PROSPECTS FOR EARLY MANNED INTERPLANETARY FLIGHTS, Astronautics Aerospace Eng., 1, 16-21 (1963).

A variety of possible manned missionsto Mars and Venus for the 1970's is presented.

Gilvarry, J.J., THE POSSIBILITY OF A PRISTINE LUNAR LIFE, J. Theoret. Biol., 6, 325-346 (1964).

The theory of Gilvarry suggesting the former existence of a hydrosphere and atmosphere lasting several billion years on the moon after its formation, and thereby yielding a complete correlation of the dimensions of the lunar craters and circular maria, is reviewed. On this basis, the dark floors of the lunar maria represent sediments, and not lava. It is proposed to explain the dark color of the sediments as arising from carbon derived from a pristine biota. A detailed argument leading to this conclusion is presented, based on Oparin's theory of biopoesis. Two positive clues derived from direct observation of the lunar surface are pointed out, implying a former lunar life. One of these is the apparent recession of the dark material in a circular mare from the bases of the encircling mountains, and the other is the spectrographic observations of Kozyrev implying the presence of carbon on the lunar surface. If this theory is correct, it is shown that the effect of the solar wind and flare particles since the lunar hydrosphere and atmosphere dissipated is to leave elemental carbon distributed superficially and at shallow depth in the rocks of the maria. Because of the effect of cosmic rays over the ages, fossils relatively undamaged by radiation cannot be found less than about 3 to 5 m below the surface of a mare.

Houck, T., ORBITING ASTRONOMICAL OBSERVATORY: THE WISCONSIN EXPERIMENT PACKAGE, Space World, A-11, 4-9 (1964).

During 1965 the first major telescope system will be put into orbit. The OAO (orbiting astronomical observatory) will contain two scientific packages. The Smithsonian package is designed to construct a star map in the ultra-violet spectrum. The University of Wisconsin experiment calls for observations in the 800 to 4,200 Angstrom unit range on representative stars and several emission nebulae. A description of the instruments included in the Wisconsin package is presented.

Hunter II, M.W., FUTURE UNMANNED EXPLORATION OF THE SOLAR SYSTEM, Astronautics & Aeronautics, 2, 16-26 (1964).

The whole solar system can be opened to scientific space exploration by developing a single chemical rocket vehicle with a versatile payload and a communication package specifically for this purpose.

Jaffe, L.D., STERILIZING UNMANNED SPACECRAFT, Astronautics Aerospace Eng., 1, 22-29 (1963).

This paper attempts an engineering examination of the problems of sterilization in unmanned exploration.

Kardashev, N.S., TRANSMISSION OF INFORMATION BY EXTRATERRESTRIAL CIVILIZATIONS, Soviet Astronomy-AJ, 8, 217-221 (1964).

The protracted duration of signal propagation is a determining factor in the one-way transmission of information through space. Reliable reception, or any reception at all, of signals by unknown subscribers necessarily requires an isotropic emission. The optimum signal spectrum for transmitting the maximum amount of information in the presence of quantum noise and the background of cosmic radio-frequency emission has been calculated. It is shown that a civilization located at any distance in the universe and in possession of power on the order of $L_{\odot} \approx 4 \times 10^{33}$ erg/sec or more, which it is capable of transmitting in a coded isotropic radio-frequency signal, may be detected by conventional radio astronomical techniques. The expected distinguishing properties of artificial sources of cosmic radio-frequency emission are enumerated. It is speculated that even some sources known to us today (notably CTA-21 and CTA-102) may be artificial radio sources.

Kuiper, G.P., THE LUNAR AND PLANETRAY LABORATORY-II, Sky and Telescope, 27, 88-92 (1964).

This article outlines some of the scientific results obtained at the Lunar and Planetary Laboratory at the University of Arizona. These results include Mars infrared spectra which record the isotopic $C^{13}O_2$ band but the relative abundances of C^{13} and C^{14} in the Martian atmosphere requires improved data. The atmospheric pressure at the surface of Mars has been determined as equal to about 7 millimeters of mercury - nearly 10 times lower than has been supposed from polarization and scattering measurements.

Larson, R.R., E.J. Dwornik, I. Adler, ELECTRONPROBE ANALYSIS OF "COSMIC" PARTICLES, Ann. N.Y. Acad. Sci., 119, 282-286 (1964).

In the course of our application of the electronprobe to the analysis of fine particles, we have analyzed some spherules believed to be of extraterrestrial origin. The source of many others is doubtful. They may have been derived from smelters or other industrial smokes, or more probably from volcanic emanations. Perhaps continued analysis of many more particles from carefully monitored and selected collecting stations may eventually suggest meaningful patterns. However, criteria are badly needed for distinguishing cosmic (extraterrestrial) from terrestrial samples.

We have demonstrated the feasibility and usefulness of the ultramicrotome in sample preparation. Although preliminary electronprobe analysis may be performed on whole spherules to detect major elements, optical study of the internal structure is essential in planning meaningful probe analyses. In addition, we have suggested a practical method for eliminating some of the unnecessary handling of small samples with consequent decrease in the attendant risks of losing them.

Mueller, R.F., STABILITY OF HYDROGEN COMPOUNDS ON VENUS, Nature, 203, 625-626 (1964).

Evaluation of the stabilities of simple hydrocarbons causes the author to conclude that it is unlikely that any significant quantities of hydrocarbons could occur on the surface and lower atmosphere of Venus.

Newell, H.E., THE KEY AND THE QUEST, Aerospace, 2, 18-24 (1964).

The scientific instruments and the mission objectives of the Orbiting observatories are reviewed.

Siegel, S.M., C. Giumarro, R. Latterell, BEHAVIOR OF PLANTS UNDER EXTRA-TERRESTRIAL CONDITIONS: SEED GERMINATION IN THE ATMOSPHERES CONTAINING NITROGEN OXIDES, Proc. Nat. Acad. Sci., 52, 11-13 (1964).

Seeds of common plant species can be germinated in rarefied nitrogen atmospheres containing high proportions of individual nitrogen oxides (N_2O, NO, NO_2) or their mixtures. A buffering substratum of $CaCO_3$ is especially beneficial, and the best responses were given thereon by rice and sorghum in the presence of certain nitrogen oxides as compared with nitrogen alone. Cell division in the sorghum shoot in N_2/NO was demonstrated. Nitrogen dioxide was inhibitory under anaerobic conditons but much less so when O_2 was present.

We conclude that, if ordinary terrestrial flora unselected for tolerance to the oxides of nitrogen are taken as a model, their prospects for growth in a nitrogen oxide-rich atmosphere would be good indeed, provided that the substratum prevents excess acidity and that NO_2 is not present in overly great quantities.

Stambler, I., INTERPLANETARY PROBES, Space Aeronautics, 42, 36-45 (1964).

Four months from now a new Mariner vehicle will be shot toward Mars on a TV flyby mission. Somewhat heavier unmanned vehicles capable of landing instrumented capsules on the surface will follow later in the sixties, and the seventies will see the much heavier, more sophisticated Voyagers orbiting and landing on Mars and eventually visiting Venus, Mercury, and Jupiter as well.

Stambler, I., THE ORBITING OBSERVATORIES, Space Aeronautics, 42, 34-42 (1964).

Delayed by technical problems and somewhat reduced in magnitude by funding cutbacks, NASA's ambitious earth-orbiting observatory program now appears set for a series of significant launches over the next several years. The sun, planets, stars, and earth itself will be scrutinized by the telescopes and other sensors carried by these versatile stabilized platforms beyond earth's atmosphere.

Thatcher, J. W., DEEP SPACE COMMUNICATION, Space Aeronautics, 42, 54-63 (1964).

How will we communicate with vehicles ranging out to the far planets and eventually beyond our solar system? This side of Pluto the present state-of-the-art seems capable of meeting the requirements for data acquisition, command, and tracking. To go further, we'll need relay satellites and more transmitter power on our spacecraft.

Wildey, R. L., PHOTOMETRY OF THE EARTH FROM MARINER 2, J. Geophys. Res., 69, 4661-4672 (1964).

The earth tracking system aboard the Mariner 2 spacecraft has collected photometric observations of the earth as a by-product of its navigational duties on the flight to Venus. The observations show good agreement with the phase curve for the earth that was previously found by observing the earth-lit moon. Diurnal variations in brightness are correlated with the fraction of the earth's disk covered by land.

Willard, M., A. Alexander, A SELF-STERILIZING COATING FOR SPACECRAFT SURFACES, Nature, 202, No. 4933, 658-659 (1964).

The coating formulation used was a water-base inorganic material comprised of potassium silicate binder and aluminum silicate pigment. To provide self-sterilizing activity, 3.7 per cent formaldehyde was added to the coating. Test results demonstrated the sterilizing properties of the formaldehyde-paint mixture.

Wright, F. W., P. W. Hodge, COMPOSITIONAL STUDIES OF EXTRATERRESTRIAL PARTICLES, Ann. N. Y. Acad. Sci., 119, Art. I, 287-297 (1964).

Particles of known meteoritic origin show a wide range in their Ni/Fe ratio, even for the same meteoritic fall. Most known meteoretic dust particles contained Ni, but for some it was not detected. In none of the cases was the composition of the artificial spherules of various origins similar to that of the suspected meteoritic spherules. Volcanic spherules analyzed had compositions similar to those of a few of the possibly meteoretic spherules, but none was found to resemble in this respect the iron rich objects the authors had previously considered most likely to be of cosmic origin.

SECTION 18

SPECTROMETRY

18.1 GENERAL

Cerbón, J., NUCLEAR MAGNETIC RESONANCE OF WATER IN MICROORGANISMS, Biochim. Biophys. Acta, 88, 444-447 (1964).

This paper demonstrates the advantages of NMR (nuclear magnetic resonance) spectrometry in the study of water content and structure in "normal" microorganisms (with cell wall intact and not plasmolyzed). Information about the orientation of molecules on the rigid cell wall during various physiological conditions was also obtained.

Grenier, R.P., R. R. Samuelson, TOTAL ABSORPTION COINCIDENCE SPECTROMETER, Rev. Sci. Instr., 35, No. 11, 1575-1582 (1964).

A total absorption beta-gamma coincidence spectrometer utilizing anticoincidence shielding is described. The main detector assembly consists of two NaI(Tl) well crystals each 22.9 cm in diameter by 12.7 cm thick. The wells in the crystals are each 5 cm in diameter by 3.8 cm deep. The crystals are positioned to face each other and present a 4π geometry to the source of activity. A 4π beta chamber operated in the Geiger region is positioned inside the wells. A 7.6-cm-thick plastic phosphor serves as an anticoincidence guard. The system may be used in a variety of double and triple coincidence configurations. The responses of the crystals to gamma rays under various coincidence conditions are included. The facile determination of absolute disintegration rates obtainable with this system by using the coincidence technique and detectors that present a uniform sensitivity to the source of activity is discussed. Experimentally determined total gamma efficiency and peak-to-total ratio vs. energy curves are presented and the techniques and isotopes used to obtain them are discussed. In the region from 70 to 2800 keV the 4π crystals have gamma efficiencies ranging from 0.765 to 0.645, respectively, with a max efficiency at 530 keV of 0.895. The peak-to-total ratio ranges from 0.92 at 70 keV to 0.47 at 2800 keV.

Hill, R. A., E. H. Beckner, A RAPID SCAN SPECTROGRAPH FOR PLASMA SPECTROSCOPY, Appl. Optics, 3, No. 8, 929-932 (1964).

An ultrarapid scanning spectrograph having a spectral scan speed of from 10 to 200 Å/µsec and a scanning range of 210 Å, is described. This spectrograph was employed to obtain time-resolved H_α, H_β, and H_γ line profiles, and line-to-continuum ratios, in a shock-heated hydrogen plasma. Electron densities were determined at various times behind the shock front from the Stark-broadened lines and the plasma temperature was obtained from the line-to-continuum ratio. The electron densities obtained from the three lines were found to compare remarkably well. In addition, it was possible to utilize the Saha equation and correlate the time-behavior of the electron density with the temperature and atom density measurements.

Nagasawa, H., A NEW TYPE SPECTROMETER FOR NUCLEAR MAGNETIC RESONANCE DISPERSION USING GATED BEAM TUBE, Japan J. Appl. Opt., 3, No. 8, 476-479 (1964).

A new type of nuclear magnetic resonance dispersion spectrometer using a gated beam tube is described. The characteristic feature of this spectrometer is its low noise figure of about three at the comparatively high r.f. level of 4V. This new spectrometer is much easier to be used than an r.f. bridge because there is no delicate balance adjustment and it is free from any balance drifting. An r.f. amplifier and a detector are no longer necessary because of the amplification and detecting properties of the gated beam tube and it is possible to sweep the frequency simply by sweeping the signal generator. The frequency sweep range is about 200 Kc/sec without any adjustment of the spectrometer.

Paulsen, P.J., W.D. Cooke, QUANTITATIVE DETERMINATION OF HYDROGEN AND FLUORINE IN ORGANIC COMPOUNDS BY NUCLEAR MAGNETIC RESONANCE SPECTROMETRY, Anal. Chem., 36, No. 9, 1713-1721 (1964).

Various procedures have been evaluated for quantitative intensity measurements of NMR spectra. The only method offering a practical solution to the problem involves the use of reference standards and area ratio measurements at experimentally determined power levels and scan rates. The procedure has been applied to elemental analysis and to compound as well as functional group determinations. A probe and integrator, operating at 15,000 c.p.s., has been designed and applied to the measurement of fluorine intensities.

Simpson, J.A., HIGH RESOLUTION, LOW ENERGY ELECTRON SPECTROMETER, Rev. Sci. Instr., 35, No. 12, 1698-1704 (1964).

An electron spectrograph consisting of an electron source, an electron monochromator, a gas cell, and an electron energy analyzer is described. The electron energy spread from the monochromator as seen by the analyzer is 0.005 eV at 3.35 eV primary energy. It is shown that space charge within the beam requires operation of the energy selectors at the lowest possible energy if high current, together with high resolution, is required.

Smith, D.M., CONFERENCE ON LIMITATIONS OF DETECTION IN SPECTROCHEMICAL ANALYSIS, EXETER, JULY 1964, Brit. J. Appl. Phys., 15, 1267-1270 (1964).

The main object of the Conference of the Spectroscopy Group of The Institute of Physics and The Physical Society, held at the Washington Singer Laboratories, Exeter University, 2nd-3rd July 1964, was to discuss unresolved problems rather than achievements. Nevertheless, some original material was presented and this report appraises the current state of limitations imposed by instrumental parameters and sample form and present methods of determining limits of detection.

Uchida, Y., EXTREME ULTRAVIOLET SPECTROSCOPIC OPTICS IN JAPAN, Appl. Optics, 3, No. 7, 799-804 (1964).

A brief review is presented of the work recently carried out in Japan in the field of the extreme ultraviolet spectroscopic optics. It also includes names of people and organizations active in the research.

18.2 INFRARED

Averkov, S.I., V.I. Anikin, V.Ya. Ryadov, N.I. Furashov, ASTRONOMICAL STATION FOR FAR-INFRARED OBSERVATIONS, Soviet Astronomy-AJ, 8, No. 3, 432-434 (1964).

The apparatus developed for astronomical research in the far-infrared region of the spectrum is described. The basic characteristics of this equipment and the results of the first observations of solar radiation carried out by its use are given.

Bartz, A.M., H.D. Ruhl, RAPID SCANNING INFRARED-GAS CHROMATOGRAPHY INSTRUMENT, Anal. Chem., 36, No. 10, 1892-1896 (1964).

This instrument was designed to utilize the ability of gas chromatography (GC) to physically separate a multicomponent chemical sample into its individual components and the ability of infrared spectroscopy to specifically identify reasonably pure compounds. The effluent from a GC column (vaporized sample plus helium) is passed through a heated light pipe which serves as an infrared absorption cell with a large optical path length-to-volume ratio. The infrared absorption spectrum of the vapor sample is obtained by using two single-beam grating spectrometers in parallel. One spectrometer covers the range 2.5 to 7 microns while the other scans from 6.5 to 16 microns. By using two spectrometers, a high chopping rate, and fast recorders, a complete spectrum may be obtained in 16 seconds comparable in quality to a normal 12-minute scan by commercial spectrometers. The high scanning speed is necessary if an IR spectrum is desired of each successive GC peak of a multicomponent sample.

Dolinsky, M., C.H. Wilson, QUANTITATIVE INFRARED ANALYSIS OF SOME WATER SOLUBLE ACIDS AND SALTS, Anal. Chem., 36, No. 7, 1383-1385 (1964).

Amberlite LA-2 liquid resin was used to extract water-soluble acids into non-polar solvents like carbon disulfide for quantitative analysis by infrared spectrophotometry. Using the procedure outlined it was possible to analyze quantitatively many mixtures of acids. The limitations of the method are pointed out.

Goulden, J.D.S., D.J. Manning, INFRA-RED SPECTRA OF AQUEOUS SOLUTIONS BY THE ATTENUATED TOTAL REFLECTANCE TECHNIQUE, Nature, 203, No. 4943, 403, (1964).

Authors suggest that the ATR (attenuated total reflectance) technique possesses no inherent advantage over the transmission technique for the examination of aqueous solutions.

Gray, F.B., INFRARED INSTRUMENTATION IN SPACE EXPLORATION: INTRODUCTORY REPORT, Mem. Soc. Royal Sci., Lugi, Colloq. Belgium, 9, 94-104 (1964).

There are special requirements for the components of an infrared system designed for space operation. They must be able to survive the space environment and operate satisfactorily when given the proper command. The components must be light in weight, have low power requirements and high reliability. Some of the components that have operated successfully in infrared systems are discussed.

Hannah, R.W., J.L. Dwyer, INFRARED ANLAYSIS OF SUSPENDED PARTICULATES WITH MILLIPORE FILTERS AND ATTENUATED TOTAL REFLECTION, Anal. Chem., 36, No. 12, 2341-2344 (1964).

Attenuated total reflection has been characterized as being essentially a surface effect. One implication of this is that for a given analysis only a fraction of a milligram of material properly presented to the totally reflecting face is required to produce a good spectrum. Membrane filters, because of their surface retention ability, not only accomplish a separation of particulate material from fluid media but also permit a nearly ideal presentation of the sample to the ATR crystal. In addition, substrate interferences which complicate transmission results, are reduced considerably. This method is especially valuable where the material to be examined is present in very low concentrations normally difficult to isolate from the fluid media or of a microscopic particle size. Several diverse examples are described which illustrate the utility of the technique.

Hunt, G.R., J.W. Salisbury, LUNAR SURFACE FEATURES: MID-INFRARED SPECTRAL OBSERVATIONS, Science, 146, 641-642 (1964).

The moon has been observed and spectrally scanned at mid-infrared wave lengths, in particular through the 16- to 24-micron atmospheric window. The data indicate that there are differences in mineral composition amoung several features of the lunar surface.

Jones, R.N., INFRARED SPECTROSCOPY, Intern. Sci. & Tech., p. 35-43 (1965).

By measuring the amount of infrared radiation an unknown material absorbs, which is an indication of the increase in the vibrational energy of its molecules, the modern chemist is able to identify the material as well as deduce important structural information, such as the length of the molecular bonds. Within the past few years faster and more accurate spectrometers have become commercially available. This has extended the use of infrared spectroscopy to practically every phase of the chemical and pharmaceutical industry for such applications as studying atmospheric pollution, identifying the odor and taste constituents in foods, and evaluating the quality of milk. In addition, the technique is providing insight into the structure of complex organic compounds such as the steroids. From analysis of the spectra of several thousand steroids we are helping to build a picture of how the atomic groupings in these compounds behave.

Kimmel, H. S., A. Saifer, INFRARED SPECTRA OF THE BIOLOGICALLY IMPORTANT DNP AND PTH AMINO ACIDS, Anal. Biochem., 9, 316-342 (1964).

The infrared spectra of the DNP and PTH derivatives of 27 amino acids that are important in the study of biological materials were determined. These spectra include nine DNP and five PTH amino acid derivatives not previously reported in the literature. In addition to the usual qualitative assignment of the wavelength of spectral absorption bands in the 2 to 15µ region, a quantitative study of the intensities of the major bands was made. This quantitative approach furnishes an additional parameter by means of which structurally related amino acids can be readily differentiated. The infrared spectra of DNP and PTH amino acids were shown to be a useful tool for the determination of the N-terminal residues of various peptides and proteins especially when used in conjunction with thin-layer chromatography.

Krimm, S., RECENT DEVELOPMENTS IN THE VIBRATIONAL SPECTROSCOPY OF HIGH POLYMERS, J. Polymer Sci., Part C, No. 7, 3-18 (1964).

The authors show that rotationally isomeric structures give rise to significant new absorption bands in the infrared spectra of polymers. These can be interpreted in terms of specific chain conformation, which in turn are often derivable from particular configurations.

Ladd, J. A., W. J. Orville-Thomas, SPECTROSCOPIC STUDIES. PART III. ANALYSIS OF THE ACETALDEHYDE VIBRATION-ROTATION BAND NEAR 764 CM^{-1}, J. Chem. Soc., 2689-2692, Aug. (1964).

The rotational structure of the 764 cm^{-1} band of acetaldehyde has been measured. This band has been analysed in order to correlate the observed rotational fine structure with the molecular dimensions.

Lambert, J. L., J. H. Hammons, J. A. Walter, A. Nickon, ANALYSIS FOR DEUTERIUM IN ORGANIC COMPOUNDS BY COMBUSTION - INFRARED SPECTROMETRY, Anal. Chem., 36, No. 11, 2148-2151 (1964).

A method is described for the quantitative analysis of deuterium in compounds by combustion and infrared spectrometry of the derived water sample. Combustion is effected conveniently by a dynamic combustion train, modified to remove acidic oxides and halogen from the combustion gases. The memory effect of this system has been reduced to an acceptable level. Analysis on the milligram scale is possible. Results agree well with analyses by mass spectrometry and the falling-drop method.

Larson, G.O., L.R. Sherman, INFRARED SPECTROPHOTOMETRIC ANALYSIS OF SOME CARBONYL COMPOUNDS ADSORBED ON BENTONITE CLAY, Soil Sci., 98, 328-331, (1964).

Infrared absorption spectra of several carbonyl compounds adsorbed on bentonite clay not only show expected carbonyl shifts but, in addition, an even more consistent change in the relative intensities of the "bonded" to "free" hydroxyl peaks. It is suggested that the change in relative intensities may be a useful criterion for judging the importance of hydrogen bonding to the adsorption process.

Matsunaga, Y., INFRARED SPECTRA IN THE CHARACTERIZATION OF SOME MOLECULAR COMPLEXES OF THE DATIVE TYPE, J. Chem. Phys., 41, 1609-1613 (1964).

The infrared spectra of six diamine-quinone complexes and eight azine-quinone complexes were examined and compared with those of the component quinones and the semiquinone salts. The absence of the quinone but the presence of the semiquinone ion was proved in these complexes; therefore, the complexes may be characterized as essentially of the dative type. It is pointed out that most, if not all, of the known complexes having relatively low electrical resistivity are of this type.

May, L., R.L. Boccalatte, SAMPLING OF BIOLOGICAL MATERIALS FOR INFRARED SPECTROSCOPY, Anal. Biochem., 9, 1-8 (1964).

Various methods for examining the infrared spectra of proteins have been investigated using yeast alcohol dehydrogenase and ribonuclease as typical proteins. These methods include films cast from aqueous solutions, KBr disks, and agar films. The effect of preparation method was examined by measuring the enzymic activities of these proteins. The yeast alcohol dehydrogenase loses activity in all cases, and the infrared spectra show that the enzyme is in the stretched or random coil form. Ribonuclease is not denatured as a flim but is denatured with the other sampling procedures. However, the spectra indicate no change in the structure of this latter protein. The sampling procedure to be used will depend upon the nature of the protein, and the extent of denaturation of the protein should be checked by an independent method before interpreting its infrared spectrum. Tissue spectra are unreliable for determining the structure of its protein components.

Metzler, R.K., SILVER CHLORIDE DISH TECHNIQUE FOR INFRARED SPECTRA OF AQUEOUS POLYMER SUSPENSIONS, Anal. Chem., 36, 2371-2372 (1964).

Many of the inherent difficulties of using and maintaining silver chloride for infrared spectrometry can be eliminated by the preparation of low cost, disposable pressed disks from powdered silver chloride using the type of die commonly employed for the preparation of potassium bromide pellets. A spectrum may be prepared directly from a wet film of an aqueous suspension applied to the disk, or from a film dried on the disk.

Philpotts, A.R., RECORDING THE INFRA-RED SPECTRA OF GAS-CHROMATOGRAPHY FRACTIONS, Proc. Colloq. Spectros. Intern., 10th, Univ. Maryland, pp. 577-582 (1962).

This review article is mainly concerned with the principles of reducing sample size in analysis of components of mixtures by combined gas chromatography and infra-red spectroscopy.

Richards, P.L., HIGH-RESOLUTION FOURIER TRANSFORM SPECTROSCOPY IN THE FAR-INFRARED, J. Opt. Soc. Amer., 54, 1474-1484 (1964).

The construction and performance of three far-infrared spectrometers are described. These are a large-aperture diffraction-grating monochromator using six 28x35-cm. interchangeable echellete gratings to span the frequency range from 10 to 150 cm^{-1}, a set of 30-cm.-square lamellar grating plates which can be inserted into the grating monochromator to convert it into a lamellar grating interferometer, and an 18-cm. Michelson interferometer. The two interferometers are used with an automatic digital data recording system which records the interferograms on punched cards so that the spectra can be obtained by numerical transformation on a digital computer. All three instruments have been operated with the same detector and the same source, thus providing, for the first time, a controlled test of the relative merits of these three types of spectrometers. As expected theoretically, the two interferometers performed similarly except for differences due to beamsplitter efficiency and mechanical accuracy. Owing to their ability to look at all parts of the spectrum simultaneously and to achieve high resolution with large aperture, however, both interferometers proved far superior to the grating spectrometer, giving some of the highest resolution spectra yet obtained in the far-infrared. Examples are presented demonstrating resolution of ~ 0.1 cm^{-1} over the frequency range from 3 to 80 cm^{-1}.

Schwarz, F., A. Ziolkowski, 2-CHANNEL INFRARED RADIOMETER FOR MARINER II, Infrared Phys., 4, 113-126 (1964).

The design criteria for the electronics and optics of the Mariner II infrared radiometer are detailed. Finally, the performance characteristics are presented.

Tsuboi, M., INFRARED SPECTRA OF A FEW SYNTHETIC POLYRIBONUCLEOTIDES, J. Polymer. Sci., Part C, No. 7, 125-137 (1964).

In this paper infrared spectra of four hemopolymers, polyribocytidylic acid, polyriboadenylic acid, polyribouridylic acid, and polyriboinosinic acid were analyzed. Using various methods outlined in this report, the nature of several absorption bands of the polynucleotides have now been clarified.

Yoshinaga, H., RECENT RESEARCH IN FAR INFRARED OPTICS IN JAPAN, Appl.Opt., 3, 805-811 (1964).

This article reviews recent research in far infrared optics in Japan. The report consists of three sections: (1) components of instruments, (2) far infrared instruments, and (3) optical materials and research in the far infrared region.

Zhukov, A.G., LONG-WAVELENGTH INFRARED SPECTROMETER WITH ECHELETTES OF SMALL DIMENSIONS, Optics and Spectroscopy, 148-150 (1964).

A recording vacuum spectrometer using 80 x 100 mm diffraction gratings for work in the 40-2100 μ region is described. The wavelength variation of the reflectance of the echelette (blaze angle 23°) in the zeroth order is given.

18.3 SPECTROPHOTOMETRY

Garrett, H.E., A.J. Walker, THE SPECTROPHOTOMETRIC DETERMINATION OF SILICIC ACID IN DILUTE SOLUTION, Analyst, 89, 642-650 (1964).

An improved spectrophotometric determination of silicic acid in the concentration region 10^{-5} to 10^{-4}M has been developed in which the yellow molybdosilicate complex is formed and its optical density measured at a wavelength of 329 mμ. At this wavelength the two forms of molybdosilicic acid, α and β, reported by Strickland have equal extinction coefficients and thus the measurement is independent of the form of the acid. The conditions can be varied widely and the determination can be made in solutions having pH values up to 4·6. In the presence of alcohols it is possible to extend the region of quantitative formation of molybdosilicic acid to pH 6. Under these latter conditions only the α acid appears to be formed. In more acid solutions, however, alcohols themselves produce coloured complexes with molybdic acids.

Gorden, G., H. Yamatera, SPECTROPHOTOMETRIC DETERMINATION OF HYDROGEN CONTENT IN HEAVY WATER, Anal. Chem., 36, 1866-1867 (1964).

It is possible to rapidly and routinely determine the hydrogen content of small samples of water using a spectrophotometric method based on measurement of the absorbance of the HDO band at 16,680 A.

Herschberg, I.S., PRECISE ANALYSIS OF POLYCOMPONENT MIXTURES BY UV SPECTROSCOPY, Z. Anal. Chem., 205, 180-193 (1964).

A new "spectrocolorimetric" method for the quantitative analysis of multicomponent mixtures is described. Absorbance measurements of reference and sample solutions are carried out simultaneously in order to achieve independence of calibrations. Absorbance values used are extended to the range $0 \leq a \leq 1.6$. The measurements are performed at 20 to 40 different wave lengths and the obtained system of equations is solved by means of an electronic computer. Accuracy can be raised to ten times that of usual methods. Up to six components can be determined. The method has been applied with notable success to the analysis of mixtures of isomeric aromatic sulphonic acids.

Kaye, W., F. Waska, A RAPID-SCAN FOR ULTRAVIOLET SPECTROPHOTOMETER FOR MONITORING GAS CHROMATOGRAPH EFFLUENT, Anal. Chem., 36, 2380-2381, (1964).

A Beckman DV spectrophotometer has been modified to scan the wave length interval 1600 to 2100Å in 6 seconds with a resolution better than 1Å. This instrument is particularly suited to monitoring effluent emerging from a gas chromatograph. The repetitively-recorded spectra may be used to identify eluting components as well as to discriminate among sample components unresolved by the chromatograph.

Liebman, P.A., G. Entine, SENSITIVE LOW-LIGHT-LEVEL MICROSPECTROPHOTOMETER: DETECTION OF PHOTOSENSITIVE PIGMENTS OF RETINAL CONES, J. Optical Soc. Am., 54, 1451-1459 (1964).

A microspectrophotometer of exceptional sensitivity has been constructed to record absorption spectra of visual pigments in single cells using minimum light. With this equipment, pigments of individual cones have been recorded in regions of less than 1 μ radius, with minimum bleaching. The instrument is simple and flexible in design, and uses commercially available components throughout. This paper reviews some general design considerations, the character and performance of our equipment, and some of the results obtained with retinal cones.

Rice, E.W., C.Z. Lapara, RAPID ULTRAMICROSPECTROPHOTOMETRIC DETERMINATION OF MAGNESIUM, Clin. Chim. Acta, 10, 360-364 (1964).

An improved ultramicrospectrophotometric procedure for the rapid determination of magnesium in biological fluids has been developed. It employs the "Mann" dye, sodium I-azo-2-hydroxy-3 (2,4-dimethylcarboxanilide)naphthalene-1(2-hydroxybenzene-4-sulfonate), and requires only 40 µl of sample. In contrast to titan yellow procedures the presence of gluconate does not interfere with the proposed method.

Rikmenspoel, R., THE SENSITIVITY AND ACCURACY OF DUAL-WAVELENGTH SPECTROPHOTOMETERS, Appl. Opt., 3, 351-355 (1964).

The ultimate noise limit of a double-beam spectrophotometer is determined by the shot-noise in the photocurrent of the detector. The magnitude of the photocurrents to be expected is discussed for instruments using grating and prism monochromators. It is shown that a shot-noise level $<10^{-4}$ can be obtained with both grating and prism monochromators at a bandpass of 1 mµ. The nonlinear relation between a concentration change of the substance under study and the detected signal is examined.

Stephens, B.G., F. Lindstrom, SPECTROPHOTOMETRIC DETERMINATION OF SULFUR DIOXIDE SUITABLE FOR ATMOSPHERIC ANALYSIS, Anal. Chem., 36, 1308-1312 (1964).

Sulfur dioxide can be determined by passing samples of the gas through a solution of ferric iron and 1,10-phenanthroline. It reduces the ferric iron to ferrous iron which reacts with 1,10-phenanthroline to form the orange tris (1,10 - phenanthroline) iron complex. The interfering green-orange color of excess hydrolyzed ferric iron is conveniently masked with fluoride. Nitrogen dioxide does not interfere and ozone does not interfere at levels possible in industrial or urban atmospheres. The color forms immediately in the capturing solution and is stable for several days.

SECTION 19

SYNTHESIS OF ORGANIC COMPOUNDS

Fox, S. W., S. Yuyama, DYNAMIC PHENOMENA IN MICROSPHERES FROM THERMAL PROTEINOID, Comp. Biochem. Physiol., 11, 317-321 (1964).

Time lapse photomicrographic evidence is presented for the occurrence in self-organized supramacromolecular units of: (1)Optical disappearance of interior material to leave outer boundary or membrane; (2) Brownian motion within the unit; (3) Appearance of septa which divide the units. These phenomena occur in a suspension of particles formed from thermal polyamino acid. The dynamic phenomena are triggered by an increase in pH with phosphate-citrate buffer. The formed units and the phenomena they display arise from the material which is formed also in an experimental continuum, and thus provide a model of how some precellular phenomena might have arisen spontaneously.

Fox, S. W., THERMAL POLYMERIZATION OF AMINO-ACIDS AND PRODUCTION OF FORMED MICROPARTICLES ON LAVA, Nature, 201, 336-337 (1964).

A model of hot, dry lava field was selected for experimentation to test the thermal theory of biochemical origins. Laboratory and field observations support the inferences of ruggedness and potentiality of reaction over a significant range of conditions for the sequence involving thermal polymerization and aqueous spherulization.

Harada, K., S. W. Fox, THERMAL SYNTHESIS OF NATURAL AMINO-ACIDS FROM A POSTULATED PRIMITIVE TERRESTRIAL ATMOSPHERE, Nature, 201, 335-336 (1964).

Under appropriate conditions thermal energy has been successfully used for the polycondensation of free amino acids. Comparison of the thermal reactions with those energized by electric discharge suggests the significance of thermal energy in the synthesis of natural amino acids.

Johnson, C.B., A.T. Wilson, A POSSIBLE MECHANISM FOR THE EXTRA-TERRESTRIAL SYNTHESIS OF STRAIGHT-CHAIN HYDROCARBON, Nature, 204, 181-182 (1964).

A hypothesis has been proposed by one of the authors that there exists in free space a non-biological mechanism for the synthesis of hydrocarbon in a straight chain configuration. The work reported in this communication is a demonstration in the laboratory of the synthesis of linear molecules using this mechanism.

Pasynskii, A.G., T.E. Pavlovskiya, FORMATION OF BIOCHEMICALLY IMPORTANT COMPOUNDS DURING THE PRE-BIOLOGICAL STAGE OF THE EARTH'S DEVELOPMENT, Usp. Khim., 33, 1198-1215 (1964). (In Russian)

This is a review article concerning the synthesis of different biochemically important compounds from the initial substances resembling those existed in the primary atmosphere of the Earth. For the last 10-15 years many works have been devoted to the origin of life on Earth. Their number increases rapidly. All these works are reviewed in this paper.

Ponnamperuma, C., SYNTHESIS OF DEOXYADENOSINE UNDER SIMULATED PRIMITIVE EARTH CONDITIONS, Nature, 203, 400-401 (1964).

The investigation reported here shows that deoxyadenosine in appreciable yield may be synthesized by the use of conditions which appear to be likely to have occurred in the primitive Earth.

Ponnamperuma, C., GUANINE: FORMATION DURING THE THERMAL POLYMERIZATION OF AMINO ACIDS, Science, 143, 1449-1450 (1964).

The action of heat on a mixture of amino acids was studied as a possible abiological pathway for the synthesis of purines and pyrimidines. Guanine was detected. This result is significant in the context of chemical evolution.

SECTION 20

AUTHOR INDEX