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RESEARCH

SPECTROCHEMICAL ANALYSIS, SPECTROSCOPY, SPECTOPHOTOMETERS,
SPECTROPHOTOMETRY, PHOTOMETRY, REFLECTOMETRY, COLORIMETRY,
TRI-STIMULUS COLOR, CHROMATOGRAPHY
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"SPECTROCHEMICAL ANALYSIS, SPECTROSCOPY, SPECTROPHOTOMETERS, SPECTROPHOTOMETRY, PHOTOMETRY, REFLECTOMETRY, COLORIMETRY, TRI-STIMULUS COLOR, CHROMATOGRAPHY"

Compiled By
Texas Transportation Institute

1. "The Successive Determination of Maganese, Sodium, and Potassium in Cement by Flame Photometry" C. L. Ford, <u>ASTM Bulletin</u>, No. 233 Oct. 1958, p 57-63.

   The flame photometric methods of previous investigators have been simplified to permit the successive determination of mangnese, sodium, and potassium in cement using only one sample and one set of standard solutions, the latter being the novel feature. The Beckman model DU spectrophotometer could be used for manganese but that either would be used for sodium and potassium. The effect of interfering elements is discussed. The removal of silica from solutions of cement samples was found to be unnecessary under the test conditions. Appended is a "Method of Analysis of Cement for Manganic Oxide, Sodium Oxide, and Potassium Oxide by Flame Photometry," as developed.

2. "Composition of Chromatographic and Thermal Diffusion Fractions of Typical Asphalts" H. M. Chelton and R. N. Traxler, Section V, Paper 19 Fifth World Petroleum Congress, 1959. 10 pp.

   A study was made of the chemical composition of asphaltic materials and of the chemical reactions occurring when asphalts are oxidized. Three vacuum reduced residua and one hard asphalt oxidized from each of them were studied. The base stocks were chosen to represent the gel, solgel, and sol-type asphalts. The n-pentane insoluble asphaltenes were precipitated, and the asphaltenes further separated by fractional precipitation. The pentane soluble petrolenes from each of the 6 asphalts were separated into 32 fractions by chromatography and liquid thermal diffusion. The physical properties of the fractions were obtained along with percent C, H, O, N, S, and infrared analysis.

   It was found that asphalts contain a significant amount of oxygen, nitrogen, and sulfur, and should not be considered strictly hydrocarbons. The types of compounds in which these constituents occur are unknown, but carbonyl and Hydroxyl groups are in evidence in the infrared spectra. The basic structural configuration is thought to be a highly substituted ring system. The substituents may be carbon from from other rings, resulting in condensation, or alkyl groups most of which are short, perhaps only methyl groups. Most of the paraffinic methylene groups present are probably in one side chain containing 4 to 12 groups. These chains are shorter in oxidized asphalts and asphaltenes. The oxidation reaction is considered to be aromatization resulting from dehydrogenation of naphthenes followed by condensation. In the thermal diffusion separations it was found that non-ring carbon compounds were concentrated at the top of the column while aromatic carbon and oxygen, nitrogen, and sulfur, were accumulated at the bottom of the column.

3. "Determination of Oxidation Rates of Air-Blown Asphalts by Infra-Red Spectroscopy" J. R. Wright and J. G. Campbell, Journal of Applied Chemistry

Oxidation rates for eight air-blown asphalts were determined by measuring the change in infra-red absorption at 5.88 v-mu with time of exposure to the radiant energy of a carbon arc. While all the asphalts oxidized at different rates, those from the same geographical areas had similar rates; those from different areas varied considerably. The pattern of oxidation was generally the same for each of the eight asphalts, in that there was an induction period followed by a steady oxidation rate until near the failure point, beyond which time the oxidation rate accelerated until film failure as denoted by asphalt film cracking. An inverse relationship was found between the rate of oxidation; and the accelerated weathering durability of each asphalt.

4. "Application of Infrared Spectroscopy to Bituminous Mineral Filler Evaluation" Bernard Chaiken, Woodrow J. Halstead and Robert E. Olsen, Highway Research Board Bull. n 329, 1962, pp 38-47.

This paper describes the methods used and results obtained in evaluating a specific natural mineral deposit as a possible mineral filler for bituminous pavement mixtures. By resorting to a combination of instrumental methods, physical tests, and chemical analysis, the clay mineral nature of the material and its potential behavior as a mineral filler were determined. The methods used included infrared spectroscopy; X-ray diffraction; differential thermal analysis; immersion-compression tests of bituminous concrete mixtures; and softening point tests of asphalt-filler mortars. The report emphasizes the merits of combining available tools in such an evaluation and particularly describes the use of infrared spectroscopy in this connection.

5. "Basic Principles and Apparatus of Gas Chromatography With Particular Application to Coal Research" Larry L. Anderson, Utah Eng. Exp. Sta. Univ. of Utah, Bull. No. 130, Aug. 1964, 37 pp.

This general instruction manual for gas chromatography is designed for technical people, students and analysts who wish to become acquainted with the present practices and applications of gas chromatography as an analytical method. The manual is not intended to be comprehensive because there are several books which cover the field as adequately as can be expected under its present, rapid growth. Since the "birth" of gas chromatography in 1952, new publications have been increasing at a rate which makes any comprehensive publication only temporarily so. In 1955 the papers published on gas chromatography were still fewer than one hundred, but these have reached over 2,000 in 1963; new journals have been born and others have expended to include publications in the field. Books and articles have been referred to which are more comprehensive as to both theory and detail of specific applications.

This manual is written to acquaint the reader with the apparatus available, the methods used, and the results obtained by the gas chromatography technique. Methods of calibration for qualitative and quantitative analyses are described and some special techniques utilizing gas chromatography are related.

6. "The Mass Spectrometric Analysis of Asphalt" R. J. Clerc and M. J. O'Neal, Jr. Analytical Chemistry Vol. 33, No. 3, pp 380-382, March 1961.

A preliminary investigation has indicated that mass spectrometric techniques can be applied successfully to the analysis of asphalt and other residual petroleum fractions. A High-temperature mass spectrometer was temporarily remodeled so that a sample of asphalt could be placed within the ionizing region. With such an arrangement mass spectra were obtained from mass 24 to about mass 1900. Although the distribution of the unresolved peaks was obtained. Some insight into the composition of asphalt from West Texas straight-run residue was gained. This particular sample of asphalt had a molecular weight range of 500 to 1900 with a mean value of about 900. Fragment ions indicated that certain heterocyclic and aromatic nuclei were the predominant molecular structural groups.

7. "Zinc Oxide As a Standard Substance in The Solution Calorimetry of Portland Cement" Edwin S. Newman, Journal of Research, Sect. A, Physics and Chemistry, National Bureau of Standards, Vol. 66A, No. 5, pp 381-388, Sept. - Oct. 1962.

Zinc oxide is the standard substance specified for calibrating the heat-of-solution calorimeters used in determining the heat of hydration of portland cement in several American and Foreign cement specifications. The heats of solution of zinc oxide samples from different sources and after different heat treatments have been determined in the standard mixture of nitric and hydrofluoric acids. It is concluded that the value given in the specifications is low, that heat treatment in the range 310 to 950 C is not critical, that small variations in the ZnO/acid weight ratio are without significance, and that analytical-reagent zinc oxide from various sources may safely be used. The mean value obtained for the heats of solution of zinc oxide from twelve sources determined in triplicate in $1.00HNO_3$, $o.284HF$, $26.38H_2O$ at a ZnO/acid weight ration of 7/425 at 25 C was 257.82 gal/g with a standard error of 0.015 cal/g. The thermichemical calorie of 4.1840 joules is used. The temperature coefficient based on least-square fitting to 16 data points obtained in an earlier study was -0.87 cal/g-deg, with a computed standard and temperature coefficient given in the specifications are 256.6 cal/g and -0.1 cal/g respectively.

8. "An Investigation of Shear Strength of the Clay-Water System by Radio-Frequency Spectroscopy", A. G. Pickett and M. M. Lemcoe, Journal of Research-Geophysical Union, 1515 Massachusetts Ave., N. W., Washington 5, D. C. Vol 64, no. 10 pp. 1579-86, October 1959.

This paper summarizes soil mechanics study of the clay-water system made with steady-state nuclear magnetic resonance as the analytical tool. Although the study was limited to measurements of the contribution of water-lattice strength to the shear strength of clay soils, the results demonstrate the utility of the techniques of radio-frequency spectroscopy in such investigations. The authors conclude that water-lattice strength is of negligible significance in determining the shear strength of wet clay soils.

9. "X-Ray Spectrochemical Analysis of Cement" Technical News Bulletin, National Bureau of Standards, Vol. 48, no. 5, p 73, May 1964.

A study of cements by X-ray spectrochemical analysis is being conducted at the Bureau. The purpose of this study is to determine the feasibility of using X-ray spectrochemical analysis as a routine test method for cement to replace the conventional chemical methods. The results of the work to date show that the X-ray spectrochemical method is potentially suitable for this work, but with present equipment and sample preparation, it does not reduce the overall man-hours required to perform the tests.

X-ray spectrometers are in use at a number of cement-manufacturing plants for control of raw materials and finished products, but the use of such apparatus for analysis of materials from a single source presents fewer problems than when used on products from a wide variety of compositions. It is this latter requirement that so far has made necessary the time-consuming sample preparation.

To date it has been possible to obtain the required accuracy only be eliminating the effect of crystalline structure through fusion of the sample with lithium tetraborate and subsequent grinding to a uniform particle size by a special technique. Boric acid is added as a binder to form the pellet used for analysis in the spectrometer. Although only 5 min are required to make the X-ray measurements, the time required to prepare the sample makes the total number of man-hours involved in an alaysis roughly the same as that for the conventional chemical methods. New methods of sample preparation are under study; when combined with improved equipment, they may reduce the time factor considerably.

The present study is continuing with the goals of reducing the time required for analysis and of obtaining better accuracy. Efforts will be made to improve instrumentation and to develop sample preparation methods.

10. "Analysis of Sodium in Concrete by Fluorescence Photometry" H. F. Pfug and C. F. Crupton Materials Research & Standards, Vol. 3, n 7, pp 556-560, July 1963.

The presence and distribution of sodium in hardened concrete are revealed under ultraviolet light by reacting zinc uranyl acetate with the sodium to form fluorescent sodium zinc uranyl acetate. The approximate concentration of the sodium is obtained by measuring the intensity of fluorescence of the reaction product with a reflection photometer. The procedure is rapid and simple and allows the analysis of many samples in one day. The samples do not need to be crushed, cut, or dissolved; any surface that is approximately smooth can be used. The samples do not need to be crushed, cut, or dissolved; any surface that is approximately smooth can be used. The prodedure can be applied directly to the surface of roads, bridges, dams, etc.

11. "Biodynamic Studies on Impact Protection" B. Aldmen, Acta Physiologica Scandinavica, 1963, 56 p 80. Road Abstracts, Vol 30, No. 10 p 236, Oct. 1963.

X-rays are electromagnetic radiations of very short wave length. They are produced when fast moving electoons impinge on matter or when a sample is iradiated with properly selected X-rays (secondary or Fluorescent emmission). X-rays have the property to give diffraction figures with crystallized bodies.

X-ray diffractions by crystals is the basis of diffractometry, for mineralogic analysis of crystallized compounds.

Secondary emission is the basis of X-rays fluorescent spectroscopy for quantitative and qualitative elementary analysis by irradiating a sample with primary X-rays, and studying the resulting fluorescent spectrum.

The Ponts et Chaussees Central Laboratory is using an improved Philips apparatus, allowing with these methods to work out various problems.

Pit-run sands, soils and rocks diffractometric analysis search for clay traces, etc.

Roads paints studies: Pigment mineralogic composition semi-quantitative method elementary analysis.

Proportion of crystalline phases in portland concretes by diffractometric method, and rapid quantitative elementary analysis of concretes by fluorescent spectrometric methods arc being studies.

12. "Potential Applications of Spectroscopy in The Highway Testing Laboratory" Woodrow J. Halstead and Bernard Chaiken, Public Roads, Vol. 32, No. 8, pp 186-189, June 1963.

Highway testing laboratories are confronted with an increasing volume and variety of construction materials to be tested for compliance with chemical or mineralogical requirements. In addition, many new and complex materials used in construction, such as plastics, synthetic polymers, surface active agents, and coatings, are too complex to be effectively analyzed by ordinary chemical means. The potential advantages of using spectroscopy methods to provide more rapid and accurate analyses of materials than is otherwise possible by standard chemical procedures are discussed in this article. The suitability of spectroscopic techniques to determine the nature of complex materials, which cannot be practicably analayzed by chemical methods, is also discussed. The article includes general estimates of cost and time factors involved for several of the more useful techniques.

13. "Evaluation of Infrared Spectrophotometry for Compositional Analysis of Lunar and Planetary Soils" R. J. P. Lyon, Technical Note D-1871 U. S. National Aeronautics and Space Administration, Washington 25, D. C., April 1963, 118 pp.

A preliminary feasibility study of infrared analytical techniques for the study of lunar surface has been made, including absorption studies of 370 rock and mineral samples, and reflection studies of 80 rocks. Spectral information was collected in the wavelength range 2.5 to 25 microns (4,000 to 400 cm^{-1}). Emittance spectra have been calculated from the reflectance data for several of the most important rock types. Feasibility of absorption analysis has been established and this method is recommended, particularly for use in manned laboratories.

The feasibility of near-normal specular reflection has also been established but its use also may be confined to manned laboratories because of the requirement that small, but highly polished flat surfaces must be prepared on the samples.

The feasibility of spectral emmission needs to be studied further, particularly to determine the limits of applicability to materials with porous or powdery surfaces. Rocks of low porosity and with reasonably flat surfaces are quite suitable for emission analysis, either from a stationary, surface-roving, or even an orbiting lunar vehicle.

These analytical methods are not dependent upon the crystallinity of the sample, and the composition of volcanic glasses, lavas, or crystalline rocks can be determined. The presence or absence of "water" can be determined, and its form, whether as bonded hydroxyl (OH)', or as loosely attached water molecules can be defined.

14. "Annotated Bibliography on Soft X-ray Spectroscopy" H. Yakowitz AND J. R. Cuthill, National Bureau of Standards, Monograph 52, June 29, 1962. 108 pp $1.00.

About 550 references are contained in this bibliography which includes, it is believed, a complete coverage of the soft X-ray literature since 1950 through 1960. Some references to earlier work are given but the general review references, listed separately, give an adequate coverage of the earlier work.

The emphasis is on the application of soft X-ray spectroscopy to the study of valence band electronic states in metals and alloys and therefore the spectral region of 25 to 800 angstroms involving rulled glass grating spectrometers is of principal interest. However, a wealth of data have been gathered, primarily by the Russians, on valence electronic states by means of high energy transitions where crystal spectrometere are satisfactory. These references and any X-ray work leading to the distribution of valence electronic states are included regardless of the transitions employed.

In addition to soft X-ray data, references on all pertinent aspects of the apparatus and experimental problems are included. Also listed separately are references of value in corroborating soft X-ray data with other results, such as energy band calculations.

Sufject, author, X-ray band, material and other indexes are included.

15. "Flame Photometric Determination of Magnesium Oxide in Portland Cement" T. C. Wilson, N. J. Grotinger, Am Soc Testing Matls-Bul # 189 Apr. 1953 p 56-8.

Report on method developed at Los Angeles City Bureau of Standards; sample solution may also be used for determination of sodium and potassium oxides by flame photometry and sulphur trioxide by nephelometry; insoluble residue is determined on residue retained on filter paper and in original beaker.

16. "Rapid Determination of Storntium and Manganese in Cement", J. J. Diamond, Pit & Quary v 49 n 4 Oct. 1956 p 91, 130.

National Bureau of Standards flame photometric method does not require previous chemical separation of substance; all determinations can be made on same 1-gram sample of cement, dissolved in hydrochloric acid and filtered to remove any insoluble material; experiments with pure solutions indicate that peaks in emmission of strontium occur at about 461 and 675 μ .

17. "Short Method for Flame Photometric Determination of Magnesium, Manganic, Sodium, and Potassium Oxides in Portland Cement" C. L. Ford, ASTM-Bul n 250, Dec. 1960, p 25-9.

Existing methods were modified to permit use of one set of standard calibration solutions for flame photometric determination of amounts of all four elements; supporting data show accuracy and precision.

18. "Water-Reducing Retarders for Concrete-Chemical and Spectral Analyses" W. J. Halstead, B. Chaiken, 126-35 - Symposium on Water-Reducing Retarders for Concrete, Publ. Roads V. 31 n 6 Feb. 1961, p 125-54.

Group of 3 articles relating to admixtures to retard set of material for use in road construction.