

H-216

APPLICATIONS OF ABSORPTION SPECTROSCOPY TO HIGHWAY TESTING AND RESEARCH

The main purpose of this report is to summarize current and proposed projects of the Research Laboratory involving the application of infrared, visible and ultraviolet spectroscopy to research and materials control in the Michigan State Highway Department. Selective absorption by chemical compounds of radiant energy at specific wavelengths in the region of the electromagnetic spectrum ranging from the ultraviolet through the visible to and including the near infrared provides a valuable means for identification and quantitative analysis hitherto difficult or impossible by conventional chemical methods. This is especially true in the field of organic chemistry, which includes paints, petroleum products, rubber, plastics, paper and textiles. In addition to organics, there are many other known applications to the testing of such inorganic materials as portland cement, mineral aggregates, glass, pigments, ceramics and metals.

The scope of this discussion includes infrared, visible and ultraviolet techniques because they supplement each other and all are needed in order to realize the maximum benefits from each. Besides these methods, several other instrumental methods of analysis, such as Raman spectra, X-ray diffraction, mass spectrography, and polarography, are finding increased technical and industrial applications. A sufficiently thorough study of these latter methods to determine their possible worth in highway work has not been made, but X-ray diffraction appears to offer considerable promise in the field of mineralogy by supplying valuable data on physical states of aggregation and crystal structure of polymorphic substances.

This report includes a brief description of absorption methods, a summary of present and proposed projects in the Research Laboratory program and an appended

list of equipment needed in addition to present equipment to implement the program.

General Description of Absorption Methods

The present most common use of infrared absorption is in the wavelength range of 2 to 25 microns. This range cannot be covered with a single set of optics, however. Rock salt optics are the most generally useful and cover a range of about 2 to 15 microns. Other optics are required in order to extend the range to 25 microns and to improve resolution at the lower wavelength end of the infrared band.

Selective absorption in the infrared in general uniquely characterizes individual chemical compounds. All organic and many inorganic materials give analytically useful spectra and many organic analyses formerly impossible are easily accomplished by this method. Besides its use in the identification and quantitative analysis of compounds, infrared spectroscopy can be used to monitor the quality of chemically complex materials in an empirical way without specific identification of the individual components. This is done by comparing spectra of incoming shipments with the spectrum of a reference material of standard quality and behavior. Because of its ability to identify specific functional groups within a chemical compound, the infrared spectrometer is also being used more and more to follow changes accompanying polymerization, oxidation and other degenerative reactions occurring in the breakdown of organic coatings and other materials.

Despite its great usefulness, infrared analysis has some definite limitations which should be kept in mind. It is not well suited to the examination of aqueous solutions because of water interference. One of its more serious limitations is that it frequently fails to detect very small amounts of minor components in complex systems. A third limitation of infrared is in the analysis of drying oil mixtures, where the spectra of linseed oil, cottonseed oil and soybean oil for example are practically

indistinguishable. In this latter case, the difficulty can be surmounted by combined chemical and spectroscopic techniques, using ultraviolet methods to supplement the infrared.

For the reason just mentioned, ultraviolet methods are now widely used in oil analysis and, when applicable, ultraviolet is superior to infrared in sensitivity. The ultraviolet region of the spectrum ordinarily used for analysis covers a wavelength range from about 0.2 to 0.4 micron at which latter wavelength the radiation becomes a visible violet. Because water is transparent to the ultraviolet, this method is especially well adapted to the study of aqueous solutions. As mentioned previously, it is frequently necessary to supplement infrared analysis with ultraviolet methods and chemical analysis to solve complex analytical problems.

While the portion of the ultraviolet band covered by the Beckman D U ultraviolet spectrometer is only between wavelengths of 0.2 and 0.4 micron, the instrument actually covers in addition the entire visible region (0.4 to 0.75 micron) and fills the gap beyond this in the very near infrared (0.75 to 2.0 microns) to where the infrared spectrometer takes over. Moreover, the flame and reflectance attachments make the ultraviolet spectrometer an extremely versatile instrument which can be used for the exact determination and specification of color of materials, and rapid quantitative determinations of minerals in cement and aggregates which are costly and time consuming by ordinary chemical methods. With the flame attachment it is particularly well suited to the determination of metals in trace amounts present in either organic or inorganic materials.

Research Laboratory Projects

With the above very brief discussion as a background, the various objectives being pursued or under consideration by the Research Laboratory are outlined be-

low. In a few of these, where noted, significant progress has already been made. A major portion of the projects listed is devoted to the development of time and money saving test procedures in order to conserve technical manpower and speed up acceptance tests. Others, more fundamental in nature, are designed to provide additional knowledge of the constitution and behavior of some of our highway materials without which further progress on some of our most baffling problems is uncertain or impossible.

I. PAINTS

A. Identification of Traffic Paints

In the performance method of specifying and testing traffic paints it is essential that the paint purchased from the successful bidder be the same as that submitted originally for the tests. Infrared absorption methods have provided the positive identification necessary to strengthen this weak link in procurement by performance.

Pigment, vehicle, and volatiles are separated and tested independently using a combination of physical, chemical, and spectroscopic tests. Here the empirical infrared procedure is used to provide a rapid, simple method of testing every batch of delivered paint for conformance with the reference standard.

This method was followed by the laboratory in testing 1954 purchases and will be continued next year.

B. Analysis of Traffic and Maintenance Paints

The purpose of this work is to analyze paint products, including wood preservatives and membrane curing compounds, to correlate composition with performance. Manufacturers of proprietary products generally will not dis-

close a successful formula, and complete chemical analysis is usually impossible without instrumental methods.

In most cases a complete constitutional analysis is possible by using a judicious combination of infrared and ultraviolet absorption spectroscopy supplemented by chemical tests.

The Research Laboratory has begun work on the infrared and chemical phases of such an analysis using the 22 samples of traffic paint submitted for this year's tests, and one membrane curing compound. Tests with the ultraviolet will be started as soon as a spectrometer becomes available.

C. Studies of Film Degradation

The general objective of this investigation is to study the mechanisms of film degradation and failure by following chemical changes in paint vehicles and pigments on weathering through the use of infrared and ultraviolet absorption spectroscopy.

This is a long range project which has not been started as yet in our laboratory. The du Pont Company and the Naval Research Laboratory in Washington are working on the same problem with the same kind of instruments and have already made considerable progress.

D. Color Specifications

The purpose of this work is to define color exactly for specification purposes by means of chromaticity coordinates in order to do away with visual color matching of the material with standard color chips. Reference standards change with time and even the standard color chips have to be reproduced by the visual method in the absence of photometric tests. Progressive industry is rapidly changing over to the newer method.

Procedures for colorimetry and reflectance tests have been in use by the Research Laboratory for more than 5 years using relatively crude equipment. Reflectance and color specifications for amber reflector buttons and white membrane compounds were written around these tests and are still in force. Chromaticity coordinates were determined on all batches of traffic paint delivered in 1954 with the ultimate object of including suitable chromaticity limits for white and yellow paints in the specifications. The same method can be applied to all paints and other materials where conformance with a color standard is required.

The Beckman ultraviolet spectrometer with reflectance attachment will give faster, more accurate, more reproducible results than present equipment.

II. PETROLEUM PRODUCTS

A. Identification of Asphalt Sources

The objective of this investigation is to identify asphalts by geographical source so that service records of asphalts may be tied in with their origin, and rapid identification methods set up for acceptance tests. By spectroscopic examination, both infrared and ultraviolet, of asphalts from various sources, it may be possible to find distinguishing characteristics sufficiently strong for positive identification. Some preliminary work with infrared only has already been done along this line in the Research Laboratory with inconclusive results. Strong possibilities still exist, however, of solving the identification problem through the use of preliminary separations of asphalt components by chromatography and the application of ultraviolet and flame photometry techniques.

B. Weathering Studies of Asphalts

The purpose of this study is to learn mechanisms of asphalt film degeneration on weathering and how these are related to composition and origin. A corollary objective is the possible finding of a cheap additive for the asphalt to inhibit or slow down oxidative and other degenerative changes.

By studying the constitution of asphalts through the use of chromatographic separations, instrumental analysis (infrared and ultraviolet), and chemical and physical tests, it should be possible to learn something of the nature of the chemical and physical changes which take place on weathering. When these changes are sufficiently understood, remedial measures may be explored. This is one of our most important projects because it goes straight to the roots of a major phase of the problem of the durability of bituminous construction. Some preliminary work has already been done in the Research Laboratory on the chromatographic separation of asphalt constituents with encouraging results.

C. Asphalt - Rubber in Joint Seals and Bituminous Mixtures

The purpose here is to effect a qualitative or quantitative analysis of asphalt-rubber blends for correlation with physical properties and performance in service.

Natural rubber can be distinguished from synthetics by infrared absorption, but new natural rubber cannot be distinguished from reclaimed natural rubber as yet. It may be possible to use an empirical infrared or ultraviolet survey spectrum to establish correlation with physical properties and monitor the uniformity of product. If this could be accomplished, a real saving in testing time and expense would be effected.

Very little has been done in the Research Laboratory along this line other than some preliminary work on sample preparation.

D. Miscellaneous Laboratory Applications

1. Distinguishing Cracked From Uncracked Asphalts. -- It should be possible to use infrared analysis to determine homogeneity of asphalts as affected by cracking. We have already made some progress on this in the Research Laboratory. There is a strong possibility that a simple examination in the infrared or ultraviolet could be worked out as a substitute for the longer, more involved Oliensis spot test.

2. Detection of Solvent Traces in Recovered Asphalts. -- It is important that all solvent be removed from asphalts recovered from bituminous mixtures before performing consistency tests. It seems quite possible that a spectroscopic method can be devised for detecting traces of solvent which may remain in asphalts after recovery from solution, thus doing away with the long, rather involved chemical method hitherto employed in research work.

III. PORTLAND CEMENT AND CONCRETE

A. Chemical Analysis of Cement

Standard flame photometry methods are already available to analyze cement for chemical composition to determine conformance with specifications. The alkali oxides, difficult and expensive to determine by ordinary chemical methods, are particularly amenable to rapid, accurate determination by flame photometry. Magnesium oxide in cement can be determined in one tenth the time now required. These methods may be applied in the laboratory immediately on acquisition of a Beckman ultraviolet spectrometer with flame

attachment.

B. Identification and Determination of Minerals in Aggregates

The application intended here is to supplement physical methods with absorption spectroscopy and flame photometry in the petrographic examination of mineral aggregates for evaluation of aggregate sources.

There are many times when it is of great advantage to know the mineral composition of aggregates. Examples of this are the relation of composition to weathered surface texture (skid resisting characteristics), the discovery and identification of potential cement-reactive materials, and the identification of various deleterious rock types. Absorption and flame photometry methods of analysis are generally applicable to most rock types. In conjunction with other physical and chemical methods they should advance this important phase of laboratory investigation considerably. Some preliminary work using infrared only has been done in the laboratory with present equipment.

IV. MISCELLANEOUS LABORATORY TESTS

In addition to the major projects listed, there is a host of minor applications of flame photometry to routine laboratory analysis, for example: brine solutions for various metals; nonferrous metals, clay, glass, etc. for sodium, potassium, calcium, lithium, iron, manganese, magnesium, rubidium, copper, silver, aluminum, lead, barium and others; and steels for manganese, chromium, cobalt, nickel, copper, lead and boron. These analyses, which are both rapid and accurate, are all possible with the flame attachment on a Beckman DU ultraviolet spectrometer.

General Comments and Conclusions

From the above summary it can be seen that absorption spectroscopy and flame photometry can be powerful tools in highway testing and research. This summary touches only the high spots of presently known possible applications. Unforeseen applications of such versatile methods always develop when the tools are at hand. As a case in point, the use of the infrared spectrometer for acceptance testing of traffic paint was not a specific objective of the Research Laboratory when the instrument was first purchased.

Despite their great usefulness, the methods just outlined offer no universal solution to all our analytical problems. Problems of any complexity always require companion techniques of chemical or physical separation and examination, and a great deal of laboratory work must be performed to establish a background for the interpretation of results. This fact necessarily implies a long range nature for some of the major projects. Other less complicated techniques can be put to use immediately in a practical way as soon as the proper equipment becomes available. The 1953 ASTM Standards include more than 30 test methods based on absorption spectroscopy, reflectance measurements and flame photometry. Committee D-1 on paints has also proposed a 1954 method of test for phthalic anhydride content of alkyd resins (used in better quality enamels and traffic paints) based on the use of ultraviolet spectroscopy. Their faith in this technique is attested by the fact that the proposed method takes precedence over the strictly chemical procedure as the referee method.

EQUIPMENT LIST

| Item | Wavelength Range, Microns | Use | Approximate Cost |
|--|--|--|---------------------|
| <u>Present Equipment</u> | | | |
| 1. Cenco-Sheard Photometer | 0.4 - 0.75 | Visible absorption, Colorimetry | 400.00 |
| 2. Beckman IR-2 Infrared Spectrometer | 2 - 15 | Infrared absorption | <u>7,500.00</u> |
| Total | | | 7,900.00 |
| <u>Additional Equipment Needed Now</u> | | | |
| 1. Beckman DU Ultraviolet Spectrometer | 0.2 - 2.0 | Ultraviolet Absorption Visible absorption Flame photometry Reflectance Colorimetry | 3,600.00 |
| 2. Perkin-Elmer Double Beam Infrared Spectrometer. Rock salt optics | 2 - 15 | Direct Infrared transmittance recording | 15,000.00 |
| 3. Additional Optics for Perkin-Elmer | | | |
| Potassium bromide | 0.2 - 28 | Extend infrared range | 1,500.00 |
| Calcium fluoride | 0.1 - 8.5 | Increase resolution | <u>2,100.00</u> |
| Total | | | 22,200.00 |
| <u>Possible Future Equipment</u> | | | |
| 1. X-Ray Equipment | 7×10^{-5} - 23×10^{-5} | Powder diffraction | <u>7,000.00</u> |
| Grand Total | | | 37,100.00 |