SHRP2 SOLUTIONS

# Primer

# Techniques to Fingerprint Construction Materials

## Techniques to Fingerprint Construction Materials User Guide (R06B)

---

**April 9 2019**

# Contents

## Tables

## Figures

# Definitions

| | |
|---|---|
| µm | micrometers |
| AASHTO | American Association of State Highway and Transportation Officials |
| Al | aluminum |
| As | arsenic |
| ASTM | American Society for Testing and Materials |
| ATR | attenuated total reflectance |
| C=C | double carbon bond |
| C-N | carbon-nitrogen bond |
| C=O | carbonyl |
| Ca | calcium |
| $Ca(OH)_2$ | calcium hydroxide |
| $CaCO_3$ | calcium carbonate |
| CaO | lime |
| $Cl^-$ | chloride |
| $cm^{-1}$ | inverse centimeter |
| -COOH | carboxyl |
| CSV | comma separated value |
| Cu | copper |
| DOT | Department of Transportation |
| DRIFT | diffuse reflectance |
| EDXRF | energy dispersive X-ray Fluorescence |
| FHWA | Federal Highway Administration |
| FTIR | Fourier transform infrared |
| Ge | germanium |
| HMA | hot-mix asphalt |
| IR | infrared |

| | |
|---|---|
| IRE | internal reflection element |
| LOD | limit of detection |
| Mg | magnesium |
| mg/kg | milligrams per kilograms |
| mm | millimeter |
| MS | mass spectrometer |
| $Na^+$ | sodium ion |
| $-NH_2$ | amine |
| $NH_4^+$ | ammonium ion |
| Ni | nickel |
| NIST | National Institute of Science and Technology |
| NMR | nuclear magnetic resonance |
| -O | oxygen |
| -OH | hydroxyl |
| OSHA | Occupational Safety and Health Administration |
| Pb | lead |
| PCC | Portland concrete cement |
| PDA | personal digital assistant |
| PMI | Positive material identification |
| $PO_4^{3-}$ | phosphate ion |
| ppm | parts per million |
| QA | Quality assurance |
| *R06B* | *Techniques to Fingerprint Construction Materials* |
| RAP | recycled asphalt pavement |
| S=O | sulfoxide |
| $SO_4^{2-}$ | sulfate ion |
| SBS | styrene-butadiene-styrene |
| *SHRP2* | second Strategic Highway Research Program |

| | |
|---|---|
| Si | silicon |
| $SiO_2$ | silica |
| TDOT | Tennessee Department of Transportation |
| Ti | titanium |
| U | uranium |
| UV-VIS | ultraviolet - visible |
| WDXRF | wavelength dispersive X-ray fluorescence |
| XRD | X-ray diffraction |
| XRF | X-ray fluorescence |
| Zn | zinc |
| ZnSe | zinc selenide |

# Executive Summary

*Techniques to Fingerprint Construction Materials (R06B)* was developed through the second Strategic Highway Research Program (SHRP2), which is a collaboration between the Federal Highway Administration (FHWA) and the American Association of State Highway and Transportation Officials (AASHTO). *Techniques to Fingerprint Construction Materials* evaluated portable spectroscopy technologies that can be used during construction to verify the chemical compounds or presence of certain additives or contaminants in some commonly used construction materials. This report provides guidelines for applying selected portable spectroscopy techniques to a wide range of materials commonly used in transportation infrastructure. Spectroscopy includes several methods, and only a subset of the most common ones were screened during the research phase of *Techniques to Fingerprint Construction Materials*. The most promising, field-ready technologies that apply to a large number of materials emerged to be X-ray fluorescence (XRF) and attenuated total reflectance Fourier transform infrared (ATR FTIR) spectroscopy.

XRF spectroscopy measures the elemental composition of materials, specifically metals, reporting the concentrations in milligrams per kilogram (mg/kg) of material. This method mostly applies to solid materials, but it can be used to measure metal concentrations in liquids and suspensions as well. Most hand-held XRF spectrometers can detect elements with atomic number Z between Z = 12 (magnesium [Mg]) and Z = 92 (uranium [U]); however, instruments that can also detect sodium [Na] with Z = 11 are also available at a higher price. Portable XRF analysis can be applied in trace-element mode and has detection limits between 2 and 100 mg/kg for most metals, depending on the element and the matrix, or in alloy mode to determine ore-grade concentrations (greater than 1 percent by weight). Different vendors provide different calibration sets to cover a wide range of materials and concentrations. XRF instruments are easy to operate. The analysis can be conducted in bulk samples placed in a sample cup or directly on a surface, and the duration of the test is under 3 minutes. Potential applications of XRF for construction materials include analyzing steel grade, aggregate quality, traffic paints and epoxies; identifying lead (Pb) and arsenic (As) in glass beads; identifying hazardous heavy metals in soils, aggregates, and construction debris; and identifying waste materials such as recycled engine oil bottoms in asphalt, among others. A draft AASHTO method has been developed for traffic paints, along with an ASTM International (formerly American Society for Testing and Materials [ASTM]) method (ASTM D4764 - 01(2012)).

ATR FTIR spectroscopy detects the vibrations of polar, asymmetric functional groups (-OH, C=O, C-C, C-N, $-NH_2$, $-SO_4$, and others), which appear as peaks in a recorded spectrum at characteristic wavelengths in the infrared (IR) region. Comparing an unknown spectrum with spectra of pure compounds is the basis of fingerprinting materials and their mixtures. The absorbance at the characteristic wavelengths can also be used to quantify a particular functional group in the analyzed mixture, provided that an appropriate calibration curve is set up. Thus, ATR requires a higher degree of training for spectra interpretation and acquisition of reference spectra for field utilization. ATR spectrometers are available both as portable benchtop and handheld instruments, the analysis requires little sample preparation beyond selecting a representative aliquot, and the test duration is under 5 minutes. Potential applications of ATR are identifying admixtures in Portland cement concrete; detecting lime in asphalt; detecting and semi-quantifying styrene-butadiene block (SBS) polymers in asphalt; detecting tar, oil, and organic contaminants in soils and aggregates.

# 1.0 Background

## 1.1 What is Spectroscopy

Spectroscopy is the use of light to determine material properties. The interaction between light and materials always results in the emission of secondary radiation, similar to the principle of a prism analyzing sunlight into a rainbow. The secondary radiation is captured by a detector, and the recorded signal is the spectrum, from which the properties of the material may be inferred, as illustrated on Figure 1. Typical applications of interest are identifying the material type (i.e., fingerprinting) and quantity (quantification). While the underlying physical and chemical principles behind spectroscopic techniques are complex, technology often allows us to use spectroscopy to infer material properties with equipment and software that is easily accessible to non-specialists or personnel with minimal training in physics and chemistry. The details of the qualitative and quantitative analysis methods depend on the specific type of spectroscopy and will be discussed for selected techniques. More information on additional spectroscopic techniques and their applications may be found in Zofka et al. (1).

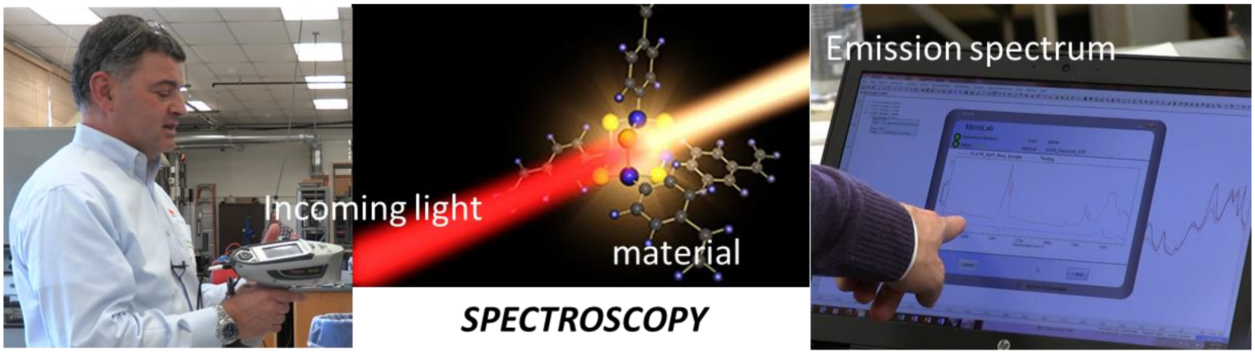

**Figure 1. Principle of Spectroscopy**

## 1.2 User Guidelines

The user guidelines depend both on the choice of the spectroscopic technique and the target application. This primer specifically focuses on the two techniques, Fourier-Transform Infrared Spectroscopy (FTIR) and X-ray Fluorescence (XRF), and is written specifically with respect to applications for construction materials. In addition to equipment operation issues that are addressed by the manufacturer operating manuals, a variety of standard methods exist for each technique, developed both by the American Society for Testing and Materials (ASTM) and AASHTO. The relevant standards will be listed for each technique in the respective section.

## 1.3 Target Users and Applications

This primer has been written considering that the main target users of spectroscopic techniques for construction materials are state highway agencies that require QA procedures to meet material specifications. However, material manufacturers and contractors are also potential end users of these techniques for the same purpose and may adopt the recommendations as well.

The target applications depend on the particular technique to be implemented. This primer focuses on XRF and FTIR spectroscopy as the two most versatile portable techniques that can be used for a variety of applications. These will be discussed for each method separately in the following chapters. An overview is provided in Table 1.

**Table 1. Overview of Potential Applications for XRF and FTIR Spectroscopic Techniques**

| XRF | FTIR |
|---|---|
| QA of traffic paints and epoxies | Identification of PCC admixtures |
| Detection of lead (Pb) and arsenic (As) in glass beads | Detection of lime in asphalt |
| Analysis of heavy metals in construction debris, old paints, aggregates, soils etc. | Evaluation of degree of asphalt oxidation (in research stage*) |
| Detection of lime and polyphosphoric acid (PPA) in asphalt | Identification and semi-quantification of SBS polymers in asphalt |
| Detection of motor oils, waste engine oils and rubber in asphalt mixes | Identification of waste engine oil and other admixtures in asphalt (in research stage*) |
| QA of Portland cement | Detection of miscellaneous additives in asphalt (crumb rubber, nanoclay and carbon admixtures –in research stage*) |
| Steel grade and metal alloy analysis | Detection of organic contaminants (diesel, tar, waste oil) in inorganic media (soils, aggregates) |

Note: * These applications have been presented in the research literature, but not vetted in the field.

# 2.0 X-Ray Fluorescence

## 2.1 Principle of XRF

XRF is a nondestructive spectroscopic method that is used to determine the **elemental composition** of materials. When atoms are struck with high-energy (X-ray) radiation, they absorb and reemit the radiation as a set of secondary X-rays of characteristic energies. Depending on the atomic number Z (i.e., the position in the periodic table), every element may be identified by the energies of these fluorescent lines and quantified on the basis of the measured intensity at each line (Figure 2). Characteristic X-ray emission energies are widely tabulated in the scientific literature, and these are used to calibrate the XRF instruments so that the end user typically does not view spectra, only measured concentrations. There are two types of XRF spectroscopies, wavelength dispersive (WDXRF) and energy dispersive (EDXRF). While WDXRF technology offers higher resolution and accuracy compared to EDXRF, it is only available in stationery equipment for laboratory use. EDXRF models are available both as benchtop and as handheld devices. This primer focuses exclusively on the use of portable equipment and thus only portable EDXRF spectrometry will be discussed.

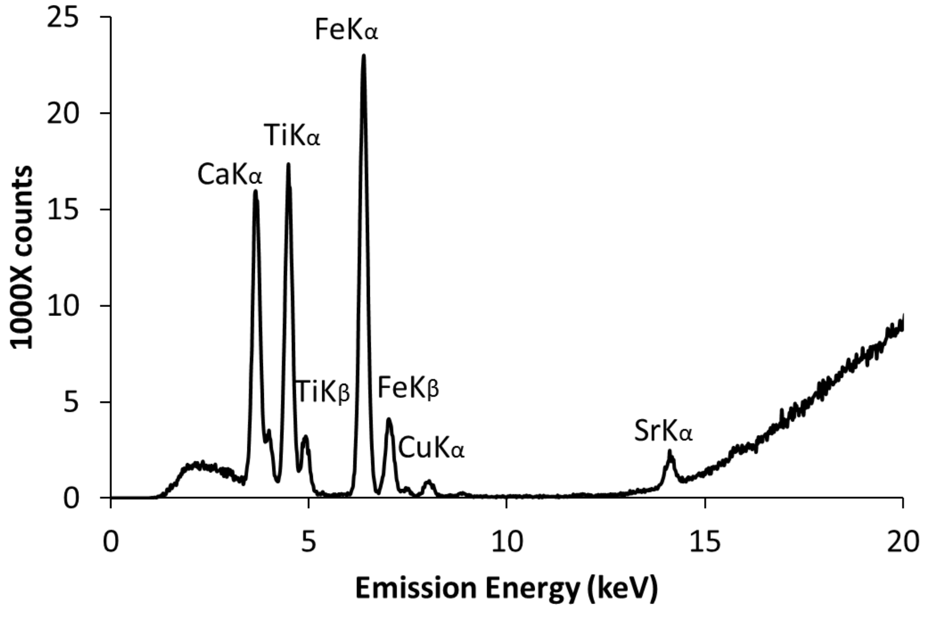

**Figure 2. Example of XRF Spectrum of Ti-Based Traffic Paint**

**Figure 3. Example of portable XRF devices, presented during a SHRP2 R06B showcase at the University of Connecticut (November 2, 2016).**

## 2.2 Applications

XRF may be used for the following several types of applications in construction and transportation materials:

- **Detecting heavy metals in solids, suspensions, or liquids—**Examples include Pb in paint, Pb and As in glass beads, metal contaminants in soils, asphalt, aggregates, and construction debris.

- **Determining steel grade—**Several manufacturers offer specific calibrations that recognize the grade and type of steel analyzed, as well as various types of metal alloys. Positive material identification (PMI) testing is a widely used term that refers to the analysis of the composition of metal alloys, including steel, and XRF is the premier method for this application.

- **Measuring chloride content in concrete—**Maine Department of Transportation (DOT) recently developed a method to detect deleterious levels of chloride in concrete using a portable XRF in a laboratory setting. The method is applied on crushed, homogenized concrete prepared as a pressed powder pellet (Figure 4).

**Figure 4. Pressed powder pellet (left and placing of the pellet in the XRF test stand for laboratory analysis (photos courtesy of Maine DOT)**

- **Measuring thickness of metal coatings (Cr, Zn, Ni)—**ASTM Method B568-98 covers this application, which is also available as built-in calibration by certain manufacturers. Measuring the zinc (Zn) coating thickness of railings is an example of the implementation of this application in transportation.

- **Detecting lime in asphalt binder—**This application may be done using the calcium (Ca) content and was employed as early as 1985 (2). A caveat to this method is that if the asphalt binder has already been mixed with the aggregate and the aggregate contains calcium, it will interfere with the detection of lime (CaO).

- **Detecting PPA in asphalt binder—**The Alabama DOT has developed a standard specification to measure PPA in asphalt binder using XRF to detect P. Federal Highway Administration (FHWA) (3) offers additional information on this application.

- **Detecting waste admixtures in asphalt mix using characteristic metals—**Both FHWA and the Texas DOT have employed XRF to identify the presence of materials such as tire rubbers and waste engine oils in asphalt mixes using elevated contents of zinc (Zn), calcium (Ca), molybdenum (Mo) and copper (Cu) as markers. Hesp and Shurvell (4) also report on applying XRF using Zn to identify waste engine oil in asphalt mix. Arnold (5) presents a comprehensive methodology to detect and estimate REOB in asphalt mix.
- **QA of paints and epoxies—***Techniques to Fingerprint Construction Materials User Guide* developed a draft AASHTO specification to use the titanium (Ti) content of paints as QA criterion. ASTM 5381-93 (5) was recently developed with the same purpose. These techniques apply to the analysis of liquid paints prior to the application on the road surface. The use of XRF to determine the Ti content of thermoplastics used in road marking is still under development. **QA of cement—**XRF is the primary method used in the cement industry to determine the composition and consistency of Portland cement. Typically stationary WDXRF equipment is utilized towards this purpose due to its ability to detect light elements (silicon [Si], aluminum [Al], magnesium [Mg]) with high precision, however modern handheld equipment may also have similar capabilities. This application has not been vetted to date.

In general, XRF may be used to fingerprint any material that has a characteristic elemental composition for the calibrated elements, or a characteristic metal, as illustrated in the examples above. Typically, developing a new application requires analyzing pure materials in the laboratory to determine the “signature” elements and associated concentrations and evaluate the lower level of admixture that could be detected by XRF.

There are several ASTM, AASHTO and EPA methods available related to XRF application on construction materials, some of which are listed below:

AASHTO methods

- AASHTO TP 106 Standard Method Of Test For Determination Of Heavy Metal Content Of Glass Beads Using X-ray Fluorescence (XRF)
- AASHTO M 85 Chemical (Oxide) Analysis by X-ray Fluorescence (XRF)
- AASHTO T 105-14 Standard Method of Test for Chemical Analysis of Hydraulic Cement (ASTM Designation: C 114-11be1)

ASTM methods

- ASTM F2980 – 13: Standard Test Method for Analysis of Heavy Metals in Glass by Field Portable X-Ray Fluorescence (XRF)

- ASTM E1361 02(2014)e1: Standard Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis
- ASTM D4294-16e1 Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry
- ASTM D5381-93(2014) Standard Guide for X-Ray Fluorescence (XRF) Spectroscopy of Pigments and Extenders
- ASTM E2120-10(2016) Standard Practice for Performance Evaluation of the Portable X-Ray Fluorescence Spectrometer for the Measurement of Lead in Paint Films
- ASTM D4764-01(2012) Standard Test Method for Determination by X-ray Fluorescence Spectroscopy of Titanium Dioxide Content in Paint
- ASTM B568-98 (2014): Standard Test Method for Measurement of Coating Thickness by X-ray Spectrometry

EPA methods

- SW-846 Test Method 6200: Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment

Users are encouraged to consult the respective websites, as new methods are continuously developed and revised for portable XRF applications.

## 2.3 Equipment

Portable XRF devices in the market are pre-calibrated for a variety of elements and concentration ranges, and operations and maintenance require only basic training. As will be discussed later, care must be taken that the built-in calibrations are appropriate for the type of application considered. While this does not affect the operation of the equipment per se, it is important for proper evaluation of the results. Certification from the Occupational Safety and Health Administration (OSHA) for operation of X-ray equipment may be a requirement; this depends on state regulations.

The test consists in attaching the equipment to the sample or surface of interest (Figure 3). The user then pulls a trigger to conduct the test, or controls the operation from a laptop when the equipment is attached to a docking station. The test duration is under 3 minutes, with most applications requiring as little as 30-60 seconds of analysis. The results are provided automatically in tabulated format for each element in the calibration range, in milligrams per kilograms (mg/kg) or percent by weight. The error associated with the XRF measurement, calculated as three times the standard deviation (3σ), is also provided. The results are stored in the equipment and can be exported as comma separate value (.csv) spreadsheets directly into a computer, an example of which is shown in Table 2. Individual spectra may also be exported, if so desired.

**Table 2. Example of Exported XRF Results**

| Sample ID | Ni | Ni +/- | Ni Pass | Ti | Ti +/- | Ti Pass |
|---|---|---|---|---|---|---|
| Sample-1 | 189 | 27 | Pass | 4784 | 248 | Pass |
| Sample-2 | Less than LOD | 70 | Pass | 6863 | 215 | Pass |
| Sample-3 | 85 | 19 | Pass | 5396 | 197 | Pass |

Note: Each element contains a column for the concentration in mg/kg, the instrument error (+/-) in mg/kg and the internal QA result (Pass/Fail). LOD = Limit of detection

Most available portable XRF equipment can detect elements between Mg (Z=12) and U (Z=92), and calibrations are typically provided for more than 30 elements. In some cases, different calibrations are required for elements that are measured in low concentrations (<10,000 mg/kg or 1% by weight) and for elements that are present in high concentrations, e.g. alloys, cements or aggregates. This depends on the manufacturer and should be discussed prior to the purchase of the equipment. The limits of detection (LODs) are specific to each element and also depend on the equipment type; users may consult with individual manufacturers to obtain tables of LODs for the particular model and calibration. In addition, LODs are sensitive to the analysis time (the longer the time, the lower the LOD) and the analyzed matrix.

Most manufacturers offer a range of handheld instruments for different applications, such as targeting ores and alloys, trace elements in soils, light elements in oil and gas exploration, and others. The type of anode (that is, the X-ray producing material) in the equipment may vary between silver [Ag], gold [Au], tungsten [W], rhodium [Rh], and others. The choice of anode depends on the target application; Rh has superior performance for light elements such as Mg, but interferes with the measurement of Cl; W offers superior performance for heavy elements such as Pb or Cadmium. Several calibration ranges (in the ppm or percentage range) are also possible for a single instrument, increasing the versatility of applications. Each calibration has a detection limit and an upper limit, above which the response is nonlinear, and the quantification results become unreliable. Users should consult on the upper limits with the manufacturer, as they are typically not provided in the accompanying documentation.

## 2.4 Test Procedure

XRF may be applied on granular samples that are placed in special XRF sample holders, or the equipment may be directly placed on the material surface, as shown on Figure 3. Test stands are available that can be used to place sample holders and perform the test without the need for an operator to hold it (Figure 5).

**Figure 5. Example of XRF test stand, with a protective shield to isolate X-rays. Samples are placed within the shield in contact with the XRF window.**

In general, the testing procedure involves the following steps:

- Initiating equipment start-up and standardization according to the directions of the manufacturer. This typically requires 10 minutes or less.
- Placing the sample holder on the XRF window (if a test stand is used) or hold the XRF window flush against the surface.
- Initiating the test by pushing the trigger or by using the software, if a test stand is used. The test may last between 30 seconds to 3 minutes. The actual time required will depend on the instrument and desired level of accuracy. The longer the testing time, the lower the LOD and the associated standard deviation.
- Receiving results displayed on the screen and exporting in a digital format.

## 2.5 Limitations

The following are the main limitations of XRF: (1) it can identify only elements, not complex compounds; and, (2) the range of elements is limited. XRF cannot be used, for example, to determine the composition of any organic material, and it cannot differentiate that contain similar elements with different structure (for example, lime and limestone are both based on Ca, but lime is calcium oxide [CaO] and limestone is calcium carbonate [$CaCO_3$]). It is possible to use XRF to detect the presence of calcium in a mixture, however differentiation between free lime and calcium carbonate is not possible. This may be especially confusing when elements are reported as oxides, i.e. CaO. This does not mean that calcium is present as free lime, but is only a reporting format for the total elemental concentration.

Beyond the method itself, there are nuances with respect to XRF interpretation that are associated with the specific type of material, for example the moisture content of a liquid paint affects the measured metal content. Also, the depth of penetration has to be considered, for example conducting a test on paint applied onto a surface will also yield signal from the underlying material, which has to be taken into account for interpretation of results. An example to illustrate both of these phenomena is shown on Figure 6 and in Table 3, obtained from a field application in Maine, conducted during Phase IV of R06B.

**Figure 6. Freshly painted concrete blocks in the laboratory (left) and freshly painted bridge on I-95 overpass in Maine (right)**

**Table 3. Example of XRF Results for samples shown on Figure 6**

| | Laboratory | | Field |
|---|---|---|---|
| | Liquid paint | Painted block | Painted bridge |
| Ti (wt.%) | 8.82 ± 0.13 | 10.06 ± 2.67 | 9.21 ± 0.29 |
| Fe (wt.%) | 0.02 ± 0.01 | 13.30 ± 3.30 | 17.83 ± 3.68 |
| Zn (wt.%) | 0.01 ± 0.01 | ND | 34.20 ± 4.85 |
| Pb (wt.%) | ND | ND | 0.02 ± 0.01 |

Note: ND = not detected

Testing the liquid paint in the laboratory resulted in an average Ti concentration of 8.8 wt.%; in this case, the paint was placed in a sample holder and tested separately. In the next step, painted wedges were prepared and tested, in order to create a more representative testing environment compared to the field testing conditions. The Ti content on the same paint immediately after application was found to be ~10%. The higher result is that during application of the water in the paint emulsion evaporates, resulting in more concentrated content of Ti in the fresh paint layer. As the paint dries out, the content keeps increasing until it stabilizes. When the same paint was tested on the freshly painted bridge, the Ti content was found to be intermediate compared to the two laboratory measurements. In addition to this observation, it may be seen from Table 3 that other elements were detected in different concentrations on the painted blocks and bridge, which were not present in the original paint. This is due to the phenomenon shown on Figure 7.

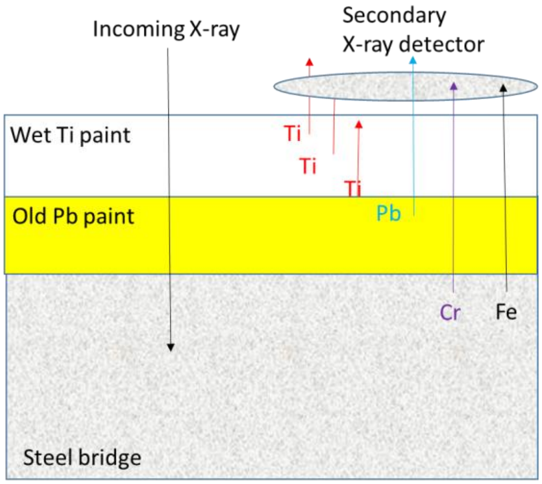

**Figure 7. Representation of the X-ray path as it is emitted from the XRF equipment, interacts and with the matrix and then re-emitted from different elements towards the detector.**

Incoming radiation has a high energy (up to 50 keV) and thus penetrates most construction materials to depths that range from several millimeters to centimeters. The X-rays then interact with the elements in the material, which emit the secondary radiation at a wavelength or energy specific to the element. In order for the element to be detected, the secondary radiation has to reach the detector, i.e. penetrate the material in the reverse direction, as shown on Figure 7. How far the radiation can travel is a function of the element that emits it and the surrounding matrix, which partially attenuates the signal as it travels towards the detector. In the application shown on Figure 7, Fe and Pb present below the paint layer are both able to be captured by the XRF and the respective concentrations reported in Table 2. The reported concentrations of the elements are not necessarily derived from the same location within the material, which is an important consideration when analyzing stratified and inhomogeneous matrices such as paint layers.

Finally, a crucial consideration is the so called “matrix effects”. This means that the nature of the material being measured influences the measurement. The first consideration when testing a new material is whether the build-in calibrations can accurately capture the behavior of the material. It is crucial that users purchase a variety of standards with properties similar to the properties of the materials to be tested. These can be used to produce material-specific calibration curves that can be programmed into the equipment as “user factors” that are specific to the material. An example of this is shown on Figure 8. The Tennessee Department of Transportation (TDOT) was interested in measuring the silica ($SiO_2$) content of aggregates using the portable XRF as a measure of aggregate quality. TDOT acquired a variety of siliceous standards from the Cement Concrete Reference Laboratory, with a range of concentrations between 18% and 60% $SiO_2$, as shown on Figure 8. Each standard was prepared with a hydraulic press and analyzed using the built-in calibration of the XRF. The results were plotted against the reference concentration of the standard. As seen on Figure 8, the XRF measurement consistently overestimated the $SiO_2$ concentration by a factor of 1.0657. This factor could then be used to automatically correct all $SiO_2$ concentrations ready by the instrument in the range 18-60%, as long as the analyzed materials were similar in nature, i.e. aluminosilicates such as soils, aggregates, cements, and pozzolans. This process was repeated using the same samples for a variety of other elements as well.

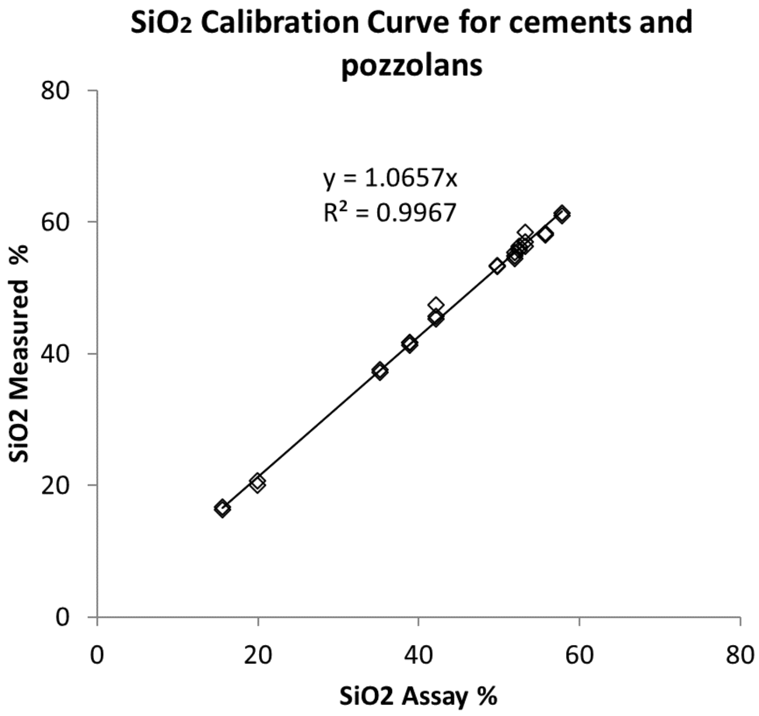

**Figure 8. Example of material-specific calibration curve for $SiO_2$ created by TDOT**

Finally, note as with any analysis method for heterogeneous materials, such as soils, aggregates, and other natural materials, users should develop robust sampling and material handling plans to insure the representativeness of the results.

# 3.0 Fourier-Transform Infrared Spectroscopy

## 3.1 Principle of FTIR

While XRF spectroscopy is largely automated, so that the user does not necessarily need to delve as much into the underlying principles, FTIR is a more nuanced technique that does require some basic understanding of the physical principles in order to conduct proper qualitative and quantitative analysis. While it is beyond the scope of this primer to provide a full analysis of FTIR theory (e.g., refer to Stuart (7) for a comprehensive presentation), we will summarize some basic principles as related to the analysis of construction materials. Such understanding is necessary to avoid pitfalls, such as false identifications and unrealistic expectations.

FTIR spectroscopy relies on the absorption of electromagnetic radiation in the infrared region (wavelength between 0.78 and 100 micrometers [µm]) by vibrating molecules or functional groups in large molecules. Fundamentally, covalent bonds between different atoms (e.g., carbon [C] and oxygen [O]) are capable of absorbing IR radiation at a specific frequency, which then induces a vibration in different directions. This is illustrated for the carbon dioxide [$CO_2$] molecule on Figure 9. The IR source emits radiation at several frequencies; only the one at approximately 2,400 inverse centimeter ($cm^{-1}$) is absorbed by the $CO_2$ molecule and used to induce a stretching vibration of the molecule. The emitted radiation that is captured then by the detector records the same intensity of other frequencies that were not changed by the molecule, whereas the IR-active frequency comes out diminished in intensity. In a transmission spectrum, this is recorded as a reduction in the percent transmission at that frequency, as shown on Figure 9. For the case of $CO_2$ stretching shown on Figure 9, this vibration occurs at 2345 $cm^{-1}$ and is observed a sharp peak in the IR spectrum. The bending vibration occurs at 665 $cm^{-1}$ and is observed as a smaller peak. The small noise observed in between is due to ambient moisture ($H_2O$), as water molecules also have characteristic frequencies in the IR region.

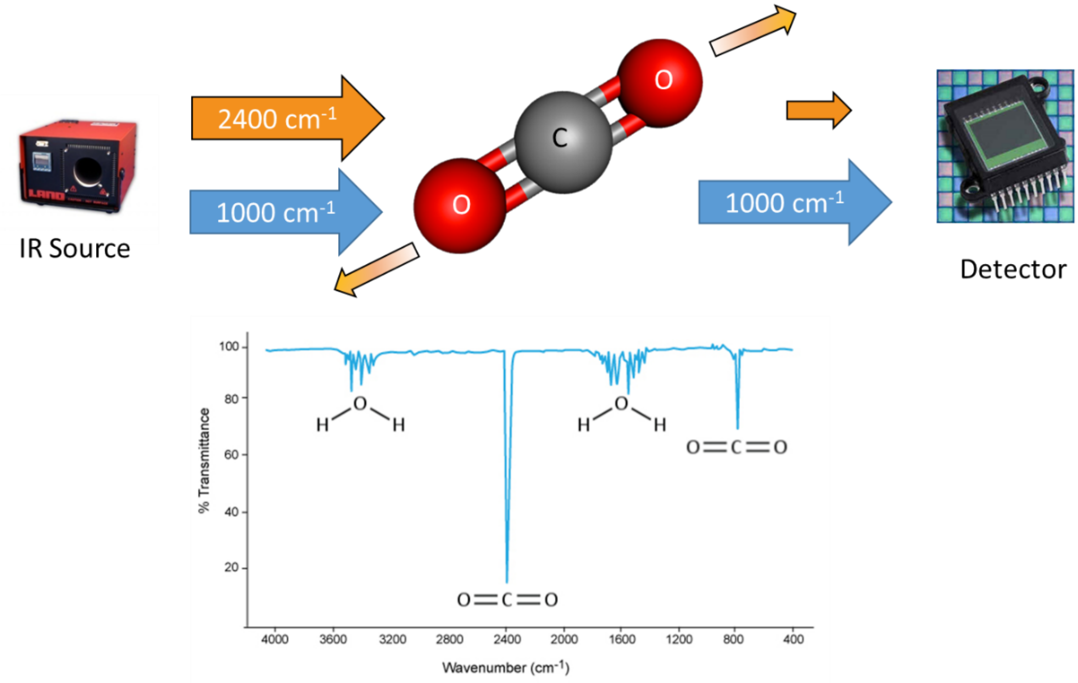

**Figure 9. Principle of molecular vibration upon IR irradiation of a $CO_2$ molecule and corresponding spectrum.**

Typically, frequencies in IR applications are given in terms of wavenumbers [$cm^{-1}$], which is the inverse wavelength ($1/\lambda$) of the frequency. IR spectra then plot either the transmission or the absorption of radiation that goes through a material as a function of the inverse wavelength of the incoming radiation.

In summary, the following principles apply:

- IR peaks are a result of the absorption of energy that is used for the vibration of bonds formed by at least two different types of atoms.
- Each vibration happens at a characteristic frequency.
- Every bond may have more than one characteristic IR peaks depending on the type of the vibration.

Another term that is frequently used in IR spectroscopy, derived from organic chemistry, is the concept of a *functional group.* A functional group is a group of atoms that have specific bonds and are typically responsible for certain chemical properties in a material. The most common functional groups relevant to construction materials and specifically asphalt are shown on Figure 10, along with the frequency regions, in which their vibrations typically appear. FTIR spectroscopy is mostly applicable to organic compounds that contain such bonds, for example

C=C, -COOH, -C=O, and others. However, inorganic compounds with similar properties are also detectable. For example, ions such as phosphate ($PO_4^{3-}$) and ammonium ($NH_4^+$) are also detectable by FTIR spectroscopy (6).

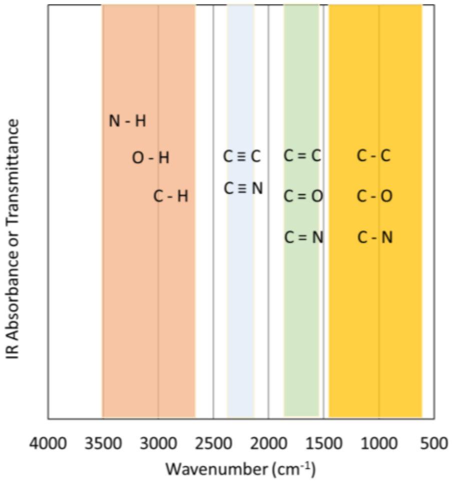

**Figure 10. Typical IR Absorption Ranges for Common Organic Functional Groups (reproduced after Wade [8])**

If the observed peaks are only vibrations of isolated functional groups, then the question becomes, how are we able to use these in order to fingerprint complex materials that may have different combinations of these groups in their structure? To accomplish this, we utilize a principle that is often applied in spectroscopic techniques to conduct qualitative and/or quantitative analysis: **through of comparison of the unknown spectra with spectra of pure compounds obtained under controlled conditions.**

This mean that FTIR analysis can only occur in a meaningful way when spectra of pure compounds are available to the user; it is not possible to detect a compound that has not been previously investigated in a pure form through this method. Databases of pure compounds are available for download or purchase, for example the National Institute of Science and Technology (NIST) has published a comprehensive database or pure IR spectra. For most applications discussed here, it is necessary to obtain spectra of pure materials in the laboratory prior to field testing.

## 3.2 Applications

FTIR technology for construction and transportation material analyses is an evolving field and different applications have different level for field readiness. More mature applications include:

- **Identifying and quantifying of polymers in asphalt—**Polymers such as SBS can be identified through characteristic peaks at 966 and 700 $cm^{-1}$ (1). Quantification is also possible at low concentrations, even though calibration curves have to be set up for individual binder types and error was found to be substantial (1).

- **Identifying curing compounds and other admixtures in PCC** (draft AASHTO method developed by *Techniques to Fingerprint Construction Materials User Guide*)— PCC admixtures include water reducers, air entraining admixtures, accelerators and retarders. This application is based on the qualitative comparison of the IR absorbance spectrum of a pure admixture sample with the spectrum of the fresh PCC-chemical mixture. The success of this method depends on whether the characteristic peaks of the admixture overlap with the PCC peaks and the level of the admixture (levels below 0.4 percent by weight are likely below the noise level).
- **Identifying lime in asphalt—**FHWA has developed an AASHTO provisional method (TP 72-08) to implement FTIR to identify lime in asphalt (9). This application relies on the same principle, i.e. it utilizes the characteristic peak of $Ca(OH)_2$ at 3640 inverse centimeters ($cm^{-1}$) to fingerprint the addition of lime (CaO), since asphalt does not contain peaks in this area of the spectrum.

Some additional applications have been identified that are still at the research stage, including:

- **Evaluating oxidation level in recycled asphalt pavement (RAP) mixtures** (draft AASHTO method developed by *Techniques to Fingerprint Construction Materials User Guide*)—Tt\his method utilizes the characteristic peaks of two functional groups that contain oxygen (carbonyl [C=O] and sulfoxide [S=O]) to evaluate the degree of oxidation of the binder, which is correlated with the presence of these oxidized groups. Abbas et al. (10) and Bowers et al. (11) used this approach to evaluate the properties of asphalt binders extracted using a solvent and mixed with RAP. When aggregate is present, the Si-O vibrations in the aggregate interfere with the S=O vibration, but not with the C=O vibration. Additional research is required to establish wider correlation of oxidation and RAP presence, especially in aged asphalt and in the presence of aggregate in order to avoid the binder extraction step.
- **Identifying recycled engine oil bottoms in asphalt—**Jia et al. (12) used FTIR to evaluate the presence of waste oil in artificial mixtures of asphalt binders and RAP, using a similar approach to the *Techniques to Fingerprint Construction Materials User Guide* method for RAP testing. While this method has not been vetted in a wide variety of samples, it does show promise for further exploration and field application.
- **Identifying miscellaneous modifiers in asphalt—**Yao et al. (13) employed the same approach as Jia et al. (12) to evaluate the presence of asphalt binders modified with nanoclay and carbon microfibers. Similar to Jia et al. (12), the sample mixtures were artificial, so that the type of admixture was known in advance. As will be described in the limitations section, the functional groups used (carbonyl and sulfoxide) are non-specific to a material (i.e., they may be derived from any admixture containing carbonyl; thus, the

type of admixture has to be known for this method to be applicable – this is rarely the case).

- **Identifying diesel, oils, tar in soils, and other inorganic media—**This may be done by identifying characteristic carbon peaks in inorganic matrices that have distinct IR vibrations.

## 3.3 Equipment

There are three types of FTIR equipment: stationary, benchtop – portable and handheld. Stationary equipment typically operate in absorption or transmission mode and are used to analyze gases, liquids and solids, while benchtop and handheld equipment operate on the basis of reflection and can be used to probe liquids and solids (6). Field equipment only utilize reflectance and will thus be discussed here. There are two main types of field FTIR equipment, using ATR or diffuse reflectance (DRIFT), Several vendors offer benchtop or handheld equipment with accessories that can switch between the two methods; examples are shown on Figure 11. Details on the principles of each method are provided by Stuart (7) and other literature sources. For construction materials discussed here, an important consideration is the amount of sample probed and sample variability.

**Figure 11. Handheld (top) and benchtop (bottom) ATR equipment presented at the R06B showcase at UCONN (November 2, 2016).**

Both ATR and DRIFT spectroscopy obtain information only from the surface of solid samples, penetrating only a few micrometers into the material (Table 4). This is especially important to keep in mind when evaluating spectra, considering the composition of the outermost thin layer of a material; the interior of grains cannot be analyzed. The difference between ATR and DRIFT lies in the number of surfaces probed to obtain the overall signal. As seen on Figure 11, the probing interface for ATR is very small, typically 1-2 mm in diameter. Obtaining a representative sample spectrum for a heterogeneous material is thus more challenging and requires the collection of multiple spectra from multiple subsamples. DRIFT spectroscopy may be performed on powdered samples without any preparation and the sample size is 1 to 2 grams (g), with IR signals obtained from a multitude of grains within that sample. This is especially useful for applications involving asphalt, concrete and soils or aggregates.

ATR spectrometers may use different internal reflection elements (IREs), with the most common being diamond, germanium [Ge] and zinc selenide [ZnSe]. The main differences between these IREs (in addition to cost) is durability, with diamond being the hardest and ZnSe the most prone to damage, and the refractive index, which limits the spectral range available and the depth of penetration (Table 4). For construction materials the spectral range of all three elements is adequate, but ZnSe is not recommended for general use, especially considering applications involving lime (basic) or PPA (acidic).

Special features provided by some manufacturers is the use of a pressure element to enhance the contact between a solid sample and the IRE, which is necessary for quality spectra acquisition, and the availability of a heating element that can soften materials such as asphalt and improve contact with the IRE.

**Table 4. Properties of the most common ATR internal reflection elements**

| | Spectral range ($cm^{-1}$) | Depth of penetration* (μm) | Resistance to acid/base | Hardness | Uses |
|---|---|---|---|---|---|
| Diamond | 25,000 to 100 | 2.01 | High | High | General and hard/caustic materials |
| ZnSe | 15,000 to 650 | 2.01 | Medium | Low | General |
| Ge | 5,500 to 675 | 0.66 | Medium/High | Medium | High absorbance materials |

**Table 4. Properties of the most common ATR internal reflection elements**

| | Spectral range ($cm^{-1}$) | Depth of penetration* (µm) | Resistance to acid/base | Hardness | Uses |
|---|---|---|---|---|---|
| | | | | | (polymers, rubber) |

Note: *at 1,000 $cm^{-1}$

In terms of portability, benchtop equipment can be used in the laboratory and in the field, for example on the back of a truck (Figure 12). This type of equipment does not offer the ability to conduct point-and-shoot analysis, bringing the IRE in contact with the surface in situ. A sample has to be extracted and placed on the equipment. Handheld equipment does offer the ability to point-and-shoot, but the user still has to take into account the small probing interface and take multiple spectra in order to obtain a representative result.  Handheld equipment often have docking stations, so that they may also be used in the laboratory with more convenience (for example during the standard development phase).

A final consideration during equipment purchase is the accompanying software, what capabilities it provides for qualitative and quantitative analysis, and how user-friendly it is. While using freeware or purchasing software separately is possible, including software acquisition and training in the equipment purchase is more cost-effective.

**Figure 12. Field Use of a benchtop ATR FTIR Spectrometer**

## 3.4 Test Procedure

In general, ATR and DRIFT do not require any sample preparation for liquid or solid samples. That said, pretreating samples to reduce matrix interferences (e.g., from aggregate material in asphalt) or obtaining a representative sample suitable to be in good contact with the IRE (e.g., by reducing particle size or sieving) may be necessary. This is, however, specific to the application and type of material analyzed and not inherent to the technique. Sample analysis includes the following steps:

- Power the instrument and provide the necessary warm up time, as required by the manufacturer.
- Clean the IRE with an appropriate solvent.
- Obtain a background spectrum, which may be air, water, or another solution, depending on the particular application. This spectrum is subtracted from the sample spectrum in order to reduce interfering peaks from water, $CO_2$ or other compounds.
- Place the sample on the IRE and insure full coverage and good contact for optimal spectrum quality.
- Use the equipment software to program the necessary parameters, including spectral range (typically 3000-400 $cm^{-1}$), spectral resolution (4 $cm^{-1}$ or higher) and number of co-averaged scans. Taking multiple scans of the same material reduces noise and increases the signal, improving the overall signal-to-noise ratio for good qualitative analysis. This number can be as low as 24 or as high as 1200 for high quality spectra; the higher the number, the longer the duration of the test. Spectra acquisition is typically a few minutes and the spectrum is displayed at the end of the test.

Spectral processing and qualitative and quantitative analysis are then performed using the software functions. Spectral processing generally includes atmospheric compensation (interference of atmospheric carbon dioxide [$CO_2$] and moisture [$H_2O$]) and background removal, if a background other than the atmosphere was used.

Qualitative analysis involves comparing the spectrum of a pure material that has been previously stored or is available in databases. There are several databases available for organic compounds, which may have some applicability to construction materials:

- https://guides.lib.utexas.edu/chemistry/spectra comprehensive list of online libraries
- NIST database (16,000 compounds):
  https://srdata.nist.gov/gateway/gateway?property=IR+spectra and
  http://webbook.nist.gov/chemistry/vib-ser.html to search by vibration energies

- EPA database (organic contaminants, solvents): https://www3.epa.gov/ttnemc01/ftir/refnam.html
- Free library for organic compounds, searchable by wavenumber: http://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre_index.cgi
- Commercial libraries such as http://www.fdmspectra.com/

In addition, the SHRP2 R06B project provided spectral libraries of materials tested during the project, available at http://www.trb.org/Main/Blurbs/167279.aspx. Finally, the analysis software provided by equipment vendors typically includes some basic libraries. In general, it is recommended to experimentally obtain reference spectra for quality assurance purposes.

There are two modes to implement FTIR: fingerprinting for QA purposes and conducting forensic analysis to identify foreign compounds in a mixture. Fingerprinting is potentially easier to conduct, as the analyst is looking for a compound with known properties. Some difficulties that can arise are:

- Interference of background matrix spectrum with compound spectrum. This principle is illustrated on Figure 13. The hot mix asphalt (HMA) mix has strong reflections in the regions around 2900 and 1500 cm$^{-1}$, which cannot be used for identification of any added compounds. The pure SBS polymer has characteristic peaks at several lower wavenumbers (963, 910, 694, 668 cm$^{-1}$). The pure HMA does not have any peaks in these regions, so that the peaks may still be identified in the spectrum of the mixture. In this case, interference of the matrix is not a problem for fingerprinting of the spectrum, however that is not always the case. Obtaining pure spectra of both the compound of interest and the matrix is critical for proper fingerprinting.
- Detection limit: In Figure 13, 6% polymer was easily observed in the mixture, however, as the concentration decreased to 1% the SBS peaks decreased to noise. In general, 1 wt.% is an average LOD for many compounds in a complex mixture.
- Change of the compound structure upon addition to the matrix. As seen on Figure 13, the SBS peaks observed at the lower wavenumbers shifted to 700 cm$^{-1}$ and only one peak is observed instead of two. This may potentially be due to the fact that the original styrene group present in SBS reacted with the HMA in some fashion, changing the bonding environment and thus the observed frequencies.

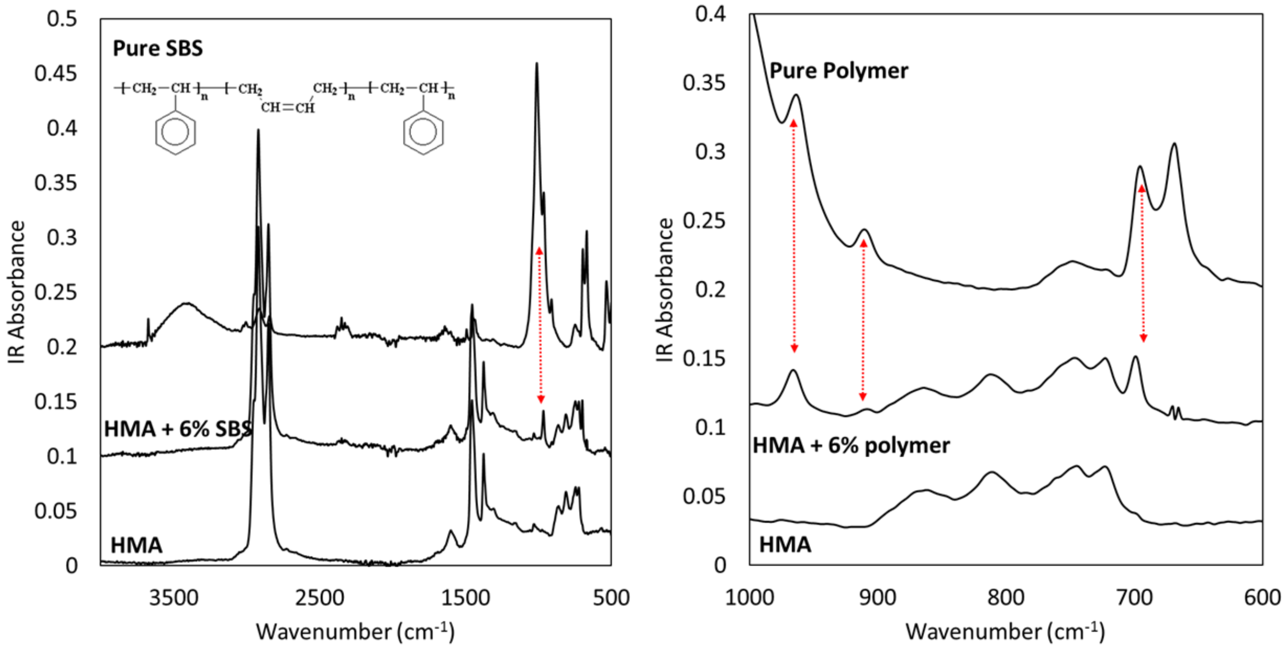

**Figure 13. Example of ATR spectrum of HMA spectrum, pure SBS polymer (structure shown) and mixture of HMA with 6% SBS. The right image shows a limited part of the spectrum for clarity.**

For forensic investigations, the objective is to determine the nature of unknown peaks present in a spectrum. An example of this is shown on Figure 14. When an asphalt binder was tested after a pavement failure, a peak was identified that was not present in the sample that the supplier had submitted for certification prior to use. Thus, the objective of this analysis was to determine the nature of the peak and examine whether its presence had any connection to the apparent failure of the pavement. It is important to distinguish between these two questions, i.e. the identification of a foreign substance does not imply correlation to failure. As with any forensic investigation, multiple lines of evidence are necessary to establish the culprit.

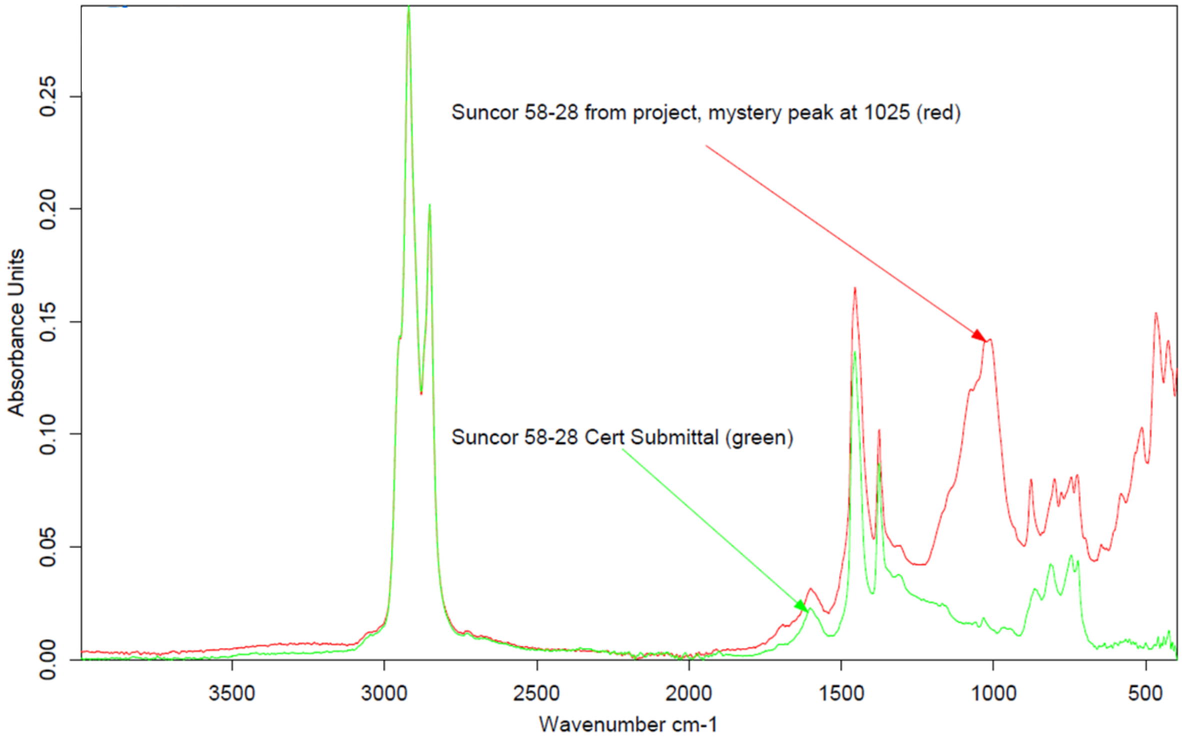

**Figure 14. Example of FTIR spectrum of asphalt binder, tested as certified sample (green) and during project application (red) (courtesy of Jerry McMahan, Vermont Agency of Transportation)**

In order to determine the nature of the peak, two avenues were pursued:

- Looking for potential admixtures (engine bottom oil, vegetable oil) that could account for this peak.
- Looking for functional groups that present peak positions in this area and then matching the chemistry of the group to a potential source.

From the second approach, it was determined that the peak could be related to two functional groups: -Si-O-Si- present in silicates and -S=O or sulfoxide. The first could potentially be present if fine aggregate was present in the material, which would be possible if the sample came from HMA. However, this sample was only asphalt binder prior to mixing with aggregate and thus silicate should not be present. The second group has been found to be related to the presence of asphalt aging and was therefore determined to be the best match for the peak. Complementary XRF to determine the presence of Si or S could help elucidate the nature of the peak in this case. Whether the presence of sulfoxide was related to the pavement failure could not be established through IR alone.

Quantitative analysis with IR is also possible, but significantly more challenging. requires building a calibration curve by using standard additions of the compound of interest to a background matrix and measuring the absorbance in the characteristic peaks of the compound. A basic introduction to qualitative and quantitative analysis is provided by Stuart (7) and software manuals. It is, however, recommended for personnel to obtain training from the specific manufacturer, if there is no prior experience with spectroscopy.

Overall, the following best practices are suggested for FTIR analysis:

- Establishing a library of reference spectra for specific material types is key
- Having a general idea of what it is you are looking for helps
- Use existing databases to narrow down the type of functional group you are looking for
- Use complementary techniques to corroborate your suspicions

## 3.5 Limitations

Following are the main limitations of FTIR:

- It is only applicable to functional groups that have molecular vibrations in the IR region, i.e. polar, asymmetric, covalent bonds.
- FTIR detects polar functional groups, not entire molecules, and as such the observed peaks are not necessarily unique to a single compound. For example, asphalt binders may contain similar concentrations of polar functional groups such as carbonyl and sulfonyl, which are observable by IR, but have different matrices that are not sensitive to IR. In addition, as discussed in the applications section, different types of asphalt admixtures may contain these functional groups, and FTIR alone cannot distinguish between them.
- Water molecules have very strong IR active vibrations, which can easily obscure IR active vibrations of other molecules when water presence is substantial, such as in aqueous solutions.

Detection of admixtures has a LOD of about 1%.

# References

1. Zofka, A., M. Chrysochoou, I. Yut, C. Johnston, M. Shaw, S.-P. Sun, J. Mahoney, S. Farquharson, and M. Donahue. *Evaluating Applications of Field Spectroscopy Devices to Fingerprint Commonly Used Construction Materials*. Report S2-R06B-RR-1, Strategic Highway Research Program 2, Transportation Research Board, 2013.

2. Ruth, B. (ed.). *Evaluation and Prevention of Water Damage to Asphalt Pavement Materials.* ASTM Special Technical Publication 899, American Society for Testing and Materials, Baltimore, MD, 1985.
3. Arnold, T. *The Use of Phosphoric Acid to Stiffen Hot Mix Asphalt Binders.* Report No. FHWA-HRT-14-086, Federal Highway Administration Pavement Materials Team (HRDI-10), McLean, VA, 2014.
4. Hesp, S.A. and H.G. Shurvell. X-ray Fluorescence Detection of Waste Engine Oil Residue in asphalt and its effect on cracking in service. *International Journal of Pavement Engineering,* Vol. 11(6), 2010, pp. 541-553.
5. Arnold, T. What's in Your Asphalt*, Public Roads,* Vol. 81(2), 2017, FHWA-HRT-17-006.
6. American Society for Testing Materials, *Standard Guide for X-Ray Fluorescence (XRF) Spectroscopy of Pigments and Extenders*, ASTM D5381 – 93, 2014.
7. Stuart, B. *Infrared Spectroscopy: Fundamentals and Applications.* John Wiley & Sons, Inc., New Jersey, 2005.
8. Wade, Jr., L.G. *Organic Chemistry, 8th* edition, Pearson Education, Upper Saddle River, NJ, 2012.
9. Arnold T., J. Rosario and J. Youtcheff. New Lime Test for Hot Mix Asphalt Unveiled. *Public Roads,* Vol. 70(5), 2007, FHWA-HRT-07-003.
10. Abbas A. R., U. A. Mannan and S. Dessouky. Effect of recycled asphalt shingles on physical and chemical properties of virgin asphalt binders. *Construction and Building Materials,* Vol. 45, 2013, pp. 162-172.
11. Bowers, B.F., B. Huang, X. Shu and B.C. Miller. Investigation of Reclaimed Asphalt Pavement blending efficiency through GPC and FTIR. *Construction and Building Materials,* Vol. 50, 2014, pp. 517-523.
12. Jia, X., B. Huang, B.F. Bowers and S. Zhao. Infrared spectra and rheological properties of asphalt cement containing waste engine oil residues. *Construction and Building Materials,* Vol. 50, 2014, pp. 683-691.
13. Yao H., Z. You, L. Li, S.W. Goh, C. H. Lee, Y. K. Yap and X. Shi. Rheological properties and chemical analysis of nanoclay and carbon microfiber modified asphalt with Fourier transform infrared spectroscopy. *Construction and Building Materials,* Vol. 38, 2013, pp. 327-337.

# Divider
# Appendix title