TECHNOTE

An Introduction to Spectroscopy for Pavement Engineers

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WHY SPECTROSCOPY?

Many tests associated with paving materials rely on the measurement of some physical engineering property, which is the approach used in Superpave® methods. While these tests may provide engineering data such as viscosity and stiffness, they tell nothing of what the tested material contains. What is in the tank? What was added to the asphalt to meet the performance grade (PG)? What is the effect of the additive on pavement life?

Spectroscopy, which is a study of interactions between matter and electromagnetic radiation that has been around for decades, provides a way of analyzing materials. Its methods can tell us exactly what a material contains and can produce unequivocal results that make it possible for highway agency personnel to quickly determine whether a material is or is not as expected or specified.

Advancements in spectroscopy have been made in recent years, resulting in the availability of handheld instruments that can be used in the field. These instruments require minimal training and are fast, providing results within a few minutes.

To date, in the paving industry, spectroscopy has been used to detect the following:

- Lime in hot mix asphalt.
- Polymers in asphalt binders.
- Vegetable oil and derivatives.
- Liquid amine antistrip additives.
- Phosphoric acid.
- Recycled engine oil bottoms (REOBs).
- Chloride in concrete bridge decks.
- Silica in limestone aggregates.
- Titanium dioxide in thermoplastic road-marking materials.
- Heavy metals in glass beads.

This list will continue to grow as more research is conducted. This TechNote serves as an introduction to spectroscopy, including explaining the science behind spectroscopic test methods. Details for developing a purchase specification for a spectrometer are also included.

Spectroscopy can be a potentially dry subject. For this reason, this TechNote is written in a very informal style in the hope that it may be easier to read and understand and perhaps more interesting for folks that may be completely new to this subject and technology.

WHAT ARE SPECTROMETERS?

Laboratory spectrometers are sophisticated, large, heavy, and expensive pieces of equipment that require knowledge and skill to operate. The power of spectrometers has been made more accessible through the recent widespread availability of handheld spectrometers, which are reliable, accurate, and require little training or skill to operate. Some handheld spectrometers can be set up to give a simple yes or no answer, indicating pass or fail when the light on the device turns red or green, respectively. Handheld spectrometers can sometimes be calibrated and programmed to do specific analyses. Once the handheld spectrometer is calibrated, the operator simply needs to position the sample, pull the trigger (or push the button), and note the reading on the screen.

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Figure 1 through figure 3 show typical laboratory spectometers. Figure 1 shows a laboratory x-ray florescence (XRF) spectrometer. The door on the front of the cabinet of the spectrometer provides access to the sampling deck, which contains approximately 50 steel cups that hold the samples and a crane to lift the samples into the x-ray chamber.

A Fourier transform infrared (FTIR) spectrometer is shown in figure 2. There is an opening at the front of the spectrometer box where the samples are placed. The sample is exposed to infrared radiation in a range of wavelengths. The spectrometer plots the absorption of the radiation against the wavelength, producing a graph called a spectrum.

Figure 3 through figure 5 show various handheld spectrometers. The handheld XRF (figure 3) and FTIR (figure 4) spectrometers are similar in appearance. They consist of a small box with a handle underneath and resemble radar speed-detecting instruments used by police officers. Figure 5 is a handheld Raman spectrometer. All three instruments have a screen for viewing test results.

The next section, Part 1: Overview of Scientific Principles, provides a simple overview of the scientific principles involved in spectroscopy. This section is followed by Part 2: Spectroscopy, which provides a technical description of each technique—FTIR, XRF, and Raman—with some practical examples of how the paving industry can use them. Part 2 focuses primarily on FTIR and XRF spectroscopy, two techniques thought to be of most use in pavement applications. Researchers at the Turner-Fairbank Highway Research Center (TFHRC) do not have much data yet on the use of Raman spectroscopy with highway construction materials. The device, however, does offer some promise in that it can "see" through plastic packaging, which opens the possibility of analyzing materials supplied in sealed polyethylene bags without having to open the bags (a technique commonly used in the pharmaceutical industry for quality control of pills sealed in bubble packs).

Figure 1. Photo. Laboratory XRF spectrometer.

Source: FHWA.

Figure 2. Photo. Laboratory FTIR spectrometer.

Source: FHWA.

Figure 3. Photo. Handheld XRF spectrometer.

Source: FHWA.

Figure 4. Photo. Handheld FTIR spectrometer.

Source: FHWA.

Figure 5. Photo. Handheld Raman spectrometer.

Source: FHWA.

PART 1: OVERVIEW OF SCIENTIFIC PRINCIPLES

What Is Spectroscopy?

Spectroscopy is the study of the interaction between electromagnetic radiation and atoms and molecules.

What Is Electromagnetic Radiation?

People use electromagnetic radiation every day. Radios, telephones, televisions, cellular phones, and microwave ovens all rely on electromagnetic radiation. According to the Encyclopedia Britannica, electromagnetic radiation can be formally defined as follows:

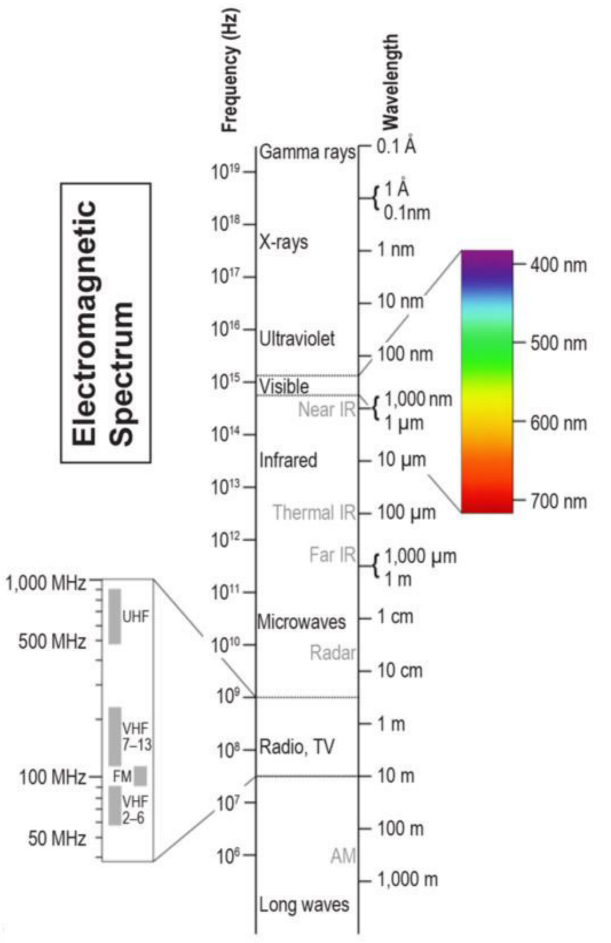
> In classical physics, it is the flow of energy through free space or a material medium in the form of electric and magnetic fields that make up electromagnetic waves such as radio waves and visible light. It exhibits many phenomena as it interacts with atoms and molecules depending upon its frequency. The spectrum of wavelengths of electromagnetic radiation extends from very low values over the range of radio waves, television waves and microwaves to visible light and substantially higher values of ultra violet light, x-rays and gamma rays.(1)

Radio waves and microwaves are usually described in terms of frequency (cycles per second or Hertz (Hz)), infrared and visible light are described in terms of wavelength (meters), and x-rays and gamma rays are described in terms of energy (thousands of electron volts (KeV)). The definition of 1 KeV is the amount of kinetic energy gained by a free electron when it passes through an electrostatic potential difference of 1,000 V in a vacuum.

Figure 6 illustrates the frequencies and wavelengths of the electromagnetic spectrum. The human eye can detect only a small portion of this spectrum called visible light. The terms light, electromagnetic waves, and radiation all refer to the same physical phenomenon: electromagnetic energy. The wavelength of an AM radio wave is approximately 100 m, a microwave about 10 cm, an infrared ray about the thickness of a sheet of paper, an x-ray about the width of a water molecule, and a gamma ray about the size of an atomic nucleus.

A wave's energy is directly proportional to its frequency. X-rays have much higher energy than microwaves. This comparison is illustrated in figure 7, which shows the range of the electromagnetic spectrum from radio to gamma rays. Figure 7 also shows a sine wave of

Figure 6. Illustration. Frequencies and wavelengths of electromagnetic radiation on the electromagnetic spectrum.[2]



Source: 2013 Wikimedia Commons (CC BY-SA 3.0 (https://creativecommons.org/licenses/by-sa/3.0)). IR = infrared.

variable wavelength. When electromagnetic radiation interacts with atoms and molecules, its behavior depends on the amount of energy it carries.

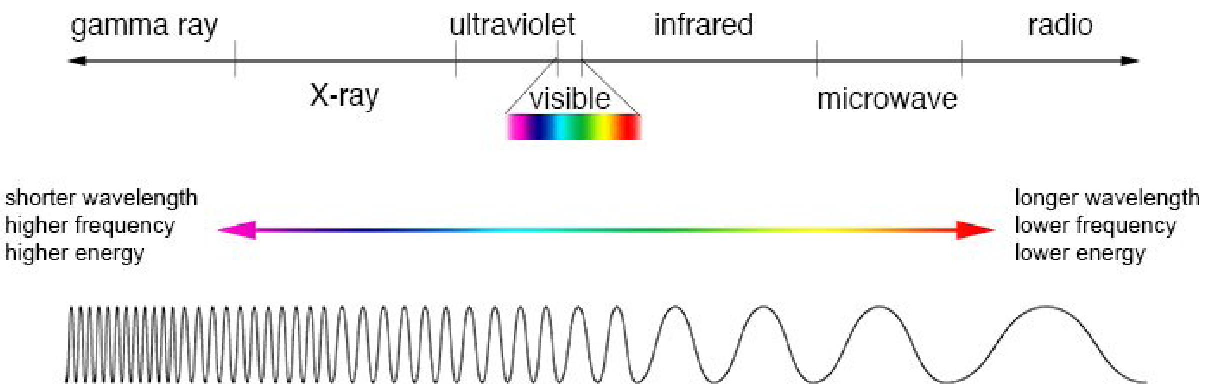
Wavelengths are important for the following reasons:

- Microwaves are radio waves of short wavelength that are used in applications such as radar and wireless networking. These waves have enough energy to be absorbed by polar molecules (like water), which causes the molecules to vibrate and rotate, resulting in bulk heating. Since microwaves can penetrate below the surface of materials, this effect is used to heat food in microwave ovens.
- Infrared waves have enough energy to cause molecules to flex and vibrate. The energy of these vibrations can be measured, and the measurements can be used to identify molecular structures.
- X-rays have enough energy to cause electronic transitions of atoms themselves. These transitions are very precise and can be used to identify the presence of elements.

What Are Atoms?

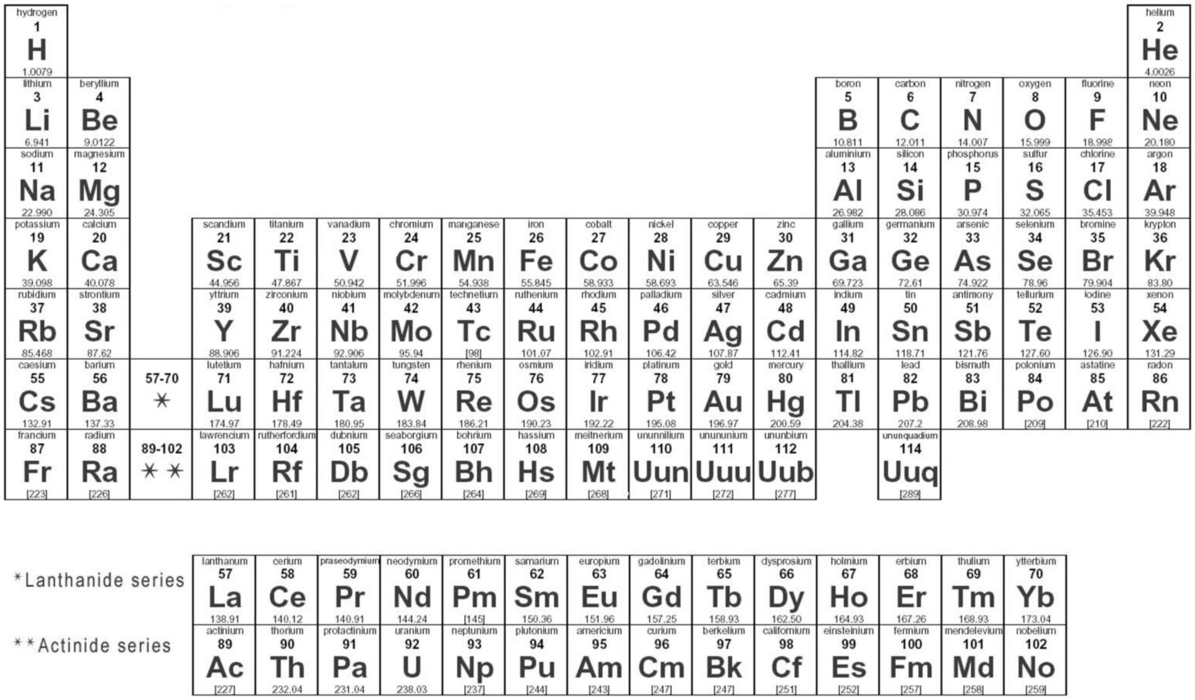
Atoms are defined as the basic unit of a chemical element. An element is a substance that cannot be broken down into simpler substances by chemical means. The periodic table, shown in figure 8, lists all known elements in order of increasing atomic number. For each element, the atomic number is listed above the chemical symbol and the atomic weight is listed below. Hydrogen, with an atomic number of 1, is the lightest element and has an atomic weight of 1.008

Figure 7. Illustration. Relationship between energy and wavelength on the electromagnetic spectrum.[3]



Source: 2013 National Aeronautics and Space Administration's Imagine the Universe.

Figure 8. Illustration. Periodic table.(4)



hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
* *Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

(nominally 1). Oxygen, with an atomic number of 8, has an atomic weight of 15.999 (nominally 16).

What Are Molecules?

A molecule is formed when two or more atoms are chemically joined together (e.g., H_2 (two hydrogen atoms) or O_2 (two oxygen atoms)). A compound is a type of molecule where two or more different atoms are joined together (e.g., H_2O (water)). The molecular weight of water is 2 × 1.008 + 15.999 = 18.015 (nominally 18). A gram molecule of water is therefore nominally 18 g. Figure 9 shows a conical glass flask containing a gram molecule (18 g) of water. A dime is placed in front of the flask for an indication of scale.

Figure 9. Photo. Glass flask containing a gram molecule of water.

Source: FHWA.

Molecules are tiny. A gram molecule of water (18 g) contains Avogadro's number (6.02×10^{23}) of molecules; for reference, that is comparable to the number of popcorn kernels that would cover the whole United States to a depth of 15 km.(5) Molecules are so tiny their individual response to radiation is too small to measure. Since all molecules in a sample are identical, they all react the same way so their collective response is large enough to be measured.

Heed this word of warning before proceeding: when using spectrometers, be sure to know what is to be measured. Spectrometers are used to measure the effect of radiation on a sample under investigation. A test sample is excited by exposure to incident radiation, and a spectrometer measures at which wavelengths the sample is excited. As the molecules become excited, they absorb radiation at specific wavelengths. A spectrometer also measures the amount of radiation a sample absorbs, which is called absorbance. After a test is complete, the spectrometer produces a chart called a spectrum, which is a plot of the absorbance on the y-axis against the wavelength of the radiation on the x-axis. An example of an infrared spectrum is shown in figure 10.

The position of peaks on the x-axis (the wavelength at which absorption occurs) indicates what is present in the sample—this measurement is known as qualitative analysis. The size of peaks indicates how much material is present in the sample—this measurement is known as quantitative analysis. Spectrometers are provided with software that links peak areas to the amount of material present in the sample. These software programs are simple to use; however, the spectrometer must first be calibrated against the material under investigation to obtain accurate results. Calibration is done by running a series of tests on reference samples that closely resemble the sample under investigation. Reference samples are samples of known composition of the same concentration range as expected in the sample under investigation. After testing reference samples, information on their composition is added to the software program in the spectrometer, and the spectrometer will link peak areas to the amount of material present. Once the calibration is complete, the spectrometer can provide the quantitative composition of the sample under investigation.

Some spectrometers are preprogrammed with quantitative analysis methods. These are catch-all programs that may have been developed with completely different materials than those under investigation. Without correct calibration, these programs will provide a quantitative analysis of unknown samples, the results of which are unlikely to be correct.

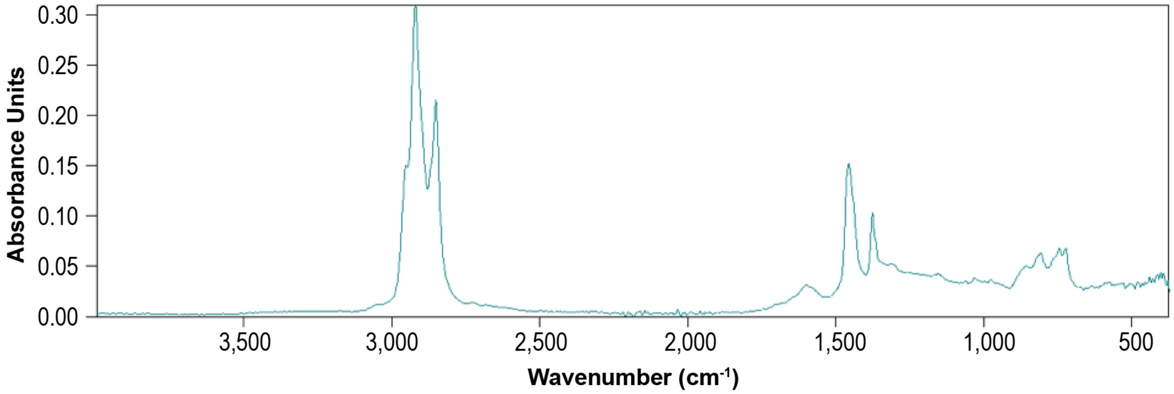
It is not possible to use the calibration from one spectrometer to another, even if they are the same model from the same manufacturer. Always calibrate the spectrometer with reference samples of known composition. Tell the spectrometer what is known so that it can provide an accurate analysis of unknown samples.

PART 2: SPECTROSCOPY

FTIR Spectroscopy

FTIR spectroscopy is used to investigate molecules. Molecules are continually moving; they flex, stretch, and

Figure 10. Spectrum. FTIR spectrum of SHRP reference asphalt AAK-1.



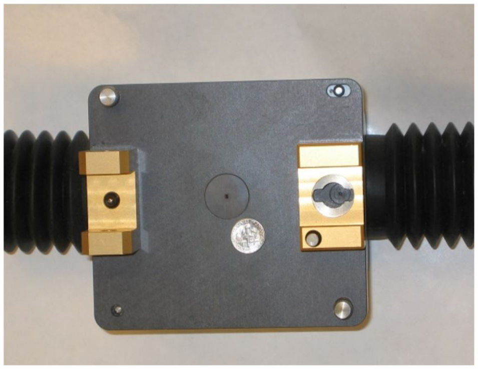
Source: FHWA.

Table 1. Typical FTIR absorption bands of chemical groups.

Absorption Band (cm^{-1})	Functional Group
3,500–3,200	O-H or N-H stretch
3,200–2,850	C-H stretch
1,350–1,480	C-H bending
1,620–1,680	C=C stretch
1,670–1,820	C=O stretch
500	C-Cl stretch
1,600	N-H bending

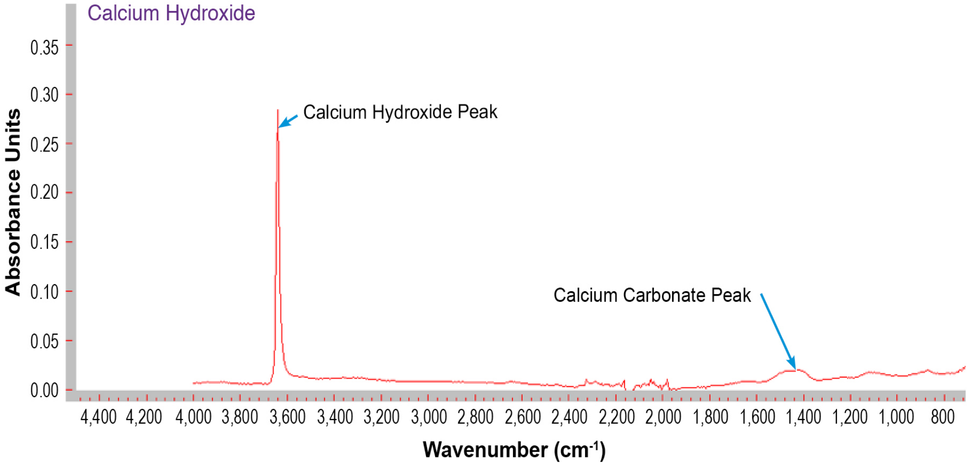
N = nitrogen; C = carbon; Cl = chlorine.

Figure 11. Photo. ATR accessory for an FTIR spectrometer.



Source: FHWA.

Figure 12. Spectrum. FTIR spectrum of lime.



Source: FHWA.

bend. Movements of pairs of atoms within a molecule are associated with specific amounts of energy and therefore resonate when excited by the incoming infrared radiation at a corresponding wavelength. Each chemical group within a molecule will absorb radiation at a different wavelength. The absorption is measured by a detector, the response of which is used to produce a spectrum, such as the one shown in figure 10. For convenience, wavelengths are generally noted as wavenumber, which is the reciprocal of a wavelength and has the unit of cm^{-1}. The FTIR spectrum for Strategic Highway Research Program (SHRP) reference asphalt AAK-1 is shown in figure 10.

Absorption wavelengths of chemical groups within molecules are well known and documented. Infrared absorption occurs in regions or bands depending on the molecule rather than at specific wavelengths. A few examples of infrared absorption bands associated with different chemical groups are given in table 1. It is not always necessary to know what all the peaks mean or what groups are present in a sample's spectrum. Often, all that is needed to answer the question of interest (i.e., is the material provided as specified?) is to match the pattern of the sample's spectrum to the spectrum of a known material. Such patterns of FTIR of known materials are widely available.

There are several ways of measuring the FTIR spectra of samples. Attenuated Total Reflectance (ATR) is the most common technique because it is the easiest to use and requires no sample preparation. The ATR accessory (figure 11) consists of a metal cube with openings on either side through which infrared radiation passes. On top of the device is a small window about 2 mm square that is usually made of diamond, which is hard and not easily damaged. The sample is placed directly on this window. For powder samples, an anvil is used to tamper the powder so that it makes intimate contact with the window. For asphalt binders, a sample of the binder is placed on the window with a spatula. Because the window is made of diamond, it is not affected by organic solvents, so asphalt binders can be readily removed by a solvent like toluene or trichloroethylene. When the ATR accessory is in use, an infrared beam passes from the source on one side of the box. Inside the box, there is usually a system of mirrors that cause the infrared beam to impinge on the sample several times. The multiple reflections increase the signal strength. The beam exits through the opposite side of the box and travels to the detector.

A simple example of the ATR technique is the generation of the FTIR spectrum of lime in figure 12. The absorbance on the y-axis is plotted against the wavenumber on the x-axis. There is a very sharp needle-like peak at 3640 cm^{-1}.

Lime is calcium hydroxide. It absorbs carbon dioxide from the air to form calcium carbonate and water, as shown in the equation in figure 13.

Figure 13. Equation. Formation of calcium carbonate.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

Where:

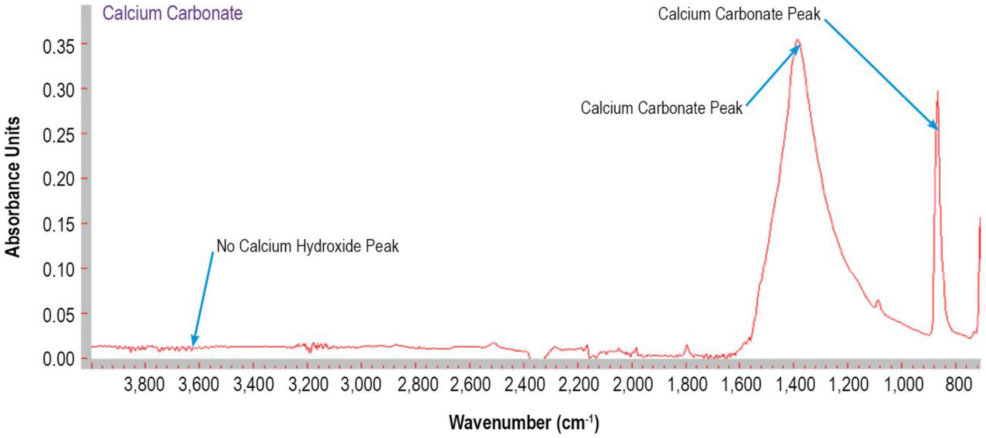
$Ca(OH)_2$ = calcium hydroxide (lime).

CO_2 = carbon dioxide.

$CaCO_3$ = calcium carbonate.

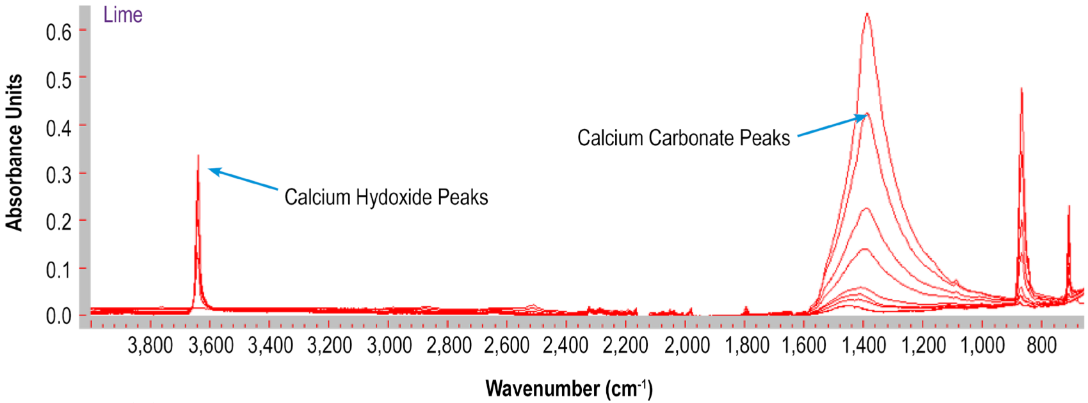
H_2O = water.

Figure 14. Spectrum. FTIR spectrum of calcium carbonate.



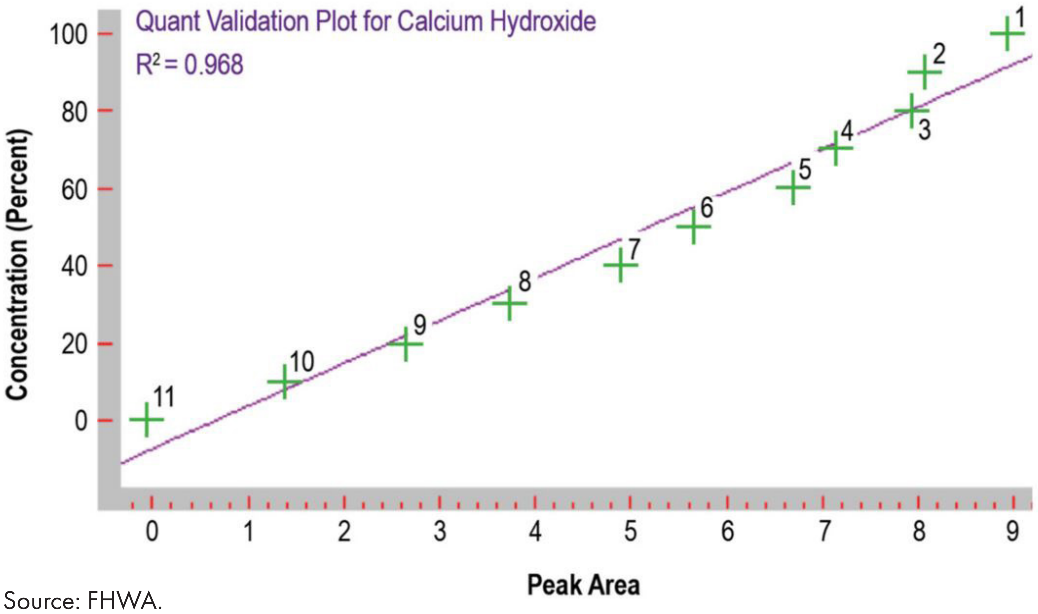
Source: FHWA.

Figure 15. Spectra. Superimposed FTIR spectra of lime/calcium carbonate blends.



Source: FHWA.

Figure 16. Graph. Peak area plotted against the lime concentration for blends of lime and calcium carbonate.

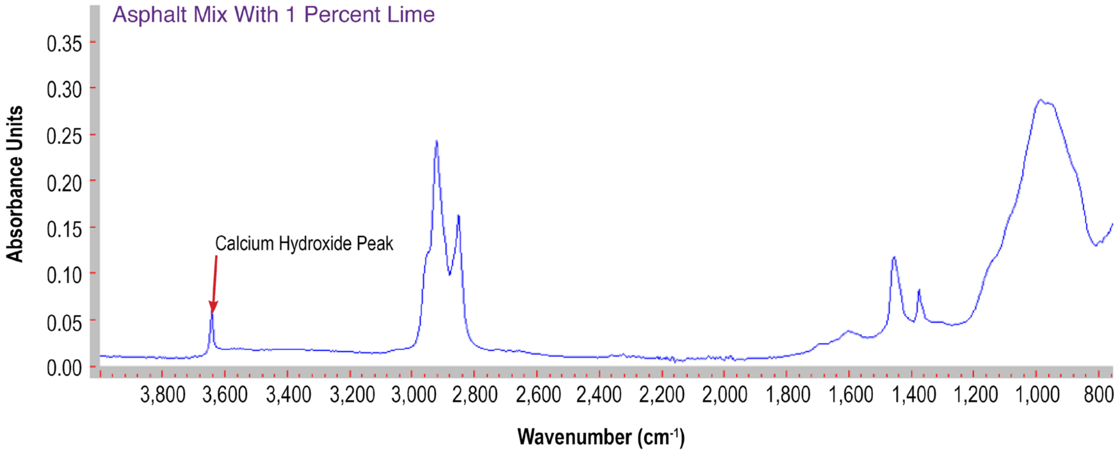


Source: FHWA.

Table 2. Quantitative FTIR analysis of lime/calcium carbonate blends.

Actual Percent Lime	Actual Percent Calcium Carbonate	Found Percent Lime (Peak at 3,640 cm^{-1})	Found Percent Calcium Carbonate (Peak at 1,390 cm^{-1})	Found Percent Calcium Carbonate (Peak at 869 cm^{-1})
90	10	77	14	14
70	30	75	25	25
50	50	52	39	39
30	70	34	70	70
10	90	9	90	88

Figure 17. Spectrum. FTIR spectrum of an asphalt binder scraped from a loose mix containing 1 percent lime.



Source: FHWA.

So, there is always a small amount of calcium carbonate present in lime. The peaks for calcium carbonate are shown in figure 14 at 1,390 and 869 cm^{-1}.

The area under the peak is proportional to the amount of material present, which is known as Beer's law. Figure 15 contains superimposed spectra of lime and calcium carbonate blends of different concentrations. The absorbance on the y-axis is plotted against the wavenumber on the x-axis. As the calcium carbonate content of the blends increase, so do the sizes of the calcium carbonate peaks. These increases are accompanied by decreases in the sizes of the calcium hydroxide peaks, although the decreases are difficult to see since the peaks are narrow.

In addition to using FTIR spectroscopy to identify materials, Beer's law can be used to obtain a quantitative estimation of components in mixtures. Figure 16 is a plot of the percentage of lime content on the y-axis against the 3,640-cm^{-1} peak area on the x-axis for blends of lime and calcium carbonate that were previously shown in figure 15. The plot has a straight line with an R^2 value of 0.968.

Knowing the peak area in a spectrum of an unknown lime/calcium carbonate blend, the percentage of lime in the mixture can be backcalculated. There are three peaks in the spectra of lime/calcium carbonate blends shown in figure 15: calcium hydroxide at 3,640 cm^{-1} and calcium carbonate at 1,390 and 869 cm^{-1}. As shown in table 2, the area under any of these three peaks can be used to determine the composition of the blends (i.e., the "found" percentage) and compared to the known composition. Spectrometers generally have quantitative analysis functions built in to automatically calculate peak areas.

Some states use lime as an antistrip additive. Figure17 shows the spectrum of a sample of asphalt binder scraped from a piece of aggregate from a loose mix containing 1 percent lime. The absorbance on the y-axis is plotted against the wavenumber on the x-axis. The size of the calcium hydroxide peak may be used as an indication of how much lime is present in the sample. For more details concerning this application, see "Determination of Lime in Hot-Mix Asphalt."(6)

Table 3. Determined percentage of lime content in samples of asphalt binders with a known percentage of lime content using FTIR spectroscopy.

Sample Number	Sample	5 Percent Known Lime Content	10 Percent Known Lime Content	15 Percent Known Lime Content	20 Percent Known Lime Content	25 Percent Known Lime Content
1	Citgo PG64-22	6.5	10.9	15.4	19.8	24.2
2	Citgo PG64-22	7.2	10.1	13.9	19.0	24.0
3	Hunt MS PG67-22	7.1	10.8	15.1	16.0	24.9
4	SHRP AAD-1	7.0	9.8	14.5	17.4	21.8
5	SHRP AAG-2	7.1	10.9	13.7	18.7	22.0
6	3 percent SBS	7.2	11.3	14.9	20.7	24.4
7	Air blown	6.3	9.9	14.2	17.9	21.9
8	EVA grafted	5.7	11.0	12.4	17.9	21.4
9	Terpolymer	5.3	8.9	14.0	18.4	21.7
All*	Maximum	7.2	11.3	15.4	20.7	24.9
All*	Minimum	5.3	8.9	12.4	16.0	21.7
All*	Average	6.6	10.4	14.2	18.4	22.9
All*	Standard deviation	0.7	0.8	0.9	1.4	1.4
All*	Coefficient of variation percentage	10.8	7.4	6.3	7.6	6.1

*All samples combined.
SBS = styrene butadiene styrene; EVA = ethylene vinyl acetate.

FTIR spectroscopy can also be used to determine whether a hot mix contains lime. It is theoretically possible to take aggregate directly from a paving machine, scrape a sample of asphalt, and run an FTIR spectrum scan, although this has not yet been done. Determination of the lime content of different asphalt binders containing various additives has been estimated and are presented in table 3.(6)

FTIR Spectra of Asphalt Binders

Since asphalt binders are a mixture of many thousands of compounds, their FTIR spectra are complex. While different crude oil sources yield asphalt binders with different chemical compositions, there are similarities between the asphalt binders and their FTIR spectra are almost identical. Even though there may be small differences between the binders, it is not possible to distinguish one asphalt binder from another simply by comparing FTIR spectra. The functional groups present in SHRP reference asphalt AAK-1 are indicated in figure 18. The absorbance on the y-axis is plotted against the wavenumber on the x-axis. The labels indicate the chemical grouping associated with each peak.

Quantitative Determination of SBS Polymer in Asphalt

Figure 19 shows the FTIR spectrum of asphalt that has been modified with SBS polymer. The presence of the polymer is indicated by two peaks: polystyrene at 700 cm^{-1} and butadiene at 965 cm^{-1}.

The areas under these peaks can be used to estimate the amount of SBS polymer in asphalt. This is the basis of the American Association of State Highway and Transportation Officials' test method T-302-4, "Polymer Content of Polymer-Modified Emulsified Asphalt Residues and Binders."(7) This test method uses the ratio of the butadiene peak (height or area) at 965 cm^{-1} to the asphalt methylene bending peak at 1,375 cm^{-1}.

Care must be taken with this test method since the size of the peak is influenced to some extent by the asphalt binder in which the polymer is dispersed. For example, the peak area for a 1-percent SBS polymer blend might vary in different asphalt binders.

Determination of Asphalt Oxidation in Reclaimed Asphalt Pavement

When asphalt oxidizes, carbonyl and sulfoxide groups are formed. In the FTIR spectrum, these appear as peaks at around 1,700 cm^{-1} for carbonyl and 1,030 cm^{-1} for sulfoxide, as shown in figure 20. Practitioners can potentially use this information to obtain some idea of how much a given sample of asphalt has aged. While this works for pure asphalt, binders recovered from reclaimed asphalt pavement (RAP) always contain traces of aggregate despite the use of a high-speed centrifuge. The overlap of the aggregate peak obscures the sulfoxide peak, making aging determination more challenging. The FTIR spectrum of some aggregate dust, shown in figure 21, illustrates this point.

Detection of Diesel Fuel in Asphalt

Diesel fuel is a hydrocarbon that contains many carbon–hydrogen bonds that are detected by FTIR spectroscopy at around 2,800 to 3,000 cm^{-1}, as shown in figure 22. Asphalt contains many carbon–hydrogen bonds as well, as previously shown in the FTIR spectrum of SHRP reference asphalt AAK-1 in figure 18. It is therefore very difficult to confirm the presence of diesel fuel in asphalt using FTIR spectroscopy.

Detection of Vegetable Oil in Asphalt

With the increasing use of RAP, it is common to add a softening agent to asphalt binders to compensate for the hardened asphalt in RAP. This addition is based on the assumption that hardened asphalt is mixed with RAP that contains fresh binder. These "rejuvenators" soften the asphalt. They come from a wide range of sources, including REOB (see the section XRF Spectroscopy), recycled swine manure, used cooking oil, and vegetable oil derivatives. Often, the compositions are not disclosed.

Animal and vegetable fats and oils are all fatty acid esters of glycerin. The ester group contains the carbonyl group C=O, which is readily detected by FTIR spectroscopy. Figure 23 shows the FTIR spectrum of used canola oil, where the carbonyl peak is clearly visible at 1,743 cm^{-1}.

The canola oil shown in figure 23 dispersed in an asphalt binder will show the same carbonyl peak, as shown in figure 24. Caution should be exercised when drawing conclusions from the presence of a carbonyl peak, as finding a carbonyl peak in the FTIR spectrum of an asphalt binder does not necessarily mean the asphalt binder contains vegetable oil. It is essential to remember that oxidized asphalt itself contains the same carbonyl group, as do many other materials. Be sure to know what material is being tested.

Detection of Liquid Amine Antistrip Additives

Liquid amine antistrip additives are generally high molecular weight amines. Amines all contain nitrogen–hydrogen bonds, which are readily detected by FTIR spectroscopy. There are many liquid amine antistrip additives sold under proprietary brand names. The amines they contain vary, and their spectra differ. When confirming that the asphalt binder contains the specified antistrip additive, it is necessary to know exactly which additive was used. To do so, it is necessary to obtain a sample of the additive from the manufacturer, make up some blends of it in asphalt, and calibrate the instrument. An example spectrum of a liquid amine antistrip is shown in figure 25.

FTIR Spectroscopy and Water

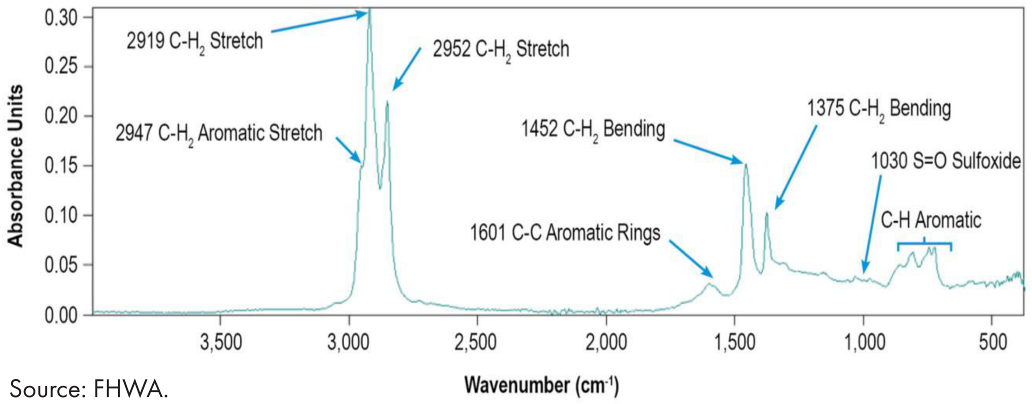
Water has an FTIR spectrum of its own (figure 26), so FTIR spectroscopy is not particularly good for the analysis of aqueous systems. Raman spectroscopy, which is further detailed in the self-named section, is a better technique to use.

Detection of Phosphoric Acid

Phosphoric acid can be used to stiffen asphalt binders. It has an FTIR spectrum with very broad peaks. As shown in figure 27, there is a very broad peak from 800 to 1,000 cm^{-1}.

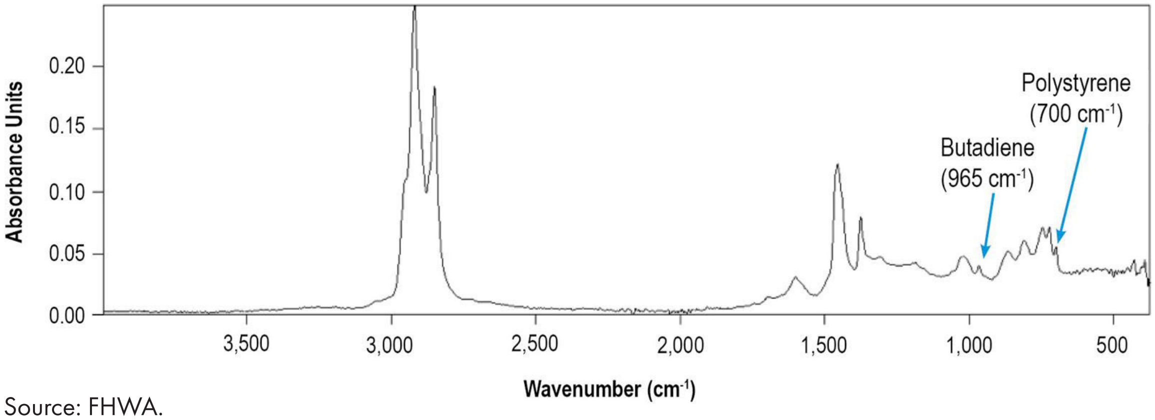
The FTIR spectrum of asphalt modified with 1.5 percent phosphoric acid is shown in figure 28. The phosphoric acid peak is buried among the asphalt peaks in the

Figure 18. Spectrum. the FTIR spectrum of SHRP reference asphalt AAK-1.



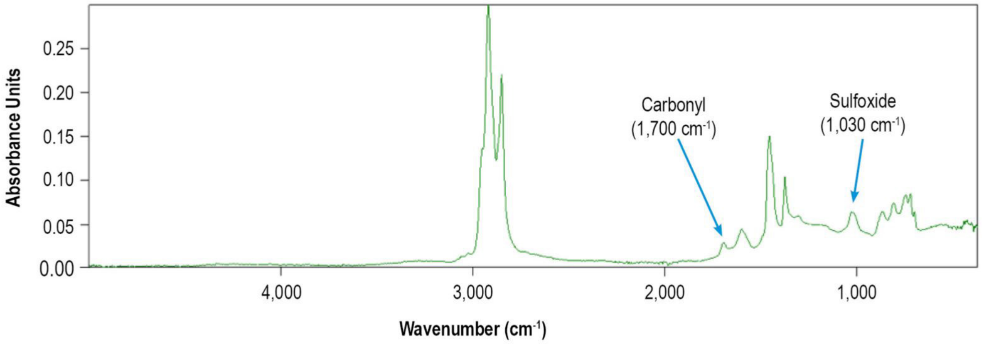
Source: FHWA.

Figure 19. Spectrum. FTIR spectrum of asphalt containing SBS polymer.



Source: FHWA.

Figure 20. Spectrum. FTIR spectrum of aged SHRP reference asphalt AAH.



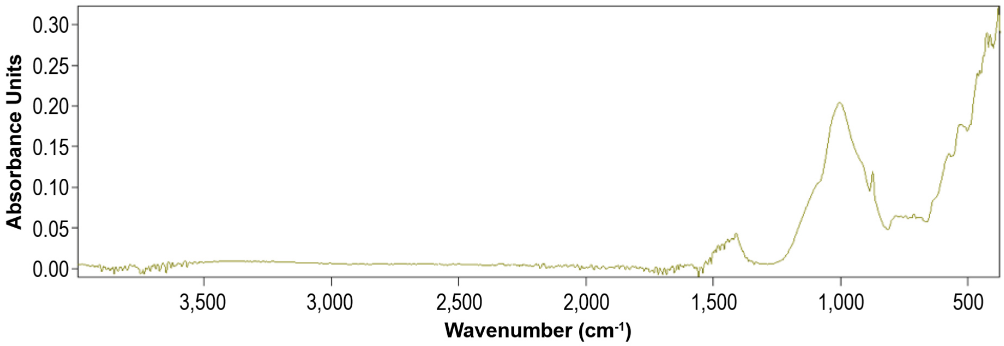
Source: FHWA.

800 to 100 cm^{-1} region and is not easy to quantify. While phosphoric acid can be detected using FTIR spectroscopy, XRF spectroscopy is a much better technique since it generates a spectrum with a very sharp peak and an accurate quantitative measure of the amount of phosphorous present in the sample.

XRF Spectroscopy

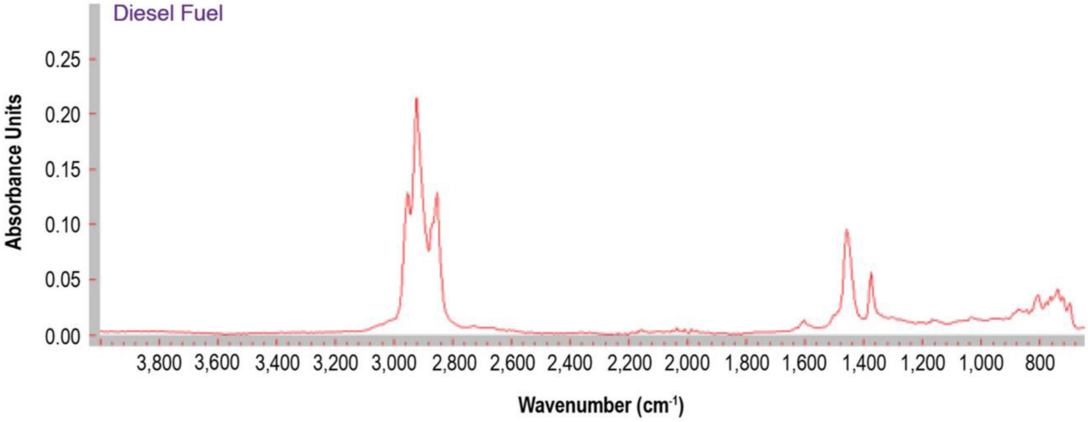
Atoms consist of a positively charged nucleus surrounded by a cloud of electrons. Electrons exist in shells or orbits of different binding energies. The further away electrons are from the nucleus, the higher their binding energy. The orbits are named outward from the nucleus as the K-shell, L-shell, and M-shell (figure 29). Electrons can

Figure 21. Spectrum. FTIR spectrum of aggregate dust.



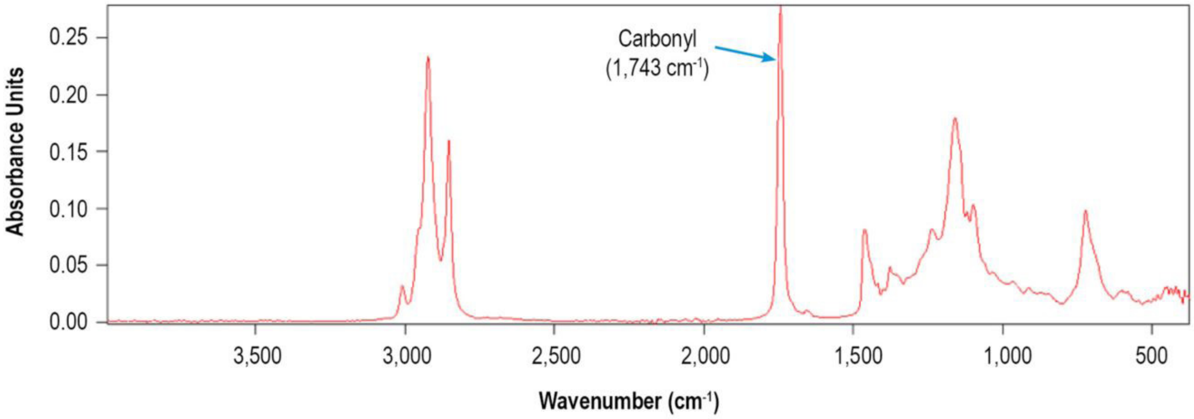
Source: FHWA.

Figure 22. Spectrum. FTIR spectrum of diesel fuel.



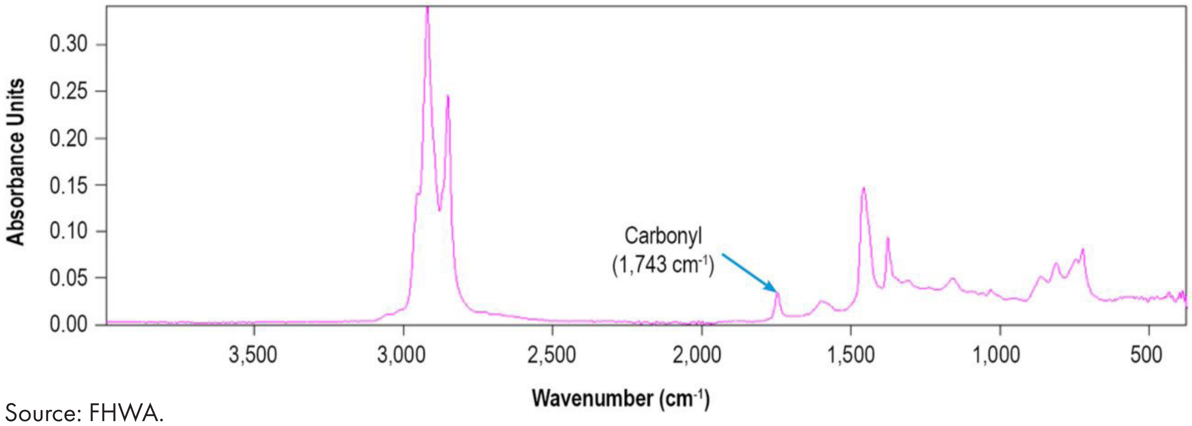
Source: FHWA.

Figure 23. Spectrum. FTIR spectrum of used canola oil.



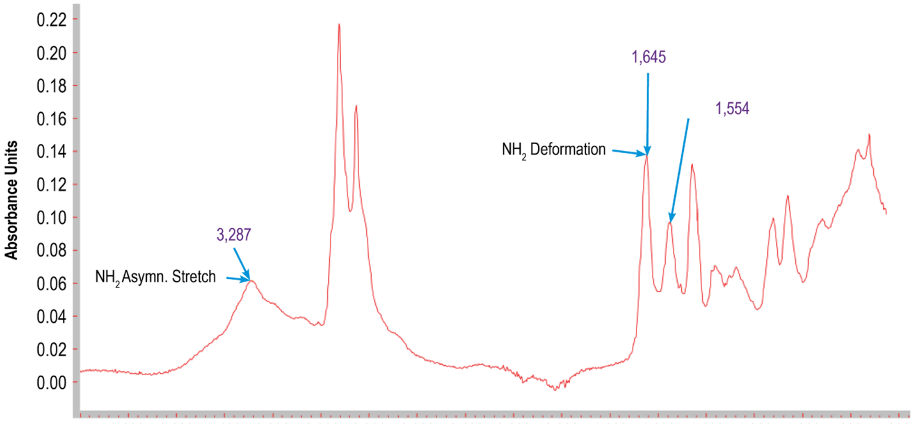
Source: FHWA.

Figure 24. Spectrum. FTIR spectrum of asphalt containing 5 percent used canola oil.



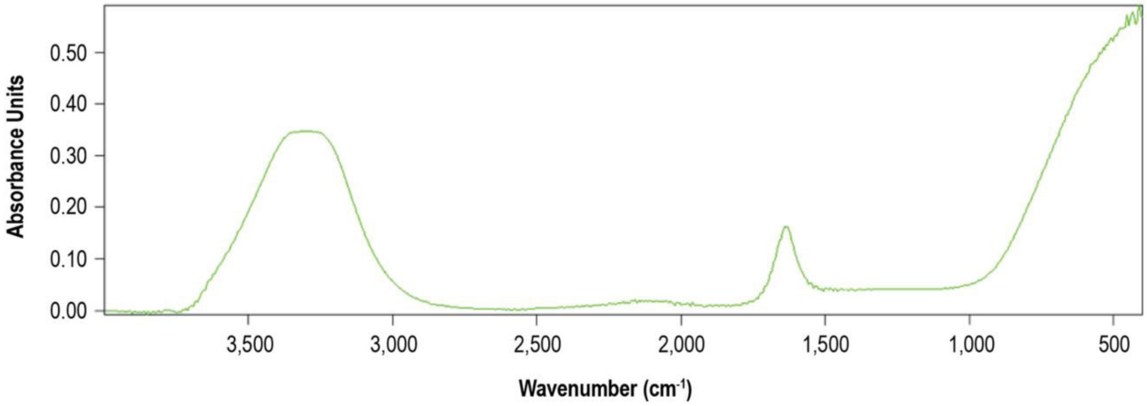
Source: FHWA.

Figure 25. Spectrum. FTIR spectrum of a liquid amine antistrip.



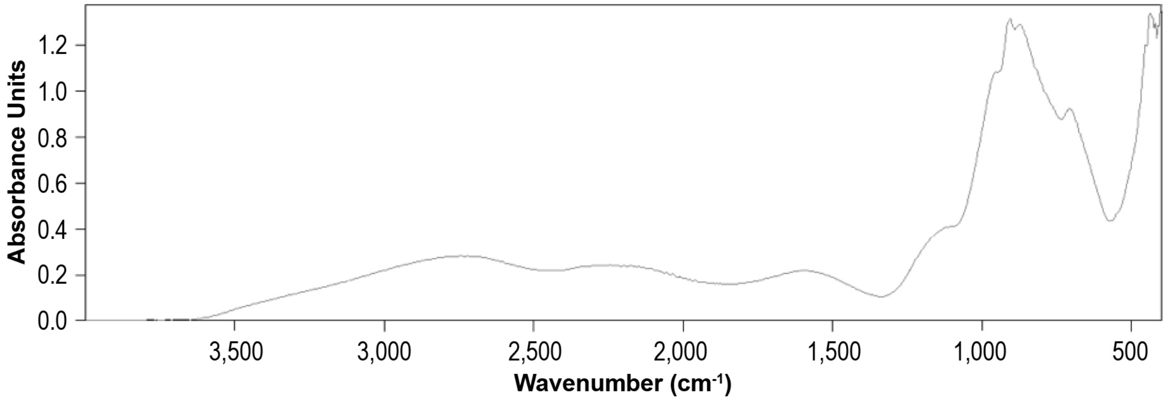
Source: FHWA.

Figure 26. Spectrum. FTIR spectrum of water.



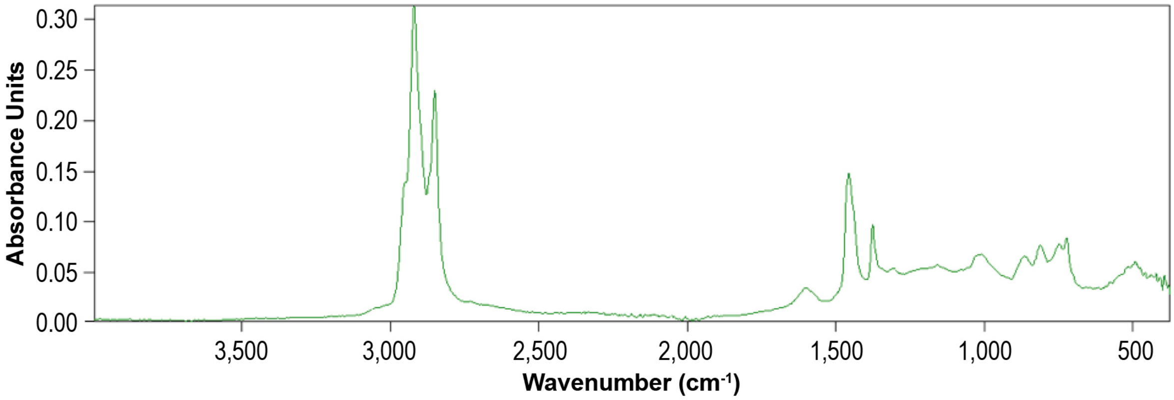
Source: FHWA.

Figure 27. Spectrum. FTIR spectrum of phosphoric acid.



Source: FHWA.

Figure 28. Spectrum. FTIR spectrum of asphalt containing 1.5 percent phosphoric acid.



Source: FHWA.

only move from one shell to the next; they cannot stop halfway between. The difference in energy between the shells is precisely fixed for each element.

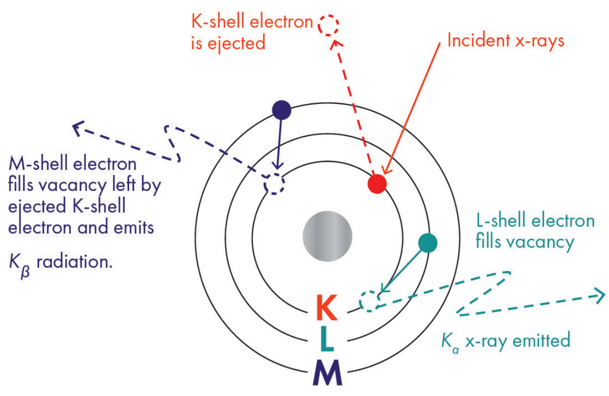
When electrons are knocked out of their orbit by irradiation with x-rays, they leave behind vacancies, which make the atom unstable. The instability is immediately corrected by an electron moving down from a higher orbit to fill the vacancy. This movement results in a release of energy equal to the energy difference of the two orbitals involved. The spacing between the orbital shells of each atom, and therefore the energy, is unique to the atoms of each element. So, the material emits radiation that has energy characteristic of the atoms present.

These electronic transitions are named depending on the orbits involved. If the electron is ejected from the K-shell, and the vacancy created is filled by an electron from the L-shell, the x-ray emitted is designated K_α. If the electron is ejected from the K-shell and the vacancy created is filled by an electron from the M-shell, the x-ray emitted is designated K_β. From the M-shell to the L-shell, it is designated L_α, and so on. This process is clearly shown in the diagram in figure 29, which represents an atomic nucleus surrounded by concentric circles representing the electron orbits. Arrows indicate the movements of electrons between orbits, the incident radiation that caused the movements, and the x-rays emitted as a result of the movements. The wavelength of the radiation emitted differs from that of the incident radiation. The emitted radiation is known as fluorescence.

Some irradiation energy results in ejection of electrons from outer shells. These ejected electrons are called auger electrons. The ratio between the number of characteristic photons to the number of auger electrons is known as the fluorescence yield (ω). The value of ω never reaches 100 percent and is a function of the atomic weight of the element. The fluorescence yield from the K-shell (ω_K) is considerably higher than that from the L-shell (ω_L).

Some of the incident x-ray energy is scattered by the sample in two ways: Rayleigh scatter and Compton scatter. Rayleigh scatter is when the energy and

Figure 29. Illustration. Electronic transitions that result in fluorescence.



Source: FHWA.

wavelength are unchanged. Compton scatter occurs when the incident radiation loses energy in a collision, resulting in emission at a longer wavelength. Both types of scatter occur more intensely in samples with a low atomic number (i.e., samples made of lighter elements). Samples made of lighter elements will produce greater Compton scatter and less Rayleigh scatter because they have many loosely bound electrons. For heavier elements, Compton scatter disappears completely and only Rayleigh scatter remains.

The energy of electronic transitions between shells increases with the atomic number and is precisely known for each element. To illustrate this concept, some examples for elements measured using K-shells are given in table 4, which lists the element name, abbreviation, atomic number, atomic weight (i.e., weight of a gram molecule), and the K_α and K_β energies measured in KeV. The XRF spectrometer can identify which elements are present in the sample.

The fluorescence radiation from lighter elements is of relatively low energy and severely attenuated if it must pass through air. For this reason, the measurement of light elements is usually carried out in a vacuum.

There are two basic types of XRF spectrometers: energy-dispersive XRF (EDXRF) and wavelength-dispersive XRF (WDXRF). Handheld XRF spectrometers are EDXRF. An EDXRF spectrometer simultaneously detects all the secondary fluorescence radiation emitted by a sample. X-rays emitted by a sample go to a solid-state detector, which produces voltage proportional to the incoming photon energies. Sodium is normally considered the lightest element that can be reliably detected by an EDXRF spectrometer. In a WDXRF spectrometer, x-rays emitted by a sample are diffracted by a crystal into individual wavelengths. The detector then measures the fluorescence energy one wavelength at a time. The advantage of a WDXRF spectrometer over an EDXRF spectrometer is that it generates a higher-resolution spectrum, resulting in fewer overlapping peaks, increased sensitivity to lighter elements, and lower background intensities.

Any time an x-ray beam is scattered off a surface, its intensity is reduced by a factor of approximately 100. While any XRF system loses intensity in the process of exciting the sample, a WDXRF system loses a factor of approximately another 100 at the diffraction device. So, to achieve similar counts at the detector, a WDXRF system needs 100 to 1,000 times the flux of a direct excitation EDXRF system. Generating this level of flux and the cost and complexity of the diffraction system causes WDXRF spectrometers to be more expensive than EDXRF spectrometers.

What Does an XRF Spectrometer Detect?

XRF measurements only identify elements present in a sample—these measurements tell nothing about the chemical structure of the sample. As seen in FTIR spectra displayed in figure 12 and figure 14, spectra of lime and calcium carbonate are quite different. Figure 30 and figure 31 show XRF spectra of these materials, respectively. The spectra are identical and show the presence of calcium, but it is not possible to distinguish the lime and calcium carbonate.

Asphalt contains significant amounts of sulfur compounds in the range of 30 to 300,000 ppm. Phosphorous and sulfur are next to each other in the periodic table, so their K_α fluorescence energies are close at 2.013 and 2.307 KeV. In figure 32, the large sulfur K_α peak overlaps the position of the phosphorous peak. Figure 33 shows a similar spectrum for the same asphalt that was modified with 1 percent super phosphoric acid. Due to the closeness of phosphorous and sulfur fluorescence energies, XRF spectrometer software may interpret the overlap of energies as due to the presence of phosphorous when there is none.

At the TFHRC chemistry laboratory, more than 1,500 samples of asphalt binders were analyzed during a study on detection of REOB.(9) Many unmodified binders were reported by the XRF spectrometer software to contain 0.1 to 0.2 percent phosphorous when none was present. WDXRF spectrometer software is better able to separate these peaks.

An XRF spectrometer can be calibrated to quantitatively measure the phosphoric acid content of asphalt binders by measuring the spectra of samples containing known concentrations. These measurements are run as "standards." When a standard is run, the spectrometer provides a calibration graph, such as the one shown in figure 34, which is a plot of XRF energy on the y-axis

Table 4. XRF energies of some elements.

Element	Abbreviation	Atomic Number	Atomic Weight	K_α (KeV)	K_β (KeV)
Lithium	Li	3	6.941	—	—
Beryllium	Be	4	9.012	0.109	—
Boron	B	5	10.81	0.183	—
Carbon	C	6	12.011	0.277	—
Nitrogen	N	7	14.007	0.392	—
Oxygen	O	8	16.000	0.525	—
Fluorine	F	9	19.000	0.677	—
Sodium	Na	11	22.990	1.041	1.067
Magnesium	Mg	12	24.31	1.253	1.302
Aluminum	Al	13	26.98	1.486	1.557
Silicon	Si	14	28.09	1.739	1.836
Phosphorous	P	15	30.794	2.013	2.139
Sulfur	S	16	32.064	2.307	2.464
Chlorine	Cl	17	35.453	2.621	2.815
Potassium	K	19	39.098	3.312	3.589
Calcium	Ca	20	40.08	3.690	4.012
Scandium	Sc	21	44.96	4.088	4.460
Titanium	Ti	22	47.90	4.508	4.931
Vanadium	V	23	50.94	4.949	5.426
Chromium	Cr	24	52.00	5.411	5.946
Manganese	Mn	25	54.94	5.894	6.489
Iron	Fe	26	55.85	6.398	7.057
Cobalt	Co	27	58.93	6.924	7.648
Nickel	Ni	28	58.71	7.471	8.263
Copper	Cu	28	63.55	8.040	8.904
Zinc	Zn	30	65.37	8.630	9.570

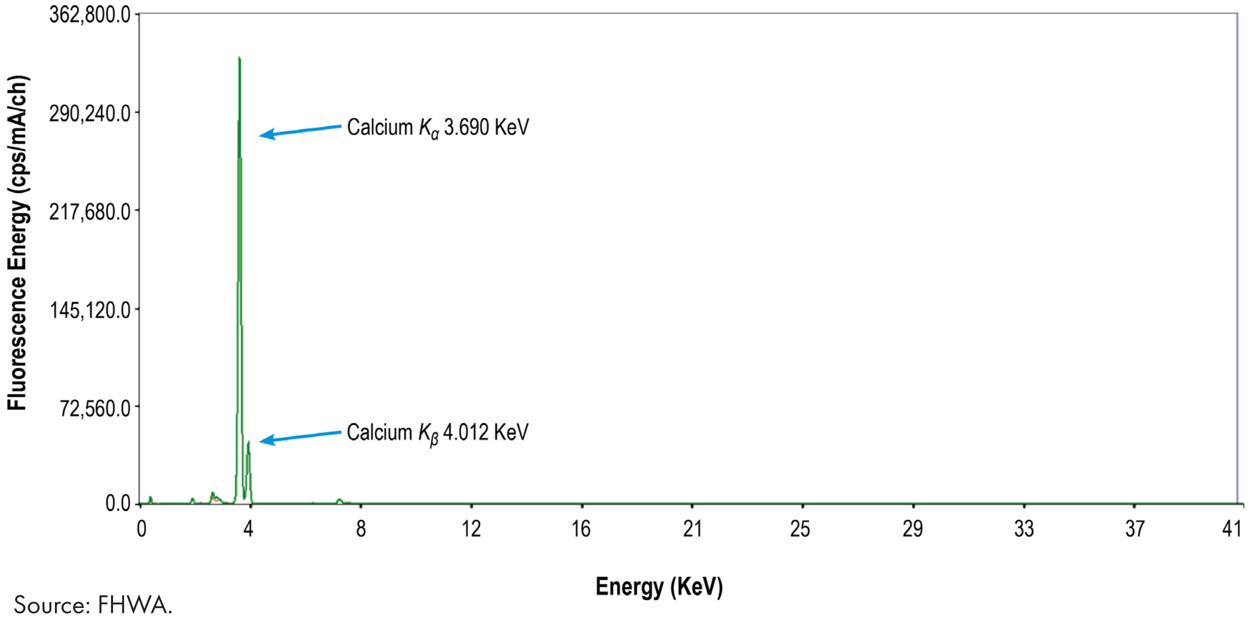
—No data.

against the phosphoric acid content on the x-axis. This calibration can be saved in the spectrometer software as a named method (e.g., "Phosphorous in Asphalt").

The calibration allows the user to compare an unknown material against the standard to determine the exact composition of the material. Figure 35 shows the actual versus found phosphoric acid content for several blends of asphalt with different levels of phosphoric acid using an EDXRF spectrometer. The left bars in the pairs represent the actual phosphoric acid content, and the right bars represent the analysis result produced from the spectrometer. Even though the phosphorous and sulfur peaks overlap, the spectrometer was still able to produce accurate analyses, as shown in the figure. For more detailed information on the analysis of asphalt binders for phosphoric acid, see *The Use of Phosphoric Acid to Stiffen Asphalt Binders.*(8)

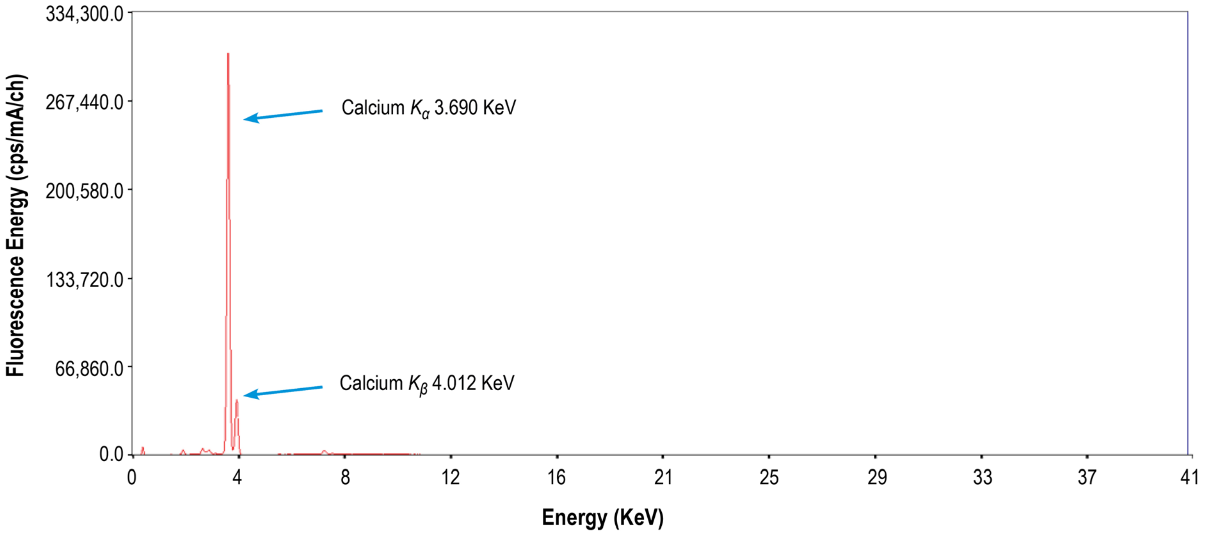
REOB has been used as an inexpensive additive to soften asphalt binders to meet Superpave specifications. Figure 36 shows the XRF spectrum of an REOB sample. It shows the energy of the emitted XRF plotted against the energy of the incident x-rays. The spectrum has several peaks, indicating the presence of the major elements plus some trace elements that are not important

Figure 30. Spectrum. XRF spectrum of lime.



Source: FHWA.

Figure 31. Spectrum. XRF spectrum of calcium carbonate.

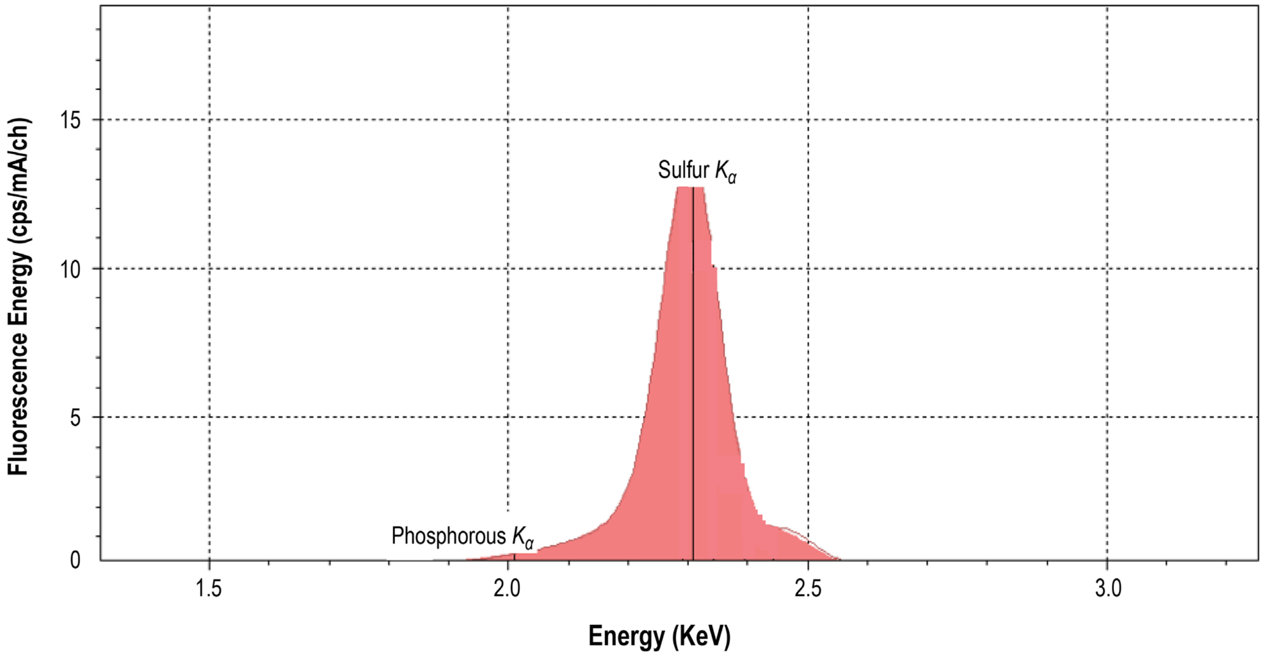


Source: FHWA.

to the analysis. Two major elements are identified in the spectrum: iron and copper compounds (Fe-K_α-C, Cu-K_α, etc.), which are wear metals from the engine; and calcium, zinc, and molybdenum compounds (Ca-K_α, Zn-K_α, Mo-K_α, etc.), which are from additives contained in the oil. Iron is not useful in the analysis since asphalt binders contain varying amounts of iron, which would affect the analysis if considered. The presence of these elements can be used to readily identify the presence of REOB in asphalt binders. For more detail on this analysis method, see *Field Analysis of Asphalt Binders for Recycled Engine Oil Bottoms (REOB) using Handheld XRF Spectrometers.*(9)

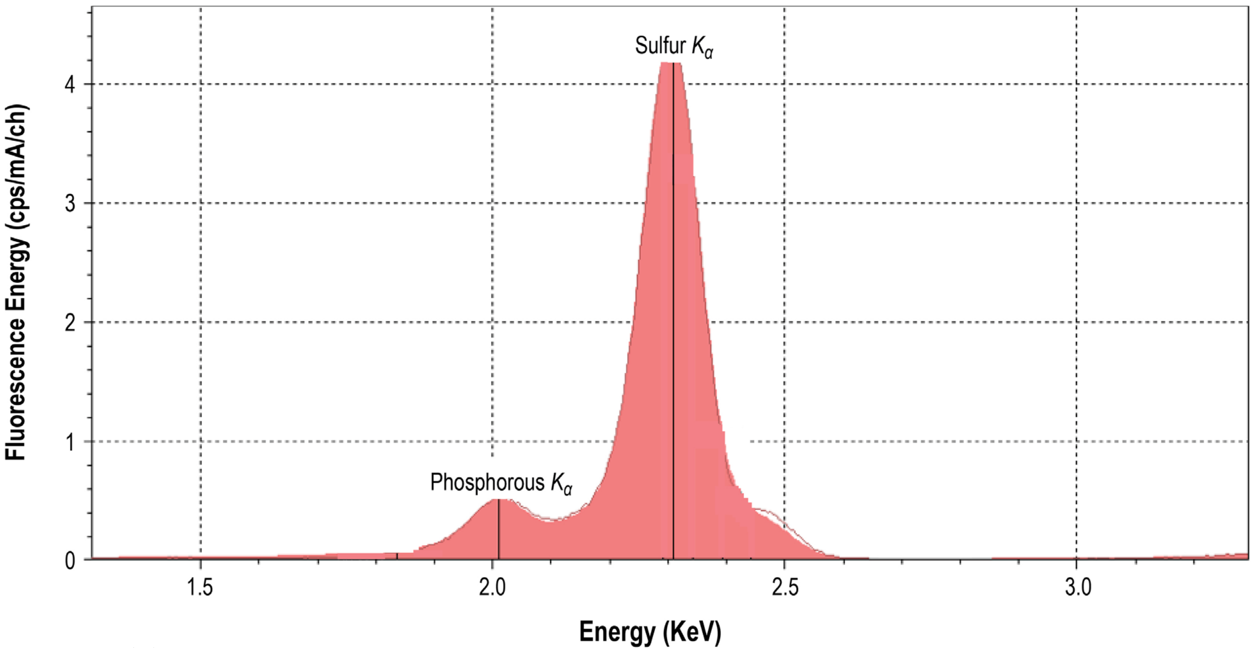
The XRF spectrum is easier to interpret than the FTIR spectrum because the analysis is provided in the form of a report, as shown in figure 37. Other than the initial calibration, no interpretation is needed.

Figure 32. Spectrum. XRF spectrum of asphalt AAB-1.



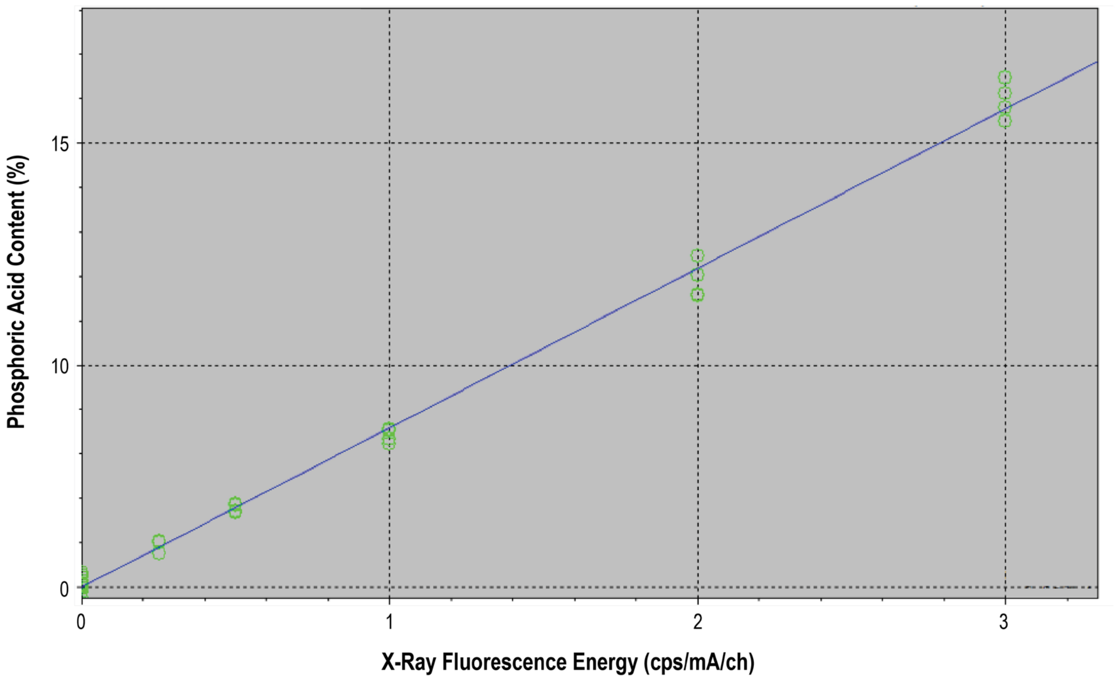
Source: FHWA.

Figure 33. Spectrum. XRF spectrum of asphalt AAB-1 containing 1 percent super phosphoric acid.



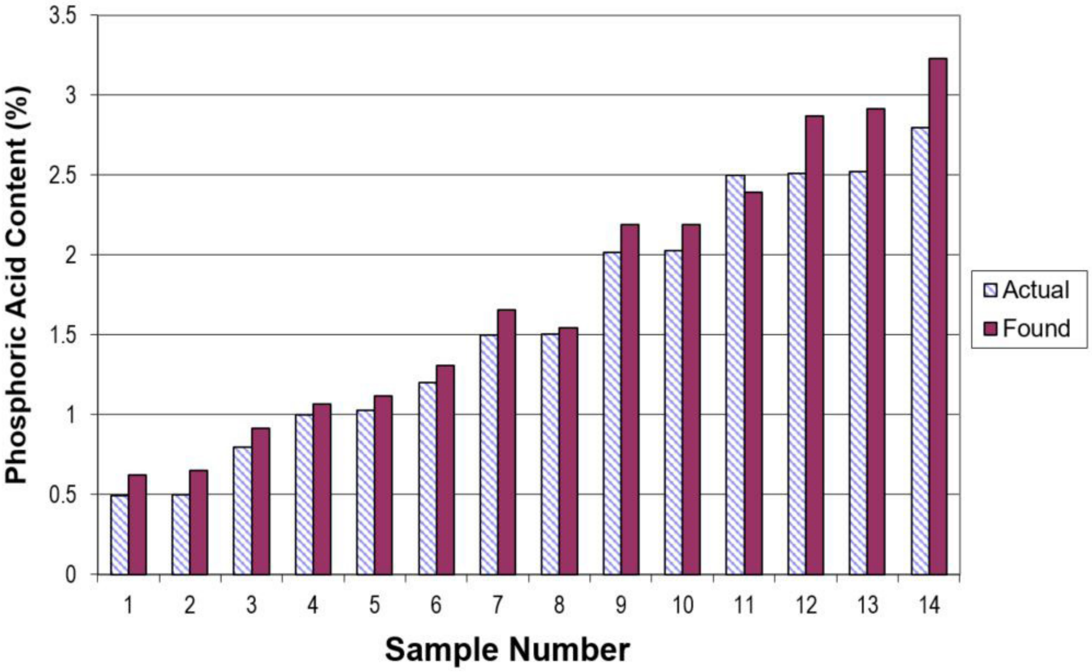
Source: FHWA.

Figure 34. Graph. Calibration of phosphoric acid modified binders.



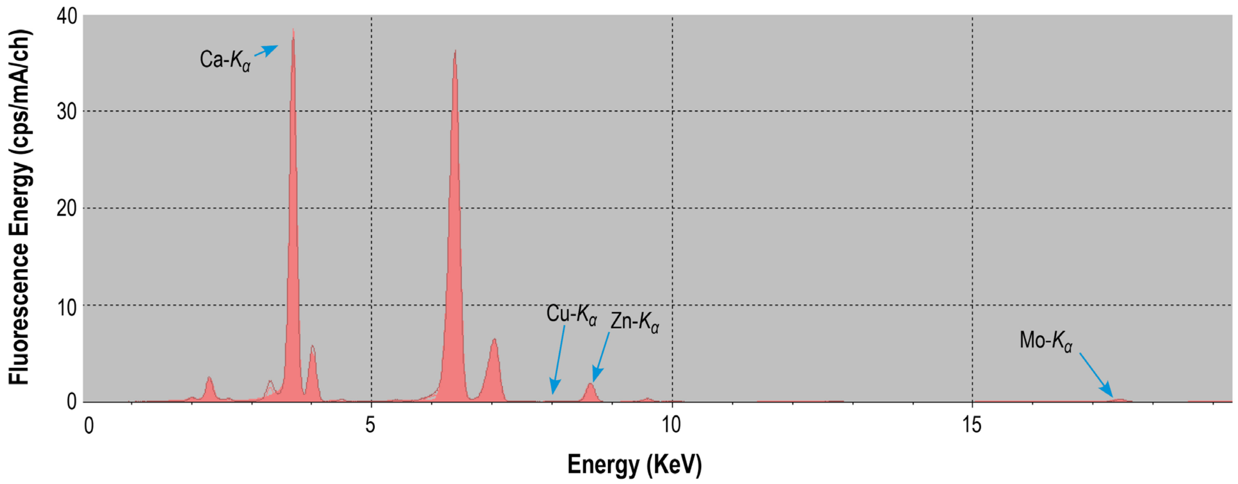
Source: FHWA.

Figure 35. Graph. XRF analysis of actual versus found levels of phosphoric acid in asphalt.



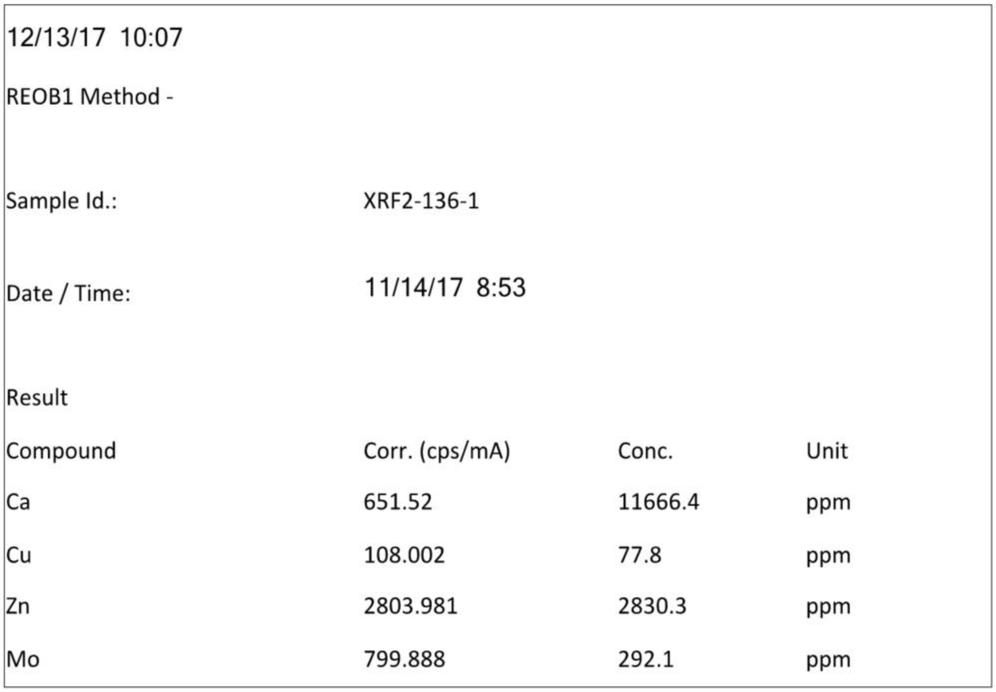
Source: FHWA.

Figure 36. Spectrum. XRF spectrum of REOB sample.



Source: FHWA.

Figure 37. Screenshot. XRF REOB analysis report.



12/13/17 10:07

REOB1 Method -

Sample Id.: XRF2-136-1

Date / Time: 11/14/17 8:53

Result

Compound	Corr. (cps/mA)	Conc.	Unit
Ca	651.52	11666.4	ppm
Cu	108.002	77.8	ppm
Zn	2803.981	2830.3	ppm
Mo	799.888	292.1	ppm

Source: FHWA.
Corr. = corrected x-ray fluorescence; Conc. = concentration in parts per million.

Raman Spectroscopy

Raman spectroscopy is an analysis technique used to measure the wavelength and intensity of inelastically scattered light (i.e., the Raman effect) from molecules. Raman scattered light occurs at wavelengths that are shifted from the incident light by the energies of molecular vibrations. Raman spectroscopy provides structural information and a fingerprint by which molecules can be identified by interactions between the laser light with molecular vibrations and other excitations on the sample. These interactions result in the energy of the laser photons being shifted up or down, which provides information about the vibrational modes and therefore the chemical structure in the system.

Raman scattering is a very weak effect. The main difficulty with Raman spectroscopy is separating the weak inelastically scattered light from the intense Rayleigh scattered light. This difficulty is exacerbated by molecules like iron oxides that fluoresce when irradiated by a laser light, drowning the Raman signal. Figure 38 illustrates energy levels and different types of scattering—Rayleigh, Stokes, and anti-Stokes—that result from the irradiation of a sample using laser light. Raman spectroscopy yields similar but complementary information to FTIR spectroscopy.

The magnitude of the Raman effect correlates with the polarizability of electrons in a molecule. The Raman effect is a form of inelastic scattering where an incident photon excites the molecule. This excitation puts the molecule into a virtual energy state for a short time before the photon is emitted. Inelastic scattering means that the emitted photon is either a higher or lower energy than the incident photon. Transitions that have large Raman intensities often have weak FTIR intensities, and vice versa.

Raman spectroscopy is used in biological applications since, unlike FTIR, it does not face interference from water molecules. It is also an efficient and nondestructive way to investigate works of art. Figure 39 through figure 41 are examples of Raman spectra for calcium carbonate, lime, and lepidocrocite (i.e., one of the iron oxide phases that occurs in rust), respectively.

SUMMARY

This document introduced the subject of spectroscopy, which has been around for decades. This TechNote specifically focused on FTIR and XRF spectroscopy, both of which are of interest to pavement engineers—especially as both methods now offer users handheld spectrometers. Overall, there are many types of spectrometers, many of which have specialized applications. However, the best spectrometer for the job depends on what is to be measured. When seeking information about a chosen spectrometer, the manufacturer is a great resource.

Figure 38. Illustration. Energy-level diagram showing states involved in Raman spectra.[10]

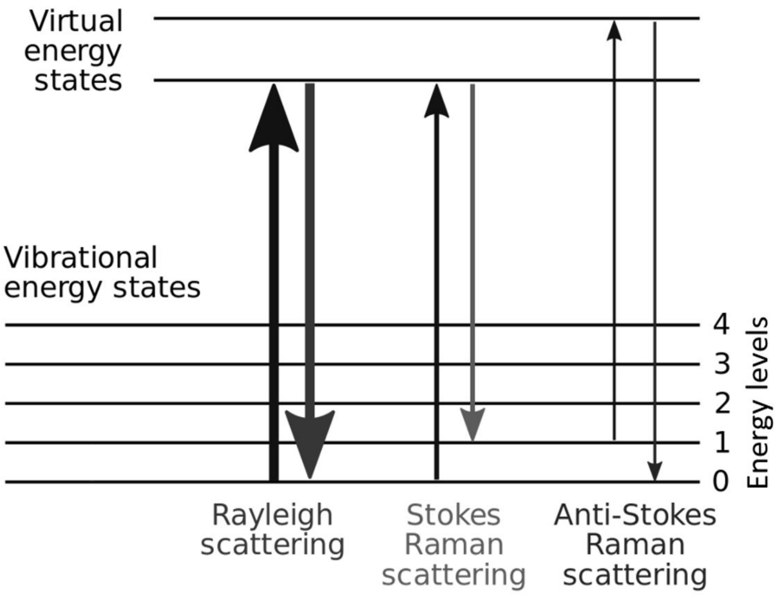


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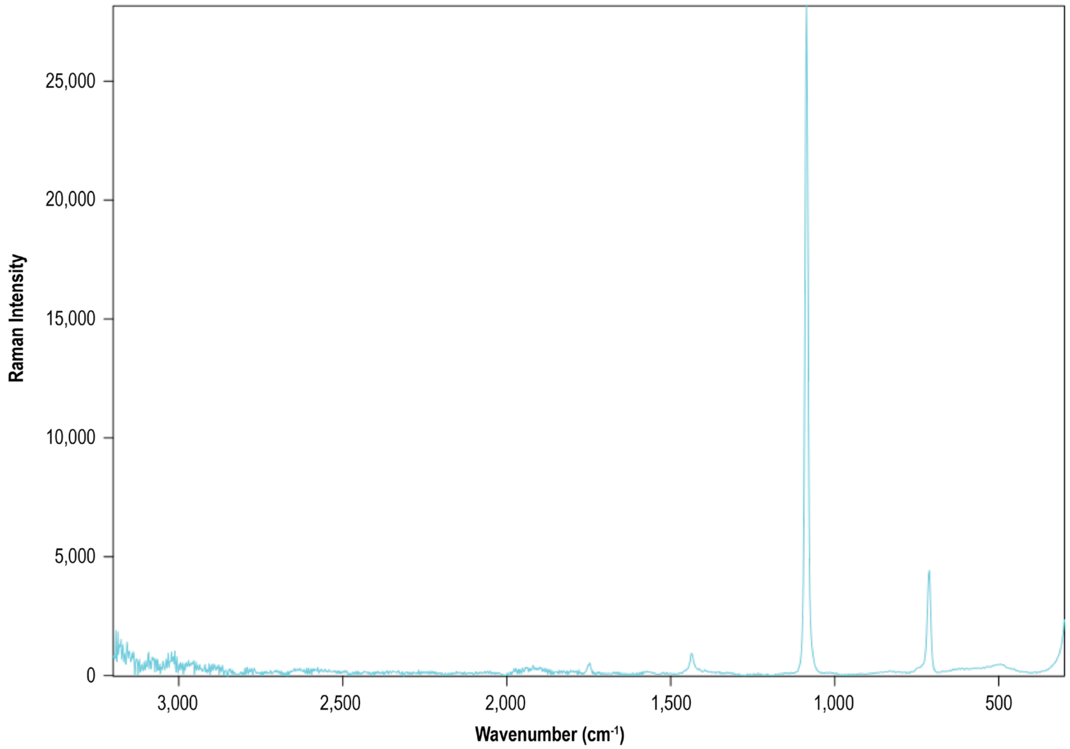
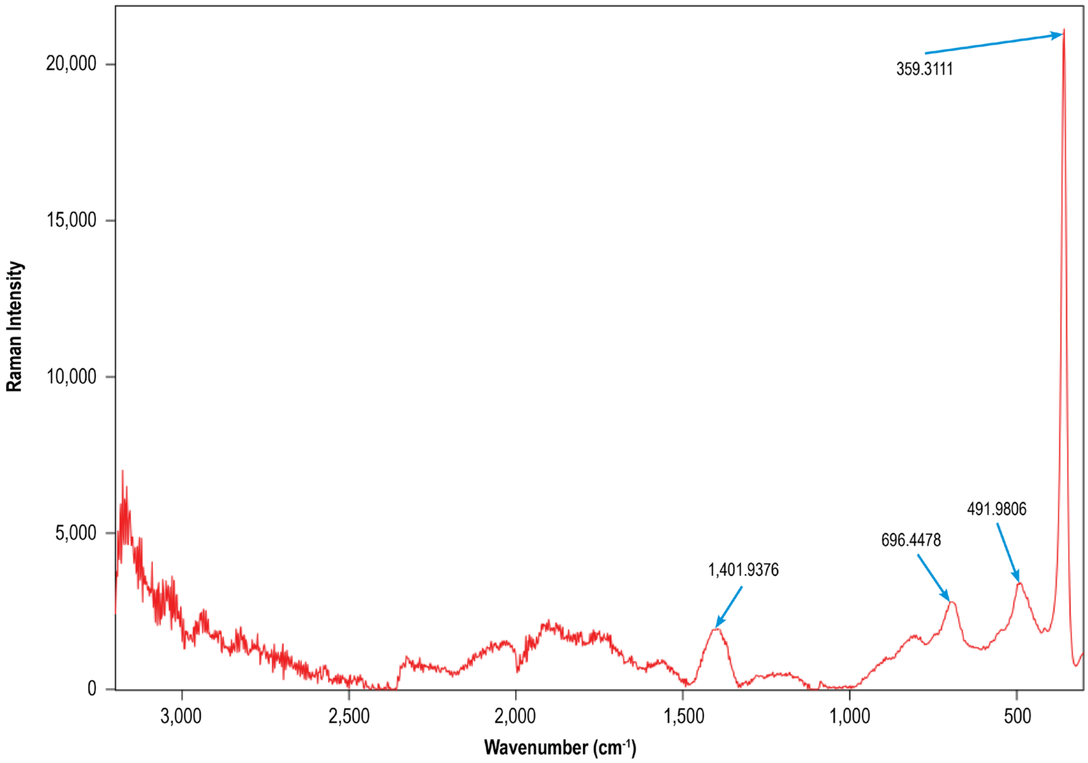
Figure 39. Spectrum. Raman spectrum of calcium carbonate.



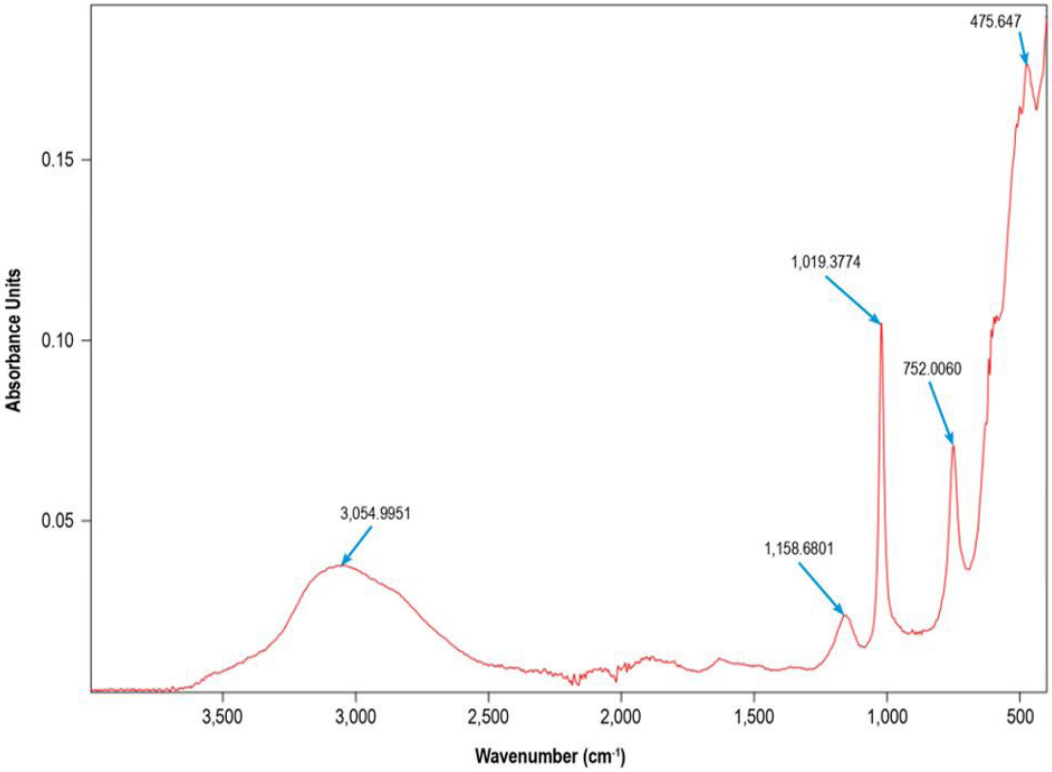
Source: FHWA.

Figure 40. Spectrum. Raman spectrum of lime.



Source: FHWA.

Figure 41. Spectrum. Raman spectrum of a rust phase lepidocrocite.



Source: FHWA.

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