Comparison of Portable FTIR Interface Technologies for the Analysis of Paints, Minerals & Concrete

Application Note

Materials research and development

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Introduction

Fourier transform infrared (FTIR) spectroscopy is a well-established and powerful instrumental technique providing detailed spectra of a wide variety of samples. Even though FTIR is a mature technology, the best fit-for-purpose sampling interface can be often overlooked simply due to previous experiences and the ease of use of attenuated total reflectance (ATR).

Traditional benchtop FTIR measurement often requires some degree of sample preparation, moderate for transmission FTIR and often onerous for benchtop diffuse reflectance. In comparison, ATR FTIR measurements seem simple and quick.

Whilst ATR is a popular technique, it does have some drawbacks: Its short sampling depth means that spectral information is obtained only from the top few microns of the sample and the technique also requires intimate contact with the sample, meaning brittle and non-pliant samples may be damaged or break. ATR is really only suitable for flat, smooth, pliant samples.

An alternative to ATR measurements is diffuse reflectance. Agilent's 4300 hand-held FTIR instrument can be fitted with a range of different interchangeable interfaces, with a diffuse reflectance interface, a 45° specular reflectance interface and an ATR interface being three of the options. By simply changing the interface, the instrument can be used to study complex solids using multiple measurement modes.

The advantage of diffuse reflectance measurements is that they require no sample preparation requirements and are completely non-destructive to the sample. Diffuse reflectance spectra can be collected with or without direct contact with the sample surface. This is often requested for art and conservation projects where minimal contact is preferred. A diffuse spectra can in fact be collected with a 1-2 mm gap between the sample surface and the diffuse reflectance interface.

This study compares data obtained using three different FTIR measurement techniques: ATR, diffuse reflectance and specular reflectance (at 45°). Three different sample types: paint, geological samples and concrete were studied.

Experimental

An Agilent 4300 hand held FTIR (shown in Figure 1) was used for this study. It was fitted with one of three different interchangeable interfaces: an ATR interface, a 45° specular reflectance interface, and a diffuse reflectance interface. Sixty-four scans per spectrum were collected with each interface, using a resolution of 4 cm^{-1}. Each spectrum was acquired in under 40 seconds.

Figure 1. The Agilent 4300 hand held FTIR instrument, with the three interchangeable interfaces used in this study.

Three different sample materials were measured:

I. A dry modern white paint containing both inorganic (mainly pigment) and organic components (mainly binder),

II. A silicate based rock – 11 different locations on the surface of the rock were measured

III. Ordinary Portland cement based concrete, after a 60 day cure. It was made using a CEM I type binder with the requisite aggregate and admixture composition, resulting in a concrete with a minimum 30 day strength class of 42.5 N [5].

Results and Discussion

Analysis of paint with FTIR ATR & External Reflectance

Spectra of 14 different formulations of white acrylic paint on a cement fibre board substrate were collected with the ATR, 45° specular reflectance and diffuse reflectance sampling interfaces. The 14 formulations cover a wide price range, with varying quantities and types of additives and fillers in each formulation. The resultant spectra are shown in Figure 2. Only the diffuse reflectance spectrum contained enough detail to allow the discrimination of the different paint formulations [1]. The ATR spectrum (shown in red) did not contain enough detail to be used for this purpose.

Also shown in Figure 2 is the peak associated with the carbonate filler (at ~2500 cm^{-1}). This appears in the two external reflectance spectra, but is missing from the ATR spectrum.

During the measurements, the ATR technique required consistent sample contact for best results. This left a permanent depression in the paint samples. A high spectra-to-spectra variance was also observed across the ATR spectra.

Conversely, both the specular 45° reflectance and the diffuse reflectance measurements required a simple "point and shoot" method to be used. They could be used without applying force onto the sample, thereby enabling longer scan periods resulting in error-free data collection and preventing any damage to the sample surface. The spectra from the two external reflectance techniques were also highly reproducible, with minimal user-induced variance. A more detailed study describes the use of diffuse spectra to differentiate between coating formulations that differ only in additives and fillers [1].

As shown in Figure 2, there are many differences between the spectra collected with the different interfaces. The spectra have not been re-scaled or manipulated and it is obvious that the diffuse spectrum contains the most spectral information, followed closely by the 45° specular reflectance interface. The ATR spectrum contains the least detail.

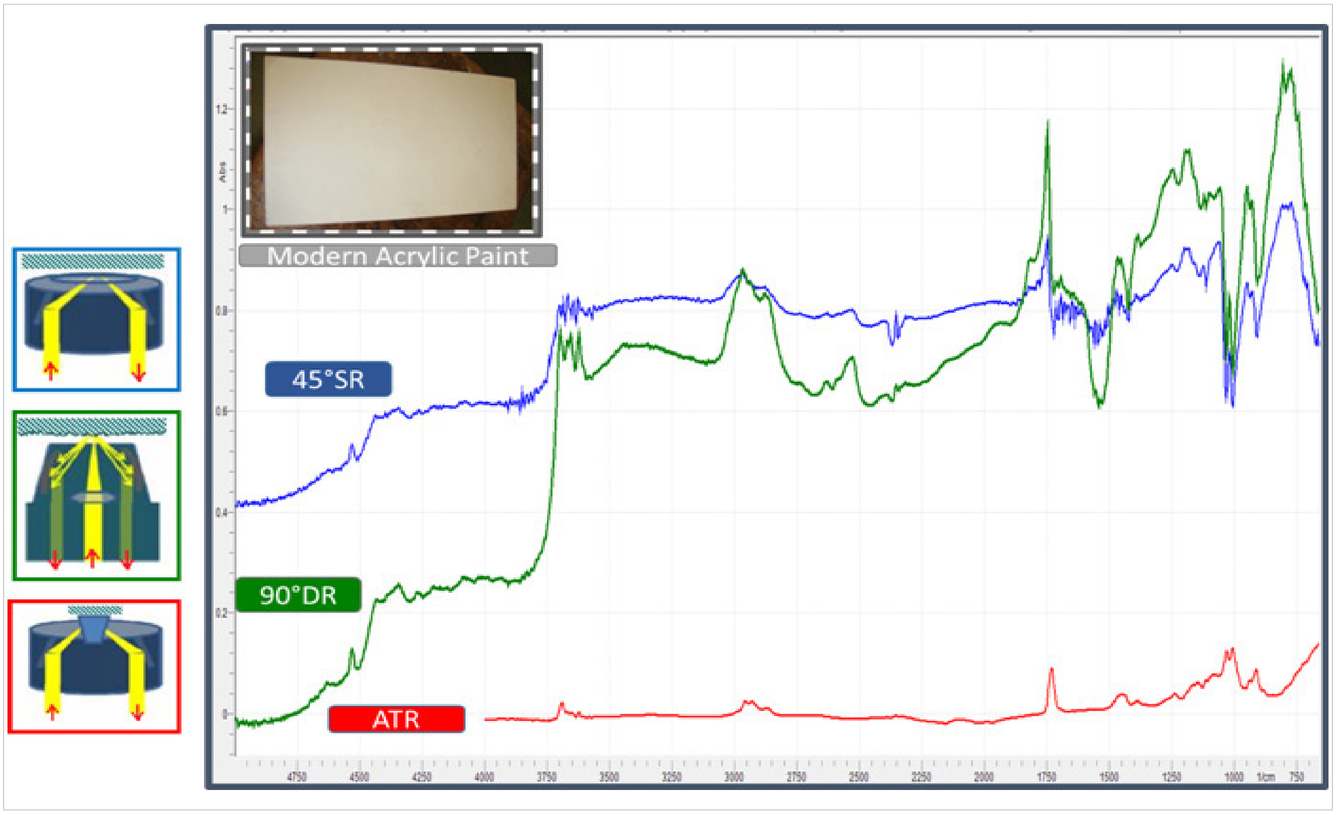

Figure 2. Spectra of a modern acrylic white paint collected by ATR (red), diffuse reflectance (green) and 45° specular reflectance (blue) interface FTIR measurement techniques. The left side bar illustrates the IR beam path of each interface type with color-coded box (red-ATR, green-diffuse reflectance & blue-45° specular reflectance)

The changes to paint that are induced by accelerated weathering has been studied non-destructively and in depth [2]. These changes are complex and the Agilent FTIR diffuse interface technique enables the same sample to be examined at intervals over the course of the ageing chamber regime. The portability of the instrument also potentially allows real-time studies of paint weathering. The more common ATR technique could be used but the requirement for surface contact could damage the sample, especially during the critical brittle failure stage of the coating's lifecycle.

Non-destructive FTIR analysis of geological samples

The sample three measurement techniques were also used to measure a geological monolithic silica based ore rock fragment, with the resultant spectra shown in Figure 3.

The ATR and specular reflectance techniques were unable to produce meaningful spectra. ATR failed due to the uneven surface of the rock sample. The rock sample had only a few point contacts for the ATR diamond, which was insufficient to collect meaningful data. An alternative would have been pulverisation of the rock prior to ATR measurements, but that would be expensive, time consuming and would have destroyed the sample. The 45° specular reflectance measurements failed due to the low reflectivity of the rock sample, which did not produce enough signal to be successfully measured by the instrument's detector.

As shown in Figure 3, the diffuse reflectance measurements of the rock sample were successful. The spectra show the primarily silicate nature of the mineral rock sample, with the peaks between 950 cm^{-1} to 1300 cm^{-1}. This is easily distinguishable from the smaller carbonate feature at 2500 cm^{-1}. There also detailed hydroxyl and resonant bands between 3,000 cm-1 – 4750 cm^{-1}.

The diffuse reflectance measurements required no sample preparation. All data was collected with an easy point and shoot manner using a Microlab PC method.

All eleven diffuse reflectance spectra of the rock sample were collected in under 10 minutes using standard instrumental conditions. Each spectrum was taken at a different location on the silicate-based rock sample. This provides information about the variation of the mineral

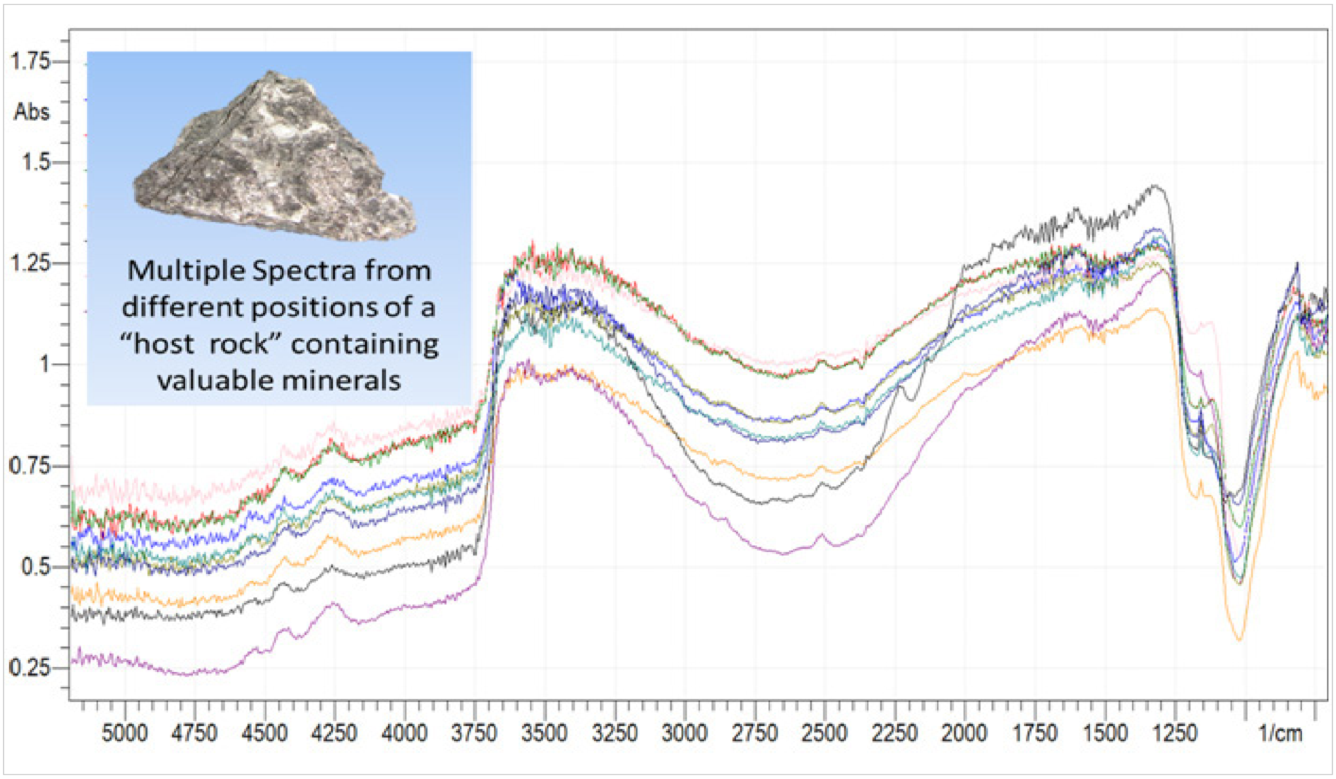

Figure 3. Diffuse reflectance spectra collected at 11 different locations on the surface of a geological monolithic ore rock fragment. Spectra were collected using an Agilent 4300 hand-held FTIR in conjunction with the diffuse reflectance interface option.

content across the rock's surface. The horizontal baseline shift is a result of the reflectivity differences across the sample, whereas the position of the peaks are directly related to the composition. The uneven, dull surface of the rock sample is ideal for diffuse reflectance measurements and incident light is widely scattered.

Hand held FTIR analysis of cured concrete

Modern concrete is by far the most commonly used construction material in the world today. It is available in a variety of grades and types, according to the presence or absence of specific additives, fillers and pozzolanic cement formulation used (the latter acts as the binder for the composite mixture). Handheld FTIR with a diffuse reflectance interface has successfully used for the non-destructive analysis of a geopolymer cement previously, effectively monitoring changes in composition and chemistry during cure [3].

The 4300 FTIR can also be used to differentiate between concrete blend types. It can even monitor the changes of these blends as a function of thermally induced chemical and physical changes and can correlate this to strength loss.

In this study, a concrete sample, cured for 60 days, was analyzed. The concrete consisted of a a composite mixture of a pozzolanic binder material and aggregates. After the addition of water, it cured to be a cross-networked solid structure interlocked with aggregates of various sizes. The complex pozzolanic cement reacts in an irreversible reaction with water forming a man-made rock. Modern concrete includes additives and aggregates, added to create various grades and types of concrete to suit specific building or engineering requirements [4].

The concrete's binder type was a CEM I type with the requisite aggregate and admixture composition resulting in a concrete with a 30 day strength class of 42.5 N [5].

We found that ATR measurements of the cured concrete sample were only possible if the sample was ground into a powder. This resulted in destruction of the sample, dilution of the concrete components and thermally induced changes. Measurements with the 45° external specular reflectance technique were not possible due to the very low reflectivity of the concrete sample.

To allow comparison of data collected with an ATR interface versus the diffuse reflectance interface, a sample of powdered concrete was measured with both. Figure 4 shows the resultant spectra. The diffuse reflectance spectrum was collected from the sample by simply pointing and shooting at the powdered sample. Collecting the ATR spectrum required drilling and subsequent ball-mill pulverisation of the drill

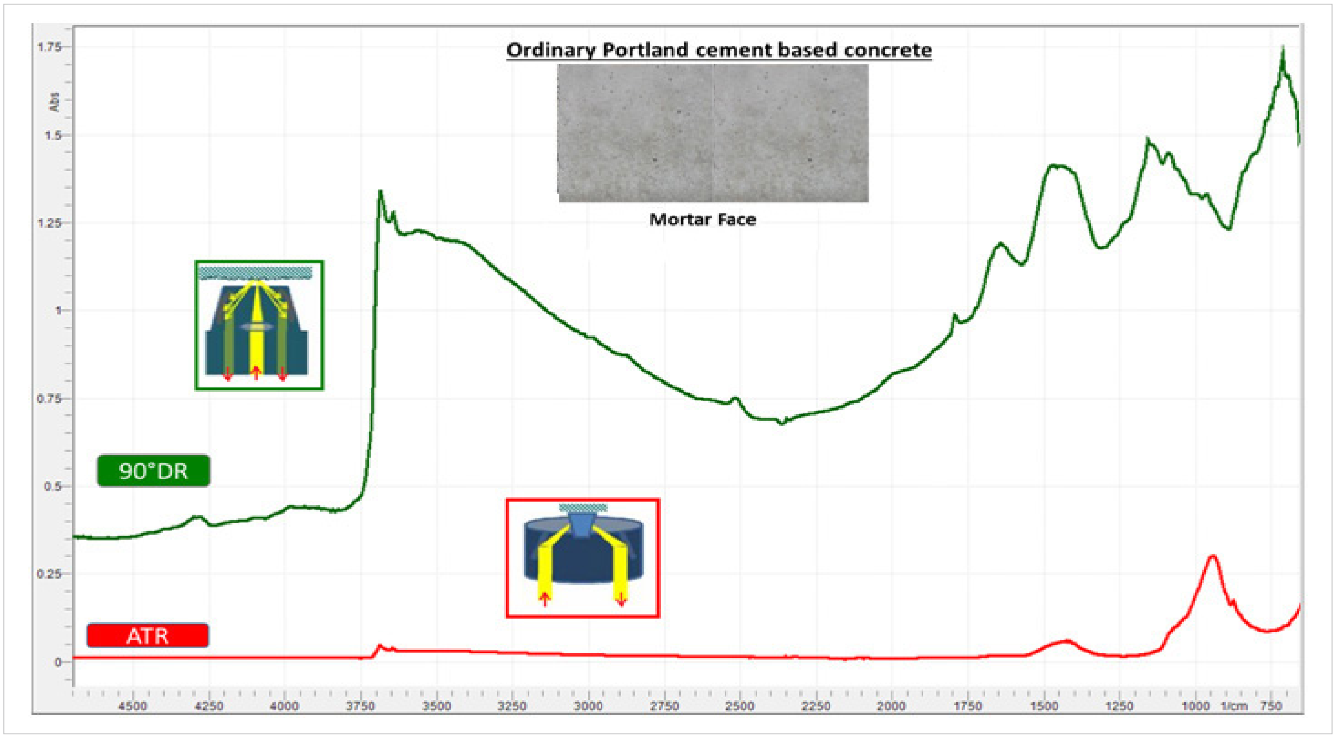

Figure 3. ATR spectra (red) of the powdered concrete and Diffuse Reflectance Spectra (green) of the mortar face of a concrete sample without any sample preparation.

debris semi-powder sample to achieve a particle size that would enable adequate intimate contact with the diamond ATR element. As shown in the figure, the diffuse reflectance spectrum contains more spectral information than the ATR spectrum. This is despite ATR measurements being the standard technique used for such analysis. The polished cross-section of the concrete samples shows visible aggregates as well as mortar (cured cement). The ingredient list of the concrete mixture is shown in Table 1.

Table 1. The material composition of the concrete block. By convention the 10/20 & 4/10 are called coarse aggregates and the 0/4 and 0/0.6 are termed the fines.

Ordinary Portland Cement (kg/m³)	**Water (mL)**	**Aggregates—coarse & fines (mm)**				**Ad-mixture (mL)**
		Sieved & sized Gabbro Rock (kg/m³)			Dune sand (kg/m³)	
		10/20	4/10	0/4	0/0.6	
380	152	702	378	630	297	2.66

A polished cross section contains mortar that acts as a binder for the aggregate fillers. The coarse fillers help bulk out and form a 3-dimensional network linked by cured cement, whilst the fines are designed to be void fillers. The aggregates are immutable in that during the cure they do not change at all, unlike the water, cement and ad-mixture which change markedly upon cure. The spectra of the light grey areas of the polished concrete are similar to those shown in Figure 4. Spectra of the aggregates and the dune sand show some marked differences due to their chemical and physical composition. The three sizes of gabbro aggregates were found on the polished section and their average spectra are shown in Figure 5, along with the dune sand. The collected reference dune sand spectra was not found in isolation on the polished cross section.

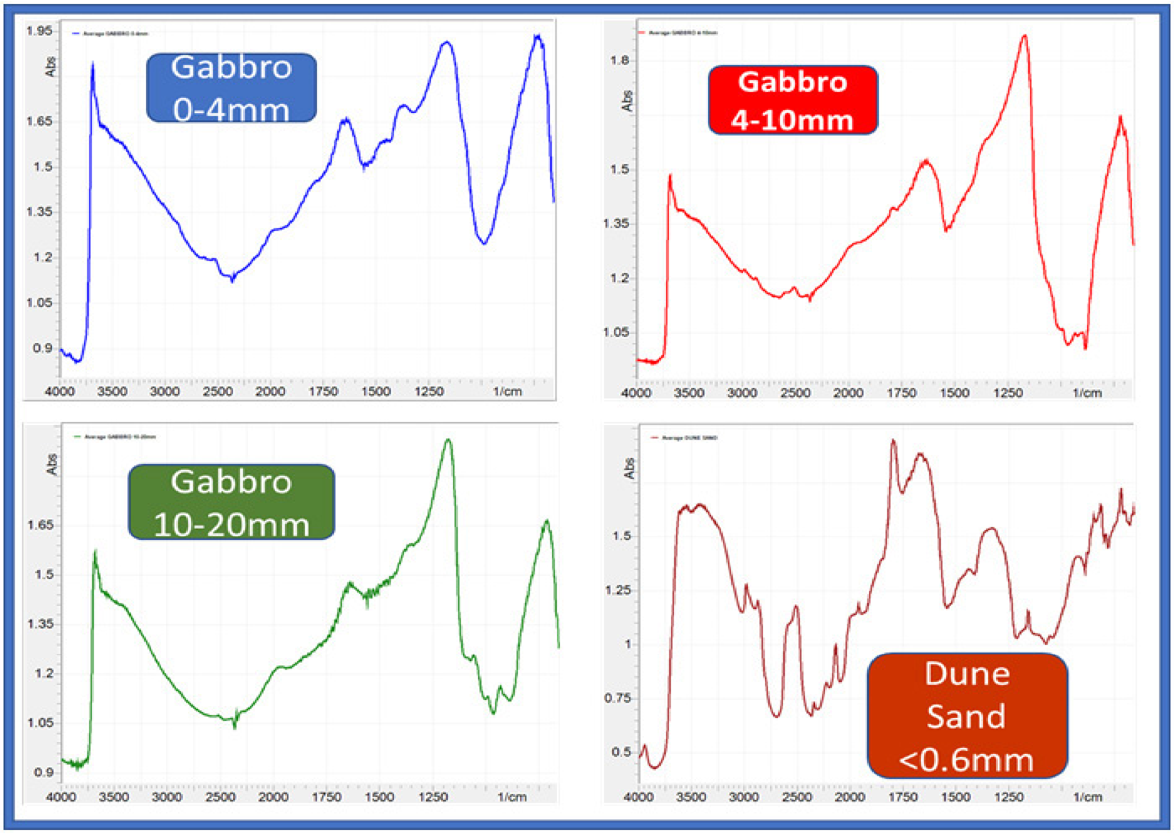

Figure 5. Diffuse FTIR spectra of the three different sized gabbro aggregates and the dune sand, all contained within a polished concrete sample.

Quantification of the thermally induced chemical and physical changes in concrete

In a separate set of measurements, diffuse reflectance spectra from 5 uncrushed/non-drilled concrete blocks were collected before and after thermal treatment. Non-destructive measurements were collected using the hand-held 4300 FTIR fitted with the diffuse reflectance interface option. Importantly, the measurements were done with no sample preparation or pre-treatment. The instrument was simply pointed at the face of the solid concrete samples.

Five concrete samples were created to investigate the changes that occur in the FTIR mid-infrared region. Each sample was cured for a full 60 days prior to being thermally treated at either 150 °C, 300 °C. 600 °C or 900 °C (one sample at each temperature). One of the samples was left untreated as a control. Full details of the study are available [4].

The diffuse reflectance spectra from the uncrushed concrete samples, collected after thermal treatment, are shown in Figure 6.

There are three notable changes shown in the spectra: First, the multiple peaks at 3600 cm^{-1} become one single peak after treatment at higher temperatures. Second, changes related to the carbonate in the sample can be seen to initially increase before complete removal at the highest temperature at 2500 cm^{-1}. This is in agreement with the decomposition temperature of calcium carbonate of ~840 °C. Thirdly, there are several structural changes related to the silicates and their forms, as evidenced by the shape changes in the fingerprint region ~1050-1300 cm^{-1} as well as region from 3,000-3750 cm^{-1}.

As the temperature changed, major differences in the spectra can be seen in the non-hydrogen bonded hydroxyl (~3600 cm^{-1} – several peaks), hydrogen bonded hydroxyl (3,000-3,400 cm^{-1}), carbonate (~2500 cm^{-1} & ~1750 cm^{-1}) and the reststrahlen inverted silicate regions (~1050-1300 cm^{-1}). These diffuse reflectance spectra correlate with TGA (thermal gravimetric analysis) and the thermograms are shown in the right. Note that the gabbro base aggregate fillers were highly carbonated with $CaCO_3$.

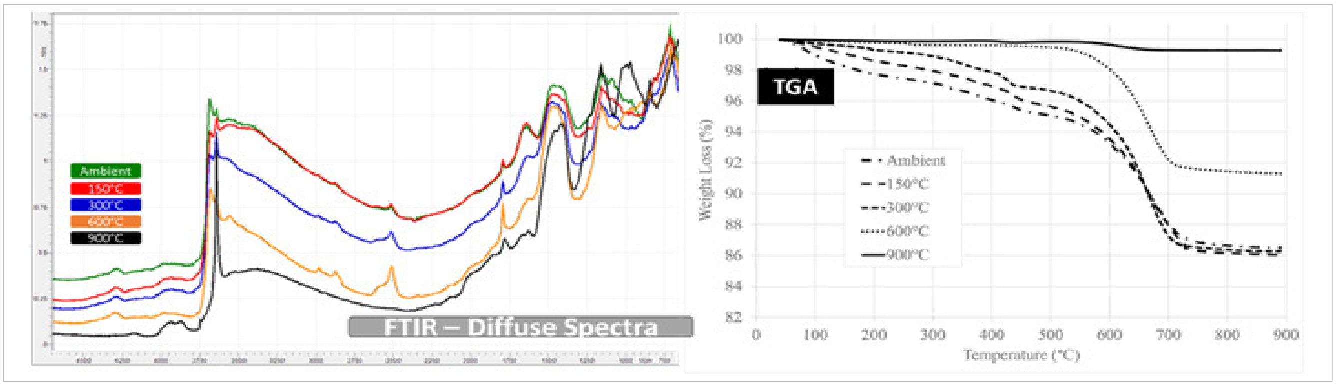

Figure 6. Left – diffuse spectra changes in a CEM I type concrete with gabbro rock aggregates at a variety of thermal treatments. Right the corresponding mass loss events for each concrete block post-thermal treatment.

Conclusion

The measurement of three different complex solids, using ATR, diffuse reflectance and specular reflectance measurement techniques revealed many differences in the data collection process and the resultant data:

- The Diffuse reflectance technique provided greater detail, higher repeatability and more in-depth information and sample penetration than ATR.
- Diffuse data collection was less prone to user error as there was no requirement for force against the sample surface.
- Thermal changes of a highly complex cement/aggregate network composite with thermal treatment revealed many measurable or quantifiable as well as identifiable changes that correspond directly with mass change events that could be elucidated without harming the sample in any way.

Contrary to popular belief and perception, the ATR technique performed poorly compared to the external reflectance techniques. The Agilent 4300 hand held FTIR instrument can be fitted with interchangeable interfaces, allowing the user to quickly change the measurement technique used. Diffuse Reflectance spectra can be collected with the instrument in-situ and without destruction of the sample and were found to have distinct advantages for paint, rocks and concrete studied here.

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