Application Note AN M138

Quality Control of Raw Materials and Formulations in Construction Industry

Introduction

Modern construction materials are products which have been optimized to fulfill demanding requirements. A wide range of admixtures is used in concrete to allow reduced construction times and to obtain a better mechanical durability of buildings, bridges, tunnels, road surfaces and so forth. Such admixtures are often organic substances which are added to the basic cement and aggregate in order to improve certain properties of the final building material. As an example polycarboxylate ethers (PCE) serve as superplasticizers that enhance the dispersion properties of the concrete suspension. Another substance class are siloxanes which are used in concrete to increase water repellence and suppress efflorescence. In certain types of concrete like asphalt concrete and polymer concrete the cementing material is completely polymeric.

Chemical Analysis of Building Materials

To control the quality of the basic inorganic construction materials like Portland cement, gypsum and limestone X-ray fluorescence (XRF) is an established and powerful analytical method. It determines the exact elemental composition of such oxides, sulfates and carbonates. As the chemical and physical properties of the building materials are mainly defined by their phase composition XRF increasingly is complemented by X-ray diffraction (XRD).

Keywords	Instrumentation and software
Building materials	ALPHA II FT-IR spectrometer
Admixtures	Platinum-ATR
Construction chemicals	OPUS spectroscopic software
Quality control	Spectrum comparison
Reverse engineering	Mixture analysis

However, the XRF/XRD techniques are not suitable for the analysis of the organic admixtures and cements. To verify the correct chemical identity of any organic raw material and also to control the chemical composition of complex formulations Fourier-Transform Infrared Spectroscopy (FT-IR) is the method of choice.

FT-IR is an established analytical method that is applied in various industries to address different questions in quality control. The IR-spectrum of a sample reflects its chemical composition – just like a chemical fingerprint (figure 1). Organic and also most inorganic components contribute to the sample spectrum. Therefore the IR-method is very well suited to identify both, pure substances and complex materials. Furthermore, it allows to quantify individual components of the analyzed material.

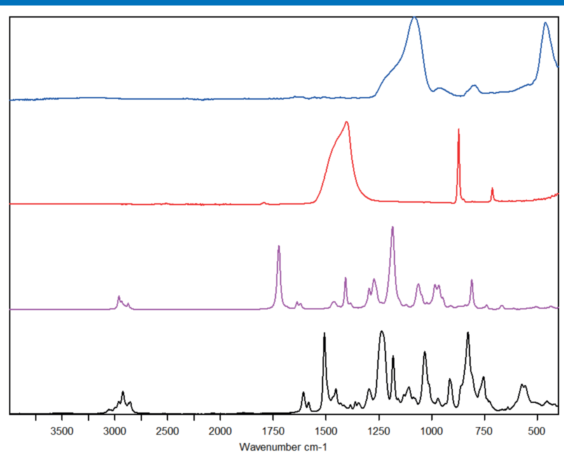


Figure 1: The IR-spectrum of a sample reveals its chemical composition – like a chemical fingerprint. Blue: silicate, red: calcium carbonate, pink: monomeric acrylate, black: epoxy resin.

Accordingly, identity and quality of the incoming raw materials used for construction materials can be tested using the FT-IR method. Moreover, the control of qualitative and quantitative quality parameters of the final formulation is possible. IR-spectroscopy also is a valuable analytical tool in product development and failure analysis as it allows to identify unknown material. By means of spectral databases the composition of a defective material or a competitive product can be determined from its IR-spectrum.

Instrumentation and Method

The compact ALPHA II FT-IR spectrometer (figure 2 top) from Bruker is the right instrument for incoming goods inspection, quality control, and product development. The measurement is performed using the Attenuated Total Reflectance (ATR) technique which is applied in an extremely comfortable and quick manner. The spectrum of any substance can be measured in seconds without any sample preparation, reagents, or consumables.

To record the IR-spectrum the sample just has to be brought into contact with the measurement element, the ATR-crystal (figure 2 below). As ATR-crystal a monolithic diamond with the dimensions of 1.5 mm x 1.5 mm is used, that is fixed in WC hard metal. The mechanical and chemical robustness of these materials guarantees a wide compatibility with samples of various kind. Due to the small dimensions of the measurement element only very little sample amounts are needed. The spectrum of a substance is measured within seconds and allows e.g. to control the quality of an incoming raw material or to analyze the composition of a competition product.

Figure 2: Left: ALPHA II FT-IR spectrometer with ATR-measurement module. Right: Principle of the ATR-measurement technique. The infrared light is guided through the diamond ATR-crystal. For measuring the IR-spectrum any liquid or solid sample just has to be brought into contact with the ATR-crystal.

Verification of Incoming Raw Materials and Formulations

To assure the quality of construction materials the use of wrong or qualitatively insufficient raw materials has to be prevented. By performing an incoming goods control using the IR-method the mix-up of materials; e.g. due to wrongly labelled packaging is avoided. Furthermore unwanted variation in the quality and composition of formulations is recognized. To verify the identity of a raw material its IR-spectrum is compared against spectra of one or several reference samples; e.g. other batches of the same material which proved to be of the required quality. Such spectra comparison is performed automatically by the used analytical software, directly after the measurement.
The example in figure 3 shows the quality control of a methyl cellulose ether. This substance class is used in cement based building materials as thickeners, binders, film formers and water-retention agents.

The correct identity and composition of the incoming raw material Hydroxypropyl methyl cellulose (HPMC) is verified by comparison of its spectrum (blue) with a previously measured spectrum of a reference batch (red). A correlation value of 99.9% indicates that the sample spectrum is in very good agreement with the reference spectrum. As the correlation of the reference and sample spectrum is above the predefined threshold value of 99% the sample is rated with an „OK“.

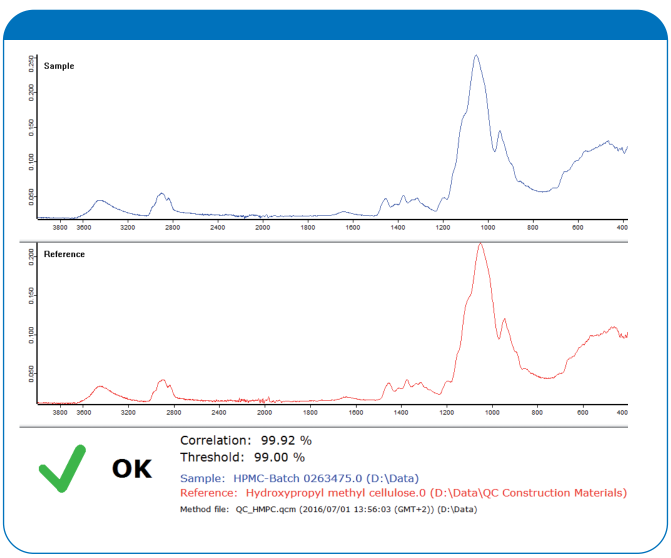


Figure 3: Incoming goods control: The result of the spectra comparison of the thickener HPMC (blue) against an according reference spectrum (red) verifies the correct identity of the material.

Quantification of a Thermoplastic Polyolefin (TPO) in a Bitumen / Limestone Formulation

Thermoplastic olefin (TPO) resins are used in building and construction e.g. for bitumen modification. In the shown example the content of a TPO in a formulation of bitumen with limestone was quantified by IR-measurement. Double measurements of each sample were performed to verify the reproducibility of the analysis. Figure 4 top, shows the spectra of defined bitumen / limestone / TPO mixtures and the reference spectrum of the used TPO. By integrating the area underneath a selected band which is specific for the TPO a calibration was generated (figure 5, down). By applying this calibration the IR-method allows to determine the amount of added TPO in unknown samples within less than a minute.

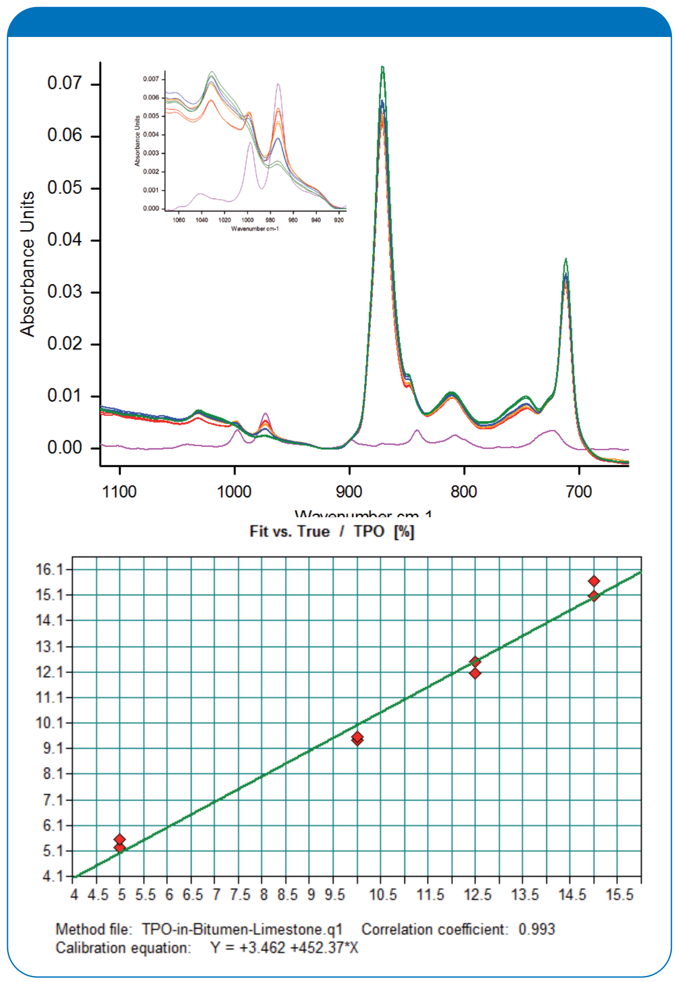


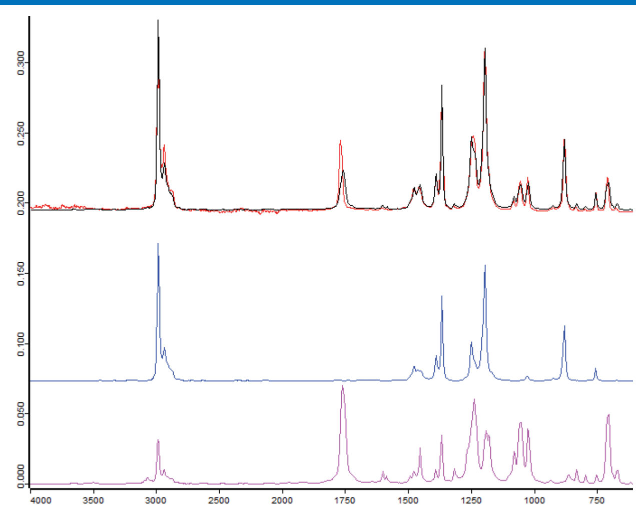
Figure 4, top: Spectra of bitumen / limestone / TPO mixtures with 5% (green), 10% (blue), 12.5% (orange) and 15% (red) TPO content. By integrating a spectral band at 973 cm^{-1} that is specific for the TPO (pure substance spectrum in pink) a linear calibration can be set up (below).

Reverse Engineering of Admixture Formulations

The analysis of competitive products can stimulate the development of own products and can help to identify patent infringement. For the identification of unknown materials, the spectrum search in reference libraries is used. The analytical software also contains a mixture analysis function for the identification of single components in complex mixtures.

Our example shows the analysis of a liquid formulation with unknown composition, which is used to initiate the polymerization process of polyester resins for synthetic marble and concrete. A drop of the liquid was placed on the diamond crystal of the ATR unit and measured. Then, the spectrum was searched in a spectral library by applying the mixture algorithm.

Figure 5 shows the result of the mixture analysis: The composite spectrum (shown in black), which is calculated from the identified single component spectra, is in a very good agreement with the measured query spectrum (red). The two identified components are di-tert-butylperoxide (blue), contributing with about 81% to the sample spectrum and tert-butyl perbenzoate (pink) that accounts for the remaining 19%.



		Color	Content [%]	Compound Name	CAS number	Molecular formula	Molecular weight
1	☑		81.4	DI-TERT-BUTYL PEROXIDE	33324-93-5	C8H18O2	146.23
2	☑		18.6	TERT-BUTYL PERBENZOATE	614-45-9	C11H14O3	194.23

Figure 5: Result of the mixture analysis of an unknown liquid formulation for preparing a polymeric resin. The composite spectrum (black) calculated from the identified components (blue and pink) shows an almost perfect match with the sample spectrum (red).

Summary

In QC/QA of modern construction materials FT-IR spectroscopy greatly complements the established XRF and XRD methods. The IR-technique allows to verify the chemical identity of organic and polymeric admixtures for incoming goods control. Furthermore checking the correct composition and even quantification of individual components in formulations and final products can be performed.

The Bruker ALPHA II FT-IR spectrometer is a compact and very easy to use system for performing routine analyses of all kinds of liquid and solid materials. A software guided workflow and intuitive hardware design allows even untrained users to work with the system after a few minutes introduction.

By means of reference spectra databases the ALPHA II can also be applied to identify unknown materials. This feature makes the system a valuable tool in product development and troubleshooting, e.g. for reverse engineering and failure analysis.

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