Application Note AN-RS-004

Raman spectroscopy analyses of road construction materials

Various solid materials used in road construction were analyzed using a handheld Raman spectrometer. The investigated materials are commonly used pigments and resins such as $CaCO_3$, TiO_2, and DEGALAN®. The measured spectra differed remarkably from each other. To evaluate the main differences in the chemical structures, the peaks of the different spectra were assigned to the functional groups causing them.

INTRODUCTION

Different materials such as paints, (white) pigments, and resins are commonly used in the construction of roads. Together with glass beads (used for night-visible road marking) and various other materials, they help us to get safely from A to B.

In this study, different roadmaking materials were analyzed using the Mira M-1 handheld Raman analyzer. The gathered spectra were compared with each other to see the main differences in the functional groups. The analysis proved that Mira M-1 is suited for the differentiation of such materials.

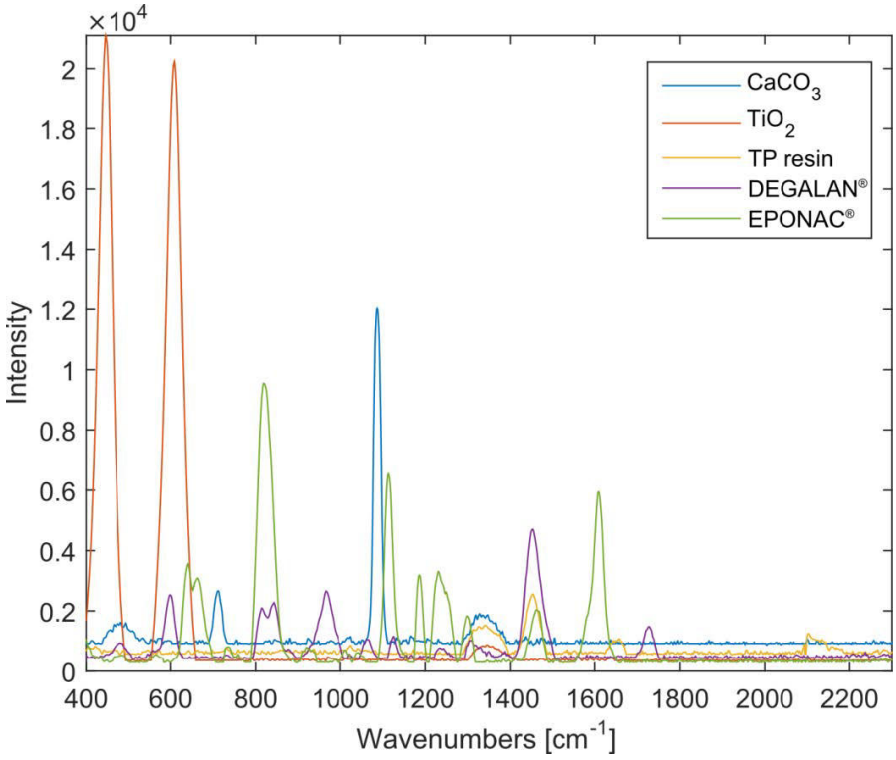

Figure 1. Overlay of spectra of different roadmaking materials

EXPERIMENTAL

All spectra were measured using the Mira M-1 Raman spectrometer in auto-acquisition mode, i.e., integration times were determined automatically. A laser wavelength of 785 nm and the Orbital-Raster-Scan (ORS) technique were applied. The measurements were done in small sample vials with the vial holder adapter.

The following samples were investigated:

1. Chalk ($CaCO_3$)
2. Titanium dioxide (TiO_2)
3. EPONAC® resin
4. TP resin
5. Pigment yellow
6. Pigment blue
7. Pgiment red
8. DEGALAN® resin

RESULTS AND DISCUSSION

The measurement of calcium carbonate furnished a clear spectrum with two main peaks at 712 cm^{-1} (symmetric O–C–O bending vibration) and 1087 cm^{-1} (symmetric stretching vibration).

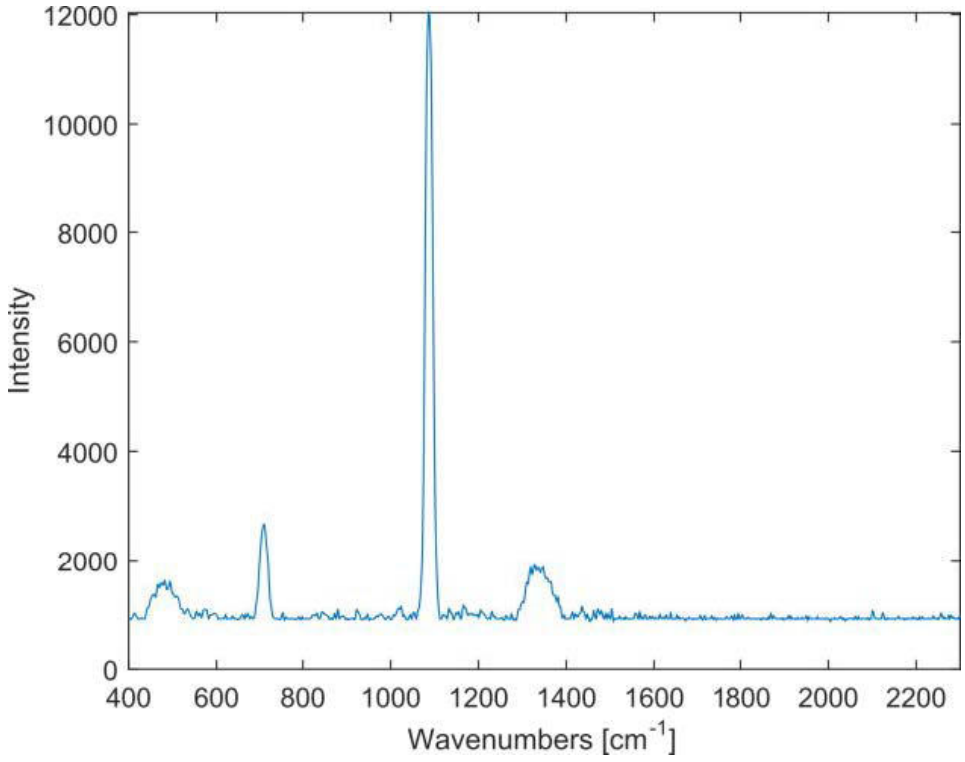

Figure 2. Spectrum of calcium carbonate.

Looking at the titanium dioxide spectrum, one can see two main peaks which give information on the present crystal modification (rutile or anatase). Two peaks represent rutile, while three peaks are typical for anatase because of its crystal symmetry.

Both peaks are symmetric stretching vibrations and belong to O–Ti–O (446 cm^{-1}) and Ti–O (609 cm^{-1}). In the case of anatase, the peak at 446 cm^{-1} is split in two. This makes it easy to differentiate between rutile and anatase.

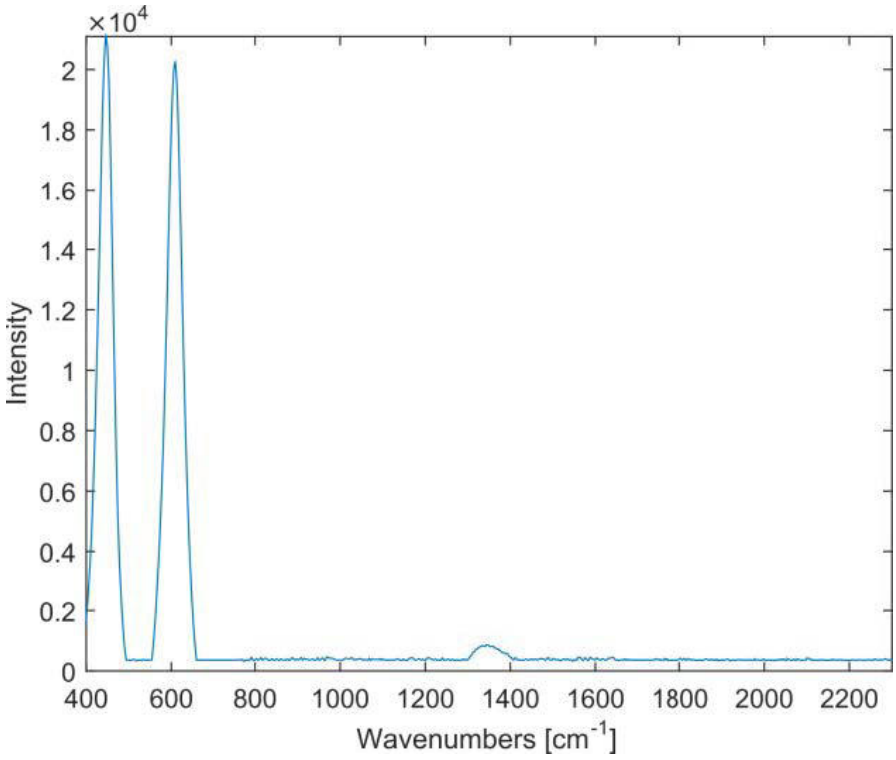

Figure 3. Spectrum of TiO2 (rutile).

A glance at the spectra of typical resins such as EPONAC® or DEGALAN® reveals nicely separated peaks which can be assigned to their corresponding functional groups (see below).

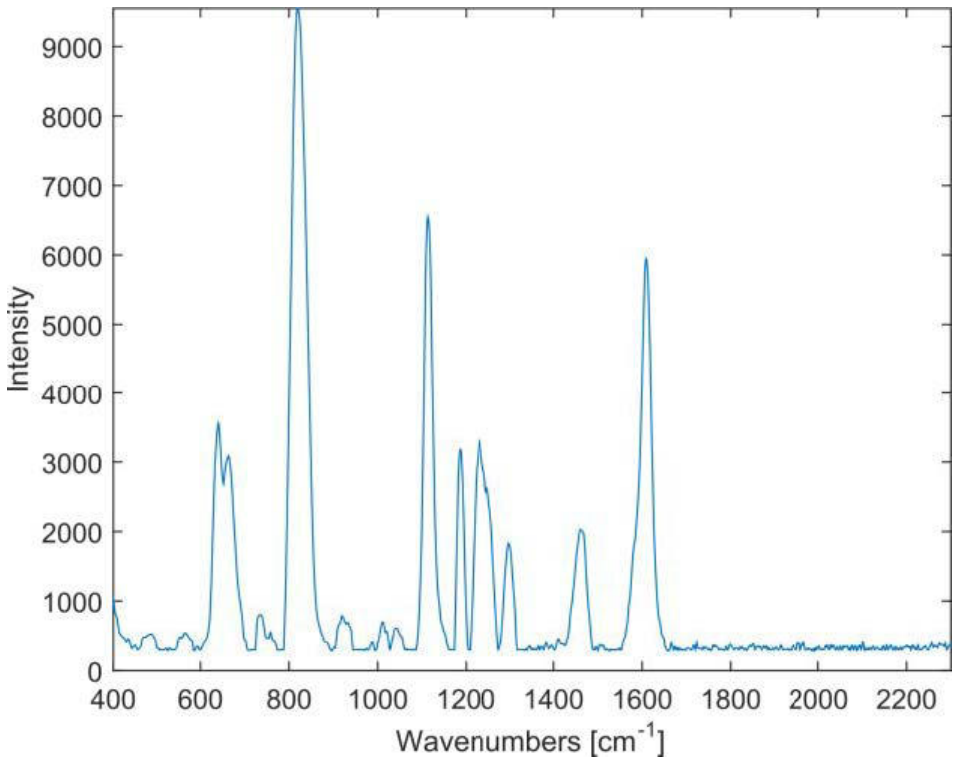

Figure 4. Spectrum of the EPONAC® resin.

Table 1. Peaks observed in the EPONAC® spectrum.

Peak [cm^{-1}]	Description
640	Cyclic vibration (para-substituted benzene)
819	C–H bending vibration (para-substituted benzene)
1000	Various C–C stretching vibrations
1113	C–OH stretching vibration
1189	C–$(CH_3)_2$ stretching vibration
1231	C–O
1248	C–H (benzene)
1298	–CH_2– twisting vibration
1461	–CH_2– bending vibration
1609	C=C

The peaks are very characteristic for para-substituted benzene and confirm that EPONAC® is a copolymer of bisphenol A (BPA) and another component.

When comparing the EPONAC® spectrum with the DEGALAN® spectrum (see Figure 5), it is obvious that the peak of the benzene at 1600 cm^{-1} is missing. The peak around 1700 cm^{-1}, together with the peaks slightly below and above 1200 cm^{-1}, is characteristic for carbonyl groups. In addition to that, the C–C peaks are more distinct for EPONAC® than for DEGALAN®.

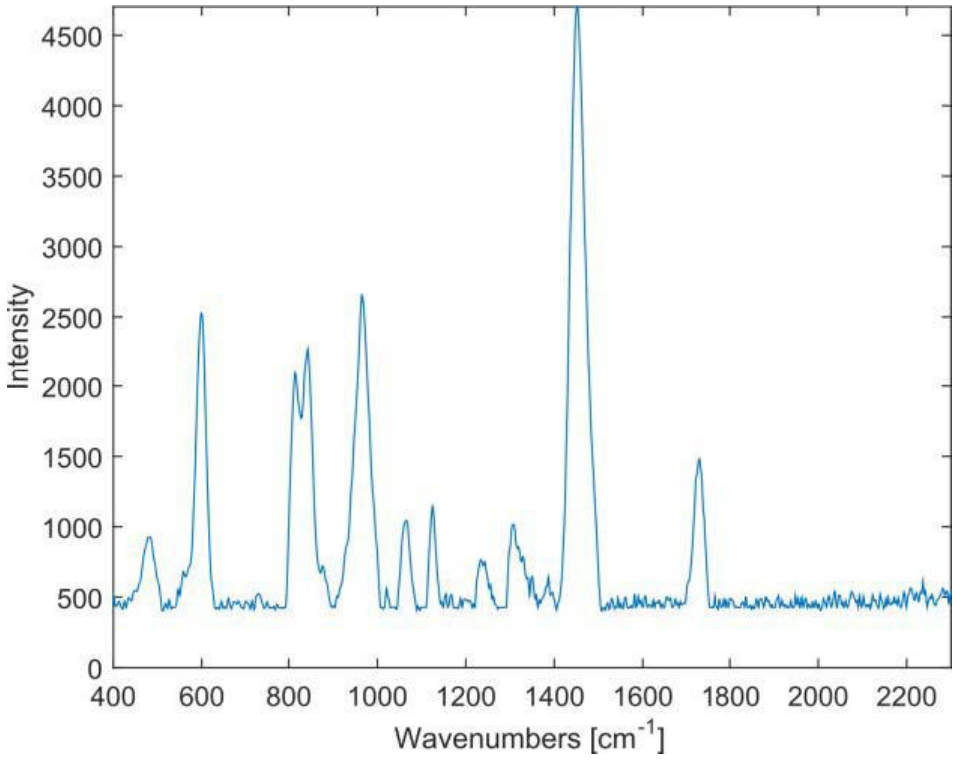

Figure 5. Spectrum of the DEGALAN® resin

Table 2. Peaks observed in the DEGALAN® spectrum.

Peak [cm^{-1}]	Description
599	–COO bending vibration
814	Propionate bending vibration
843	C–CH_3 stretching vibration
965	C–C stretching vibration
1065	C–COO stretching vibration
1125	C–O
1234	C–O
1308	–CH_2– twisting vibration
1452	–CH_2– bending vibration
1728	C=O carbonyl group, ester

Using these differences, it is easy to discriminate between the resins and also between resins and pigments (see Figure 6).

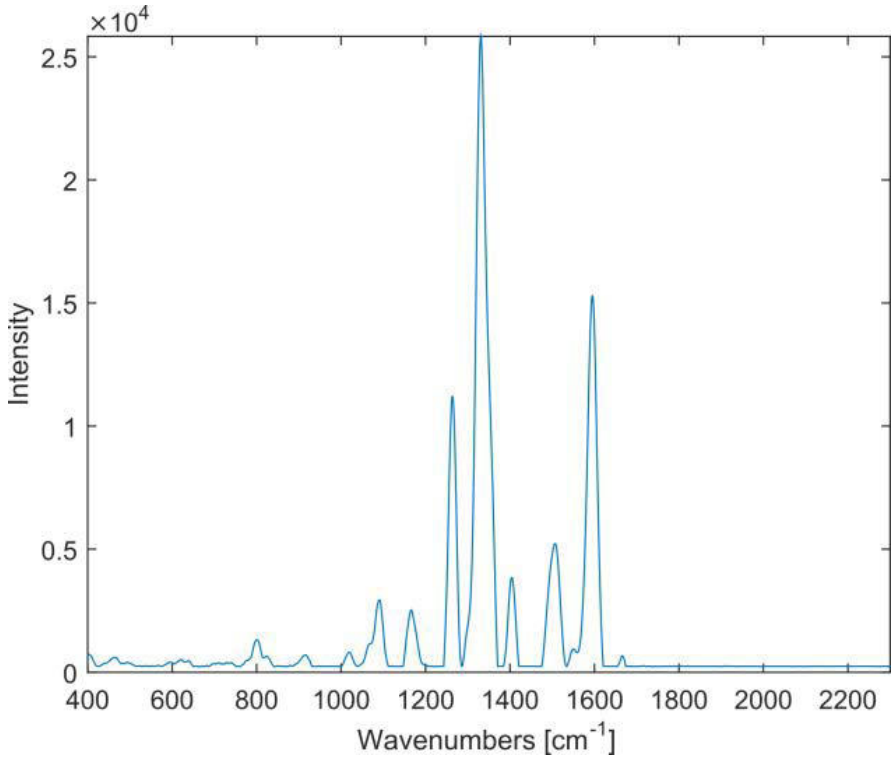

Figure 6. Spectrum of the yellow pigment «Hansa®-Brilliantgelb»

CONCLUSIONS

Because of the great differences in their spectra, handheld Raman spectroscopy is ideally suited for the analysis of materials used in road construction. The investigation of the spectra showed that there are significant differences in the functional groups of the materials, thus allowing the identification with handheld Raman systems such as Mira M-1.

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CONFIGURATION

MIRA P Advanced

The Metrohm Instant Raman Analyzer (MIRA) P is a high-performance, handheld Raman spectrometer used for rapid, nondestructive determination and verification of different material types, such as Pharmaceutical APIs and excipients. Despite the small size of the instrument, the MIRA P has a ruggedized design and features a high-efficiency spectrograph design equipped with our unique Orbital-Raster-Scan (ORS) technology. The MIRA P is fully compliant with FDA 21 CFR Part 11 regulations.

The Advanced Package includes an attachment lens for analyzing materials directly or through containers (laser class 3b), as well as a vial holder attachment for analyzing samples contained in glass vials (laser class 1).