



## FAST DETECTION OF PAH IN RECLAIMED ASPHALT USING FTIR-ATR SPECTROSCOPY

Jens Wetekam, Konrad Mollenhauer

*University of Kassel, Germany*

### Abstract

The presence of polycyclic aromatic hydrocarbons (PAH) in reclaimed asphalt (RA) is a problem for its recycling. Due to its carcinogenic compounds, which are released by vapors when heated, asphalt material with high PAH content is not recyclable in warm, or hot mix asphalt. For recycling purpose it is necessary to check the content of PAH in reclaimed asphalt. To determine this content time-consuming and costly investigations like thin layer chromatography or high-performance-liquid-chromatography are usually applied.

In order to identify an alternative method for PAH detection, 56 PAH-contaminated asphalt granulate samples with various PAH contents were measured via FTIR-ATR spectroscopy on recovered binders from the RA samples. Therefore, a cold recovery method was applied using toluene which allows to quickly recover the required small amount of binder. Additionally, the 16 PAH-EPA according to the list, which was compiled by the U.S. Environmental Protection Agency and classified as priority environmental pollutants, were measured by FTIR-ATR to compare them to the spectra of PAH-contaminated reclaimed asphalt.

To evaluate the IR-spectra, the peak areas, peak area ratios and peak height for different spectral areas in the range from 700 cm<sup>-1</sup> to 1200 cm<sup>-1</sup> were examined which made it possible to calculate index values, representing the proportion of PAH compounds.

*Keywords: ftir-atr spectroscopy, PAH detection, reclaimed asphalt, data analysis*

### 1 Introduction and Motivation

In Germany, more than 90 % of the reclaimed asphalt pavements (RAP) produced during road maintenance is reused in the production of new asphalt mix [1]. Due to this reuse, it is possible to lower the content of new materials by ~25 %, conserve natural resources, and provide the asphalt more economically. Before reusing the Asphalt granulate, it is necessary to perform some investigations and make sure that there are no harmful components inside the RAP material. One group of these harmful compounds are polycyclic aromatic hydrocarbons (PAH), which are contained in tar and can cause cancer. Until the 1980`s tar was used as a binder material for pavements, so it is and will be found in many existing flexible pavements during road maintenance and rehabilitation.

To avoid health danger to any person, which might be in contact with these materials, the recovered material from flexible pavements needs to be analysed prior to maintenance and rehabilitation works. Therefore, usually extensive examinations like thin layer chromatography or high-pressure liquid chromatography (HPLC) are performed. These extensive tests are time consuming, costly and a fast detection can't be performed directly at the asphalt plant, which demands for selected storing of material in question. To quickly determine the PAH-content, the fourier-transformation-infrared-spectroscopy (FTIR), especially combined

with attenuated total reflection (ATR) method, is a promising tool to further give additional information about the aging state or additives in the RAP material [2-6].

If it is possible to quickly characterise the RAP's harmful components with FTIR-ATR spectroscopy, it would be possible to use this information for the RAP management at asphalt mixing plants and use the material in an optimal way.

## 2 Methodology

In total 56 PAH-containing RAP materials which different PAH-contents in a range from 23 mg/kg to 8.000 mg/kg were selected from several road maintenance sites and investigated. Additionally, the 16 PAH-EPA according to the list, which was compiled by the U.S. Environmental Protection Agency and classified as priority environmental pollutants, were measured to compare them with the PAH-contaminated reclaimed asphalt.

### 2.1 Sample preparation and FTIR/ATR-measurement

For FTIR-tests only a small binder sample of 2 g has to be recovered from the RA material. Therefore, a representative sample is taken from the RAP source (for example a truck load) by selecting samples from various spots. By proper separation and homogenisation, a RAP sample of 40 g is required for recovery of the binder. The recovery of the binder was done by using Toluene at ambient temperature and separating the dissolved from the insoluble components in a centrifuge as to see in Figure 1, see also [7]. To measure the IR-Spectrum of the binder with the FTIR-ATR device, one drop of the prepared solution was placed directly onto the ATR diamond cristal. After complete evaporation of the solvent, the IR-spectrum from the binder sample was measured. For each RAP sample, one solution was prepared, from which seven sample drops were measured by FTIR-ATR.



**Figure 1** RAP sample: unsolved (left), solved in toluene (middle) and separation of binder and aggregate matter after centrifuge (right)

### 2.2 Data pre-processing

The results of the FTIR-ATR measurements are absorbance- or transmission- spectra, which both can be used for data evaluation, but for quantitative analysis the absorbance ones must be used [8]. The spectra represent the light absorbance intensities, which occur because of molecule-vibrations of the test sample at different wavelengths. To avoid atmospheric influences first, an atmospheric correction was applied, after these, a baseline correction was calculated. The last pre-processing method, which was done, is the vector normalisation.

This method makes spectra with different intensities more comparable and helps to develop an evaluation technology. Figure 2 shows an example of a transmission and the calculated and absorbance spectrum after pre-processing of a bitumen sample.

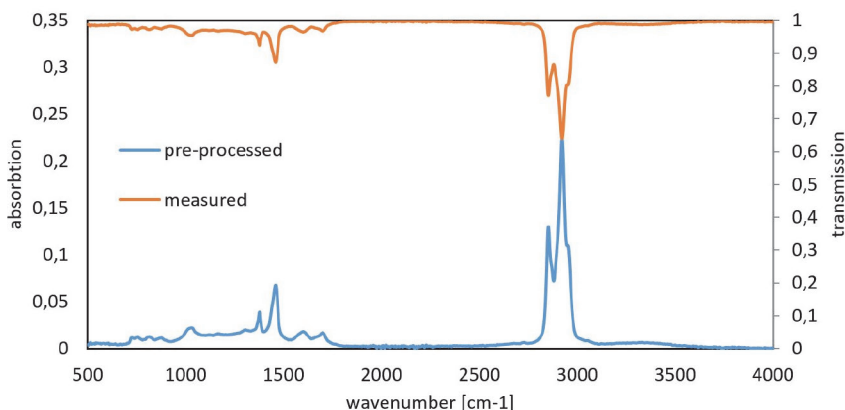


Figure 2 Measured and pre-processed spectra

### 3 Data evaluation

To extract the containing information out of the measured spectra data, different areas of the spectra need to be considered in detail. In order to find the relevant areas of the spectra, a closer look at the spectra with high PAH-content is important, see Figure 3. A first view at the whole spectra points out, that in the wavenumber area of  $3150\text{ cm}^{-1}$  to  $3500\text{ cm}^{-1}$  a wide peak is visible. Furthermore, in the area from  $1800\text{ cm}^{-1}$  to  $3100\text{ cm}^{-1}$  sharp peaks at wavenumbers of  $3050\text{ cm}^{-1}$  and  $1930\text{ cm}^{-1}$  can be seen. From wavenumber  $1800\text{ cm}^{-1}$  to  $600\text{ cm}^{-1}$  there are several sharp peaks detectable which can be evaluated. To identify the peaks that are different from bitumen-peaks and similar to PAH-peaks the measured data of all materials were considered. The main evaluation was done by considering the peak intensity, which means the amount of a specific molecule with in the whole sample.

#### 3.1 PAH and tar spectra

In Figure 3 the measured spectra of one tar-sample, one bitumen sample and naphthalene as an example for a pure PAH is plotted. In the area from  $600\text{ cm}^{-1}$  to  $1800\text{ cm}^{-1}$  many sharp peaks are visible in the spectra of PAH and tar sample, however not at the same wavenumbers. The naphthalene is just one sample, but the other PAH samples provide similar spectra with different sharp peaks at several varying wavenumbers within the same wavenumber range. The number of peaks within the bitumen sample in this area is considerably smaller.

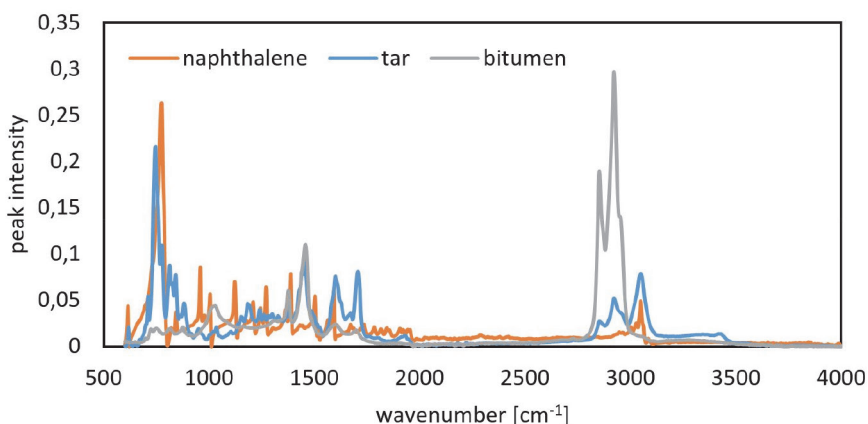


Figure 3 Spectra of naphthalene, bitumen and tar plotted against each other

### 3.2 Tar and binder spectra

To identify, if a binder sample contains PAH or not, tar and bitumen spectra were compared. All peaks of both spectra were investigated and a method was developed and applied at all other measured sample spectra. This method compares the peaks and intensities to the PAH-content within the samples. To identify the peaks in all spectra, even when they are slightly shifted, a wavenumber range was given and the peak will be found within these ranges automatically. As to see in Figure 4, the tar-spectrum has a higher number of specific peaks compared to the bitumen spectrum.

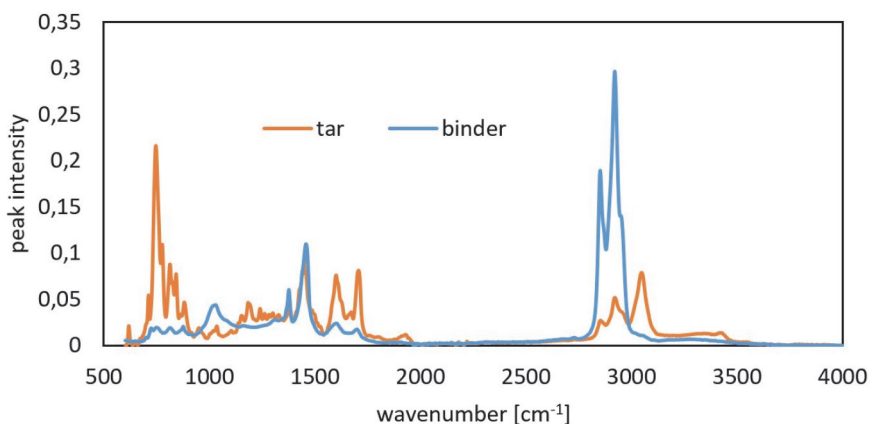


Figure 4 Spectra of a bitumen and tar sample

## 4 Results and interpretation

The results of the spectra peak intensities are calculated and compared. Due to the similarity of spectra measured on bitumen and on samples with low PAH contents, the first evaluation step was to separate the spectra of samples with high PAH-contents from sample spectra with low PAH-contents. Afterwards the spectra with low PAH contents were further analysed.

#### 4.1 Samples with high PAH contents (> 200 mg/kg)

As to be seen in Figure 5, for the samples with high PAH contents assessed by traditional methods, also the analysis by FTIR results in high values of peak intensities. Here the evaluated data is the peak intensity in a range from 768 cm<sup>-1</sup> and 791 cm<sup>-1</sup>, were in the most spectra the peak appears at the wavenumber 777 cm<sup>-1</sup>. Furthermore, four samples, which contain PAH between 100 mg/kg and 200 mg/kg could be detected, but the peak intensity does not correlate with the PAH content. This method is therefore only suitable to detect if there is a presence of PAH or not and sort out the specimen, which contain PAH.

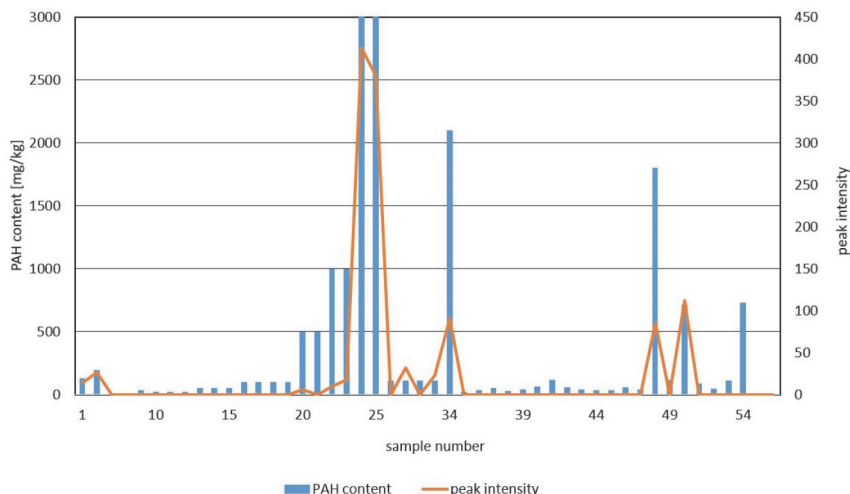


Figure 5 PAH content and peak intensity of spectra with high PAH contents

#### 4.2 Samples with low PAH contents

In the next step it was necessary to evaluate the data and find a correlation between the result of the developed method and the PAH contents of the test samples. Therefore, all samples were analysed with different statistical methods and the correlations were considered. Figure 6 shows the correlation of the peak intensity for the wavenumber range between 768 cm<sup>-1</sup> and 791 cm<sup>-1</sup>, which are also shown in figure 5. As to be seen, the correlation is quite good for all measured samples. However, for the most interesting PAH content range of < 200 mg/kg, the method results in a low correlation.

Therefore, another data evaluation method was developed and tested. This method considered different integral peak areas and the result of each peak area can be seen as a parameter. In total 45 peak areas were considered which represent the most significant peak areas of the 16 PAH(EPA). The peak areas, which doesn't show significant correlation with the PAH content, were sorted out of the data evaluation in a first step. After this was done, the remaining peak areas were examined in more detail by factorisation.

The result of these analysis is shown in Figure 7 and as to be seen it is not satisfying, as the correlation is just 0.45. Furthermore, several samples with identified critical PAH contents (> 25 mg/kg) are not identified by FTIR analysis.

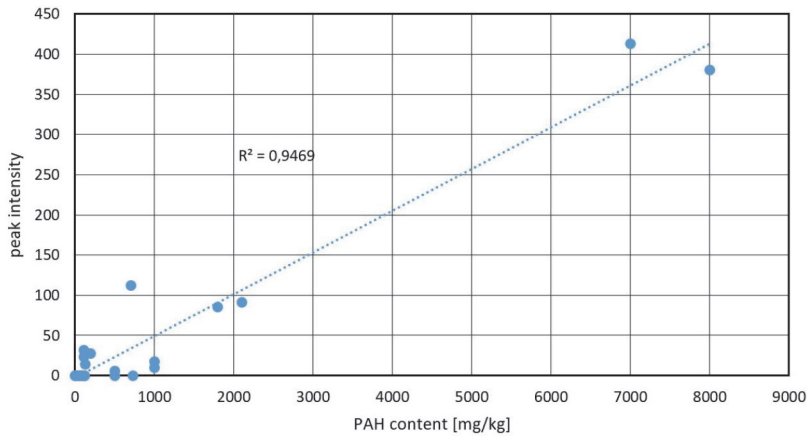


Figure 6 Correlation between the peak intensity and the PAH content

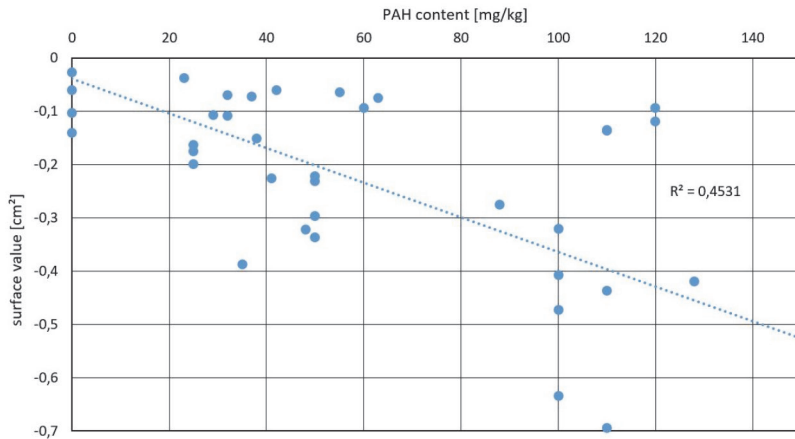


Figure 7 Correlation of low PAH containing samples and surface value

## 5 Conclusions

The presence of PAH in RAP is a serious problem when it comes to a reuse of the asphalt, because harmful components which can cause cancer will be released during mixing and while paving the asphalt. Therefore, it is necessary to detect harmful RAP and protect the worker's health. Currently, the detection of PAH is time consuming and costly, so a fast detection method was developed by using the FTIR-ATR spectroscopy. The results show that it is possible to detect samples with high PAH contents. More problematic is the detection of low PAH contents, due to the similarities of the spectra to non-contaminated samples. Therefore, it is necessary to optimise the data evaluation procedures and use all information which the FTIR-spectra contain. The final goal is a fast screening method for application on mixing sites which will allow to classify the RAP materials in critical and non-critical PAH content. However, for a third fraction, additional PAH analysis may be necessary.

## References

- [1] Deutscher Asphaltverband, Wiederverwendung: Deutscher Asphaltverband (DAV) e.V, 2022, <https://www.asphalt.de/themen/umwelt/wiederverwendung/>, 27.01.2022.
- [2] Hao, G., Huang, W., Yuan, J., Tang, N., Xiao, F.: Effect of aging on chemical and rheological properties of SBS modified asphalt with different compositions, *Construction and Building Materials*, 156 (2017), pp. 902–910
- [3] Jing, R., Varveri, A., Liu, X., Scarpas, A., Erkens, S.: Laboratory and Field Aging Effect on Bitumen Chemistry and Rheology in Porous Asphalt Mixture, *Transportation Research Record*, 2673 (2019), pp. 365–374
- [4] Kleizienė, R., Panasenkienė, M., Vaitkus, A.: Effect of Aging on Chemical Composition and Rheological Properties of Neat and Modified Bitumen, *Materials* 12 (2019)
- [5] Margaritis, A., Soenen, H., Franssen, E., Pipintakos, G., Jacobs, G., Blom, J., van den Bergh, W.: Identification of ageing state clusters of reclaimed asphalt binders using principal component analysis (PCA) and hierarchical cluster analysis (HCA) based on chemo-rheological parameters, *Construction and Building Materials*, 244 (2020) 118276
- [6] Weigel, S.: Bitumen und Chemometrie - Innovative Wege der Bitumencharakterisierung mittels FT-IR-Spektroskopie und multivariater Analysemethoden, *Dissertationsschrift*, Berlin, 2018.
- [7] Wetekam, J., Mollenhauer, K.: Sample preparation method for quick characterization of reclaimed asphalt by FTIR spectroscopy, 2022.
- [8] Hesse, M., Meier, H., Zeeh, B.: *Spektroskopische Methoden in der organischen Chemie*, 2005, 7<sup>th</sup> ed., Georg Thieme, Stuttgart