Cantilever Enhanced Photoacoustic FTIR Challenges ATR and Diffuse Reflectance Techniques

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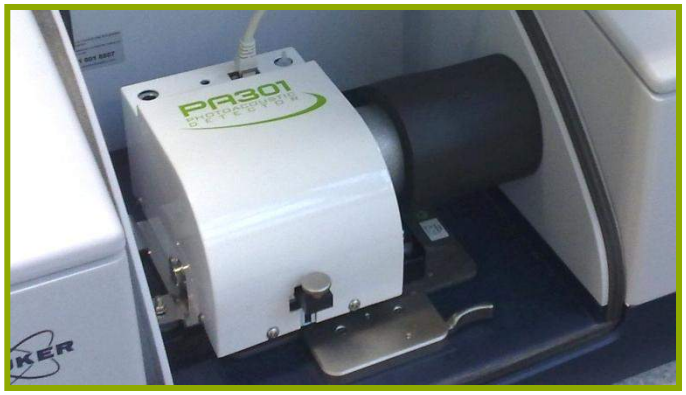
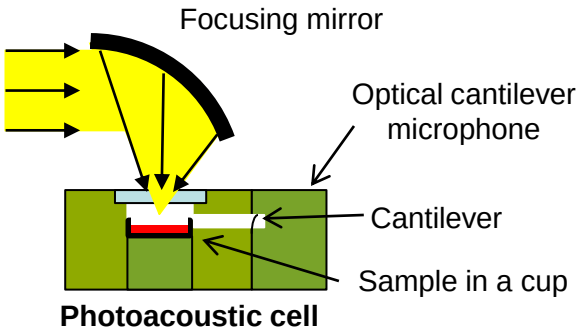
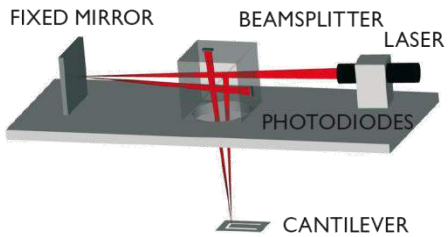
New photoacoustic FTIR accessory PA301



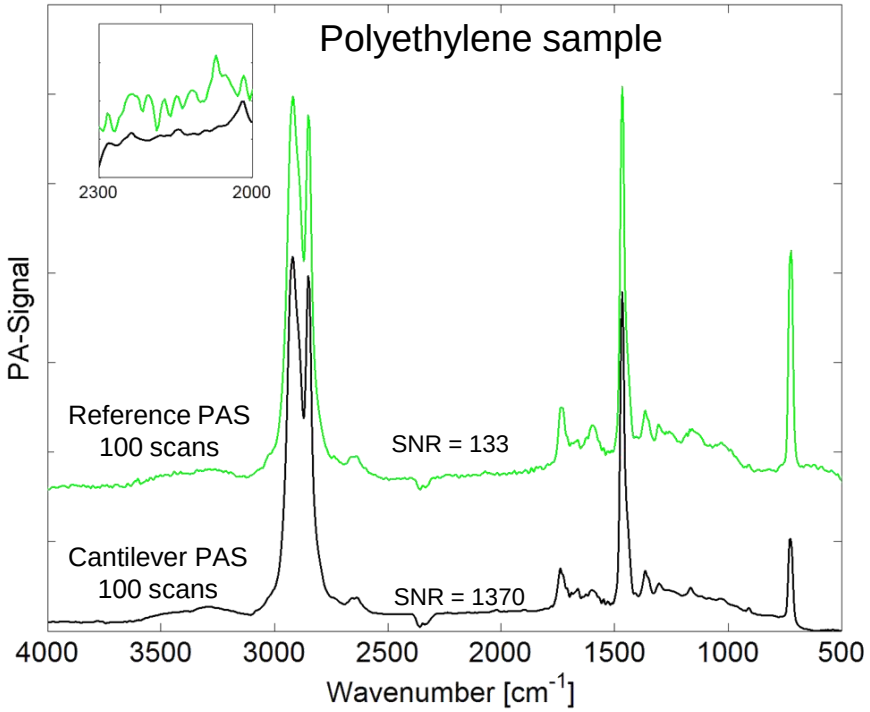


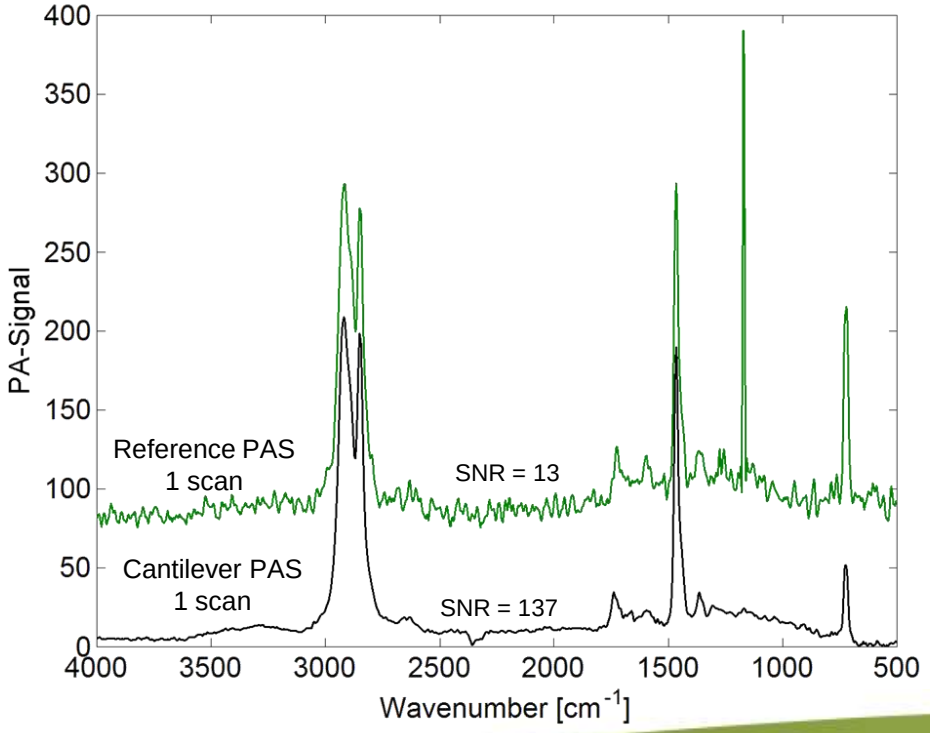


- PA301 is a new ultra sensitive FTIR accessory for measurement of solid and liquid samples.
- It relies on photoacoustic sensing.
- The high sensitivity of the detector is based on the patented optical cantilever microphone.

Superior performance compared to other PAS devices

- Photoacoustics is considered as an extremely versatile technique.
- The signal with condenser microphones has been somewhat noisy.
- Cantilever microphone removes that problem by being over 10 times more sensitive than any other photoacoustic FTIR accessory resulting in **100 times faster analysis**.





Properties of photoacoustic detection

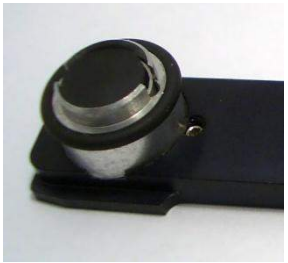
- **Versatile** – it is possible to measure any kind of samples with single accessory.
- **Easy sampling** – practically no sample preparation is needed.
- Spectrum is also **independent of sample morphology** – sample does not have to be made to fine powder.
- **Contactless and nonconsuming** – fragile and valuable samples can be measured.
- **Possibility for depth profiling** – no other FTIR accessory is capable for this.
- Suitable for **optically opaque samples**.
- And now with the **equal measurement time** than with other accessories (such as ATR).

Comparison – PAS and ATR

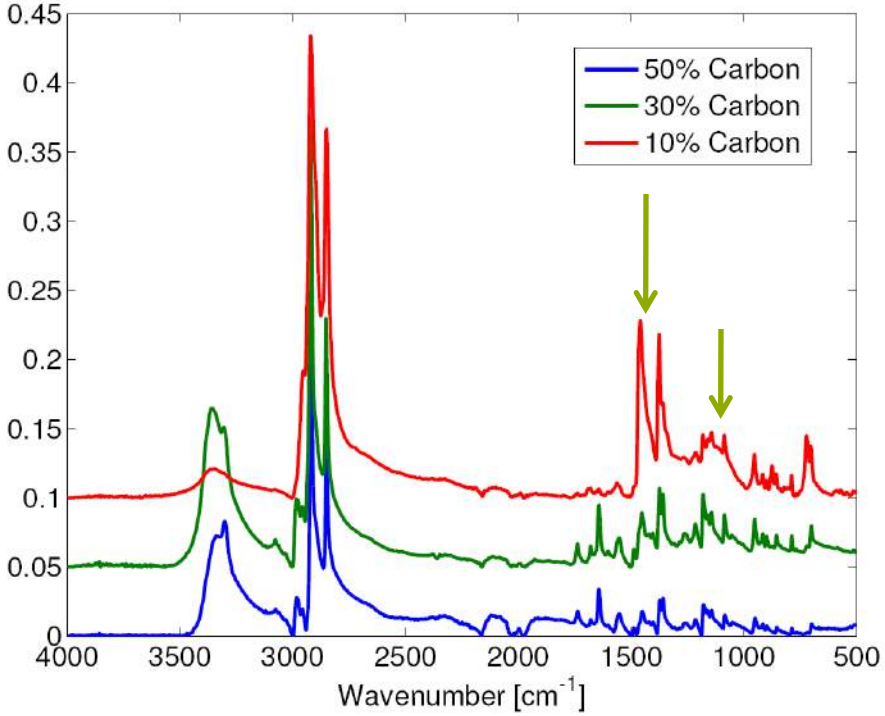
- Attenuated total reflectance (ATR) is currently regarded as the best general purpose FTIR accessory.
- It is at best with liquids and relatively soft samples that give good optical contact with ATR crystal.
- It has a very short sampling depth < 2 µm.
- A comparison of spectra with PAS and diamond ATR was done.
- It was not possible to measure some samples with ATR due to the pressing, e.g.
  - gun powder might have exploded,
  - tablets did not stand pressing.
- The interferometers in the tests were
  - Bruker Alpha with Diamond ATR
  - Thermo Antaris or Bruker Tensor 27 with PAS

Black rubber

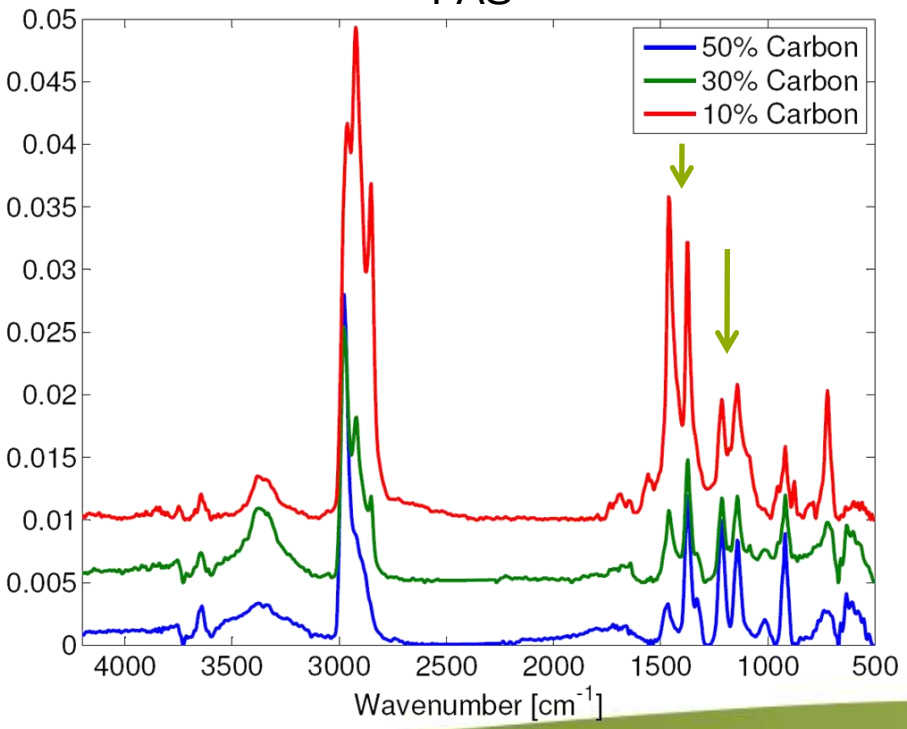
- A rubber containing 10 %, 30 % and 50 % of soot was measured.
- Spectral rangr e.g. between 1200 cm^{-1} and 1400 cm^{-1} is more informative in the photoacoustic spectrum when soot concentration is increased



ATR



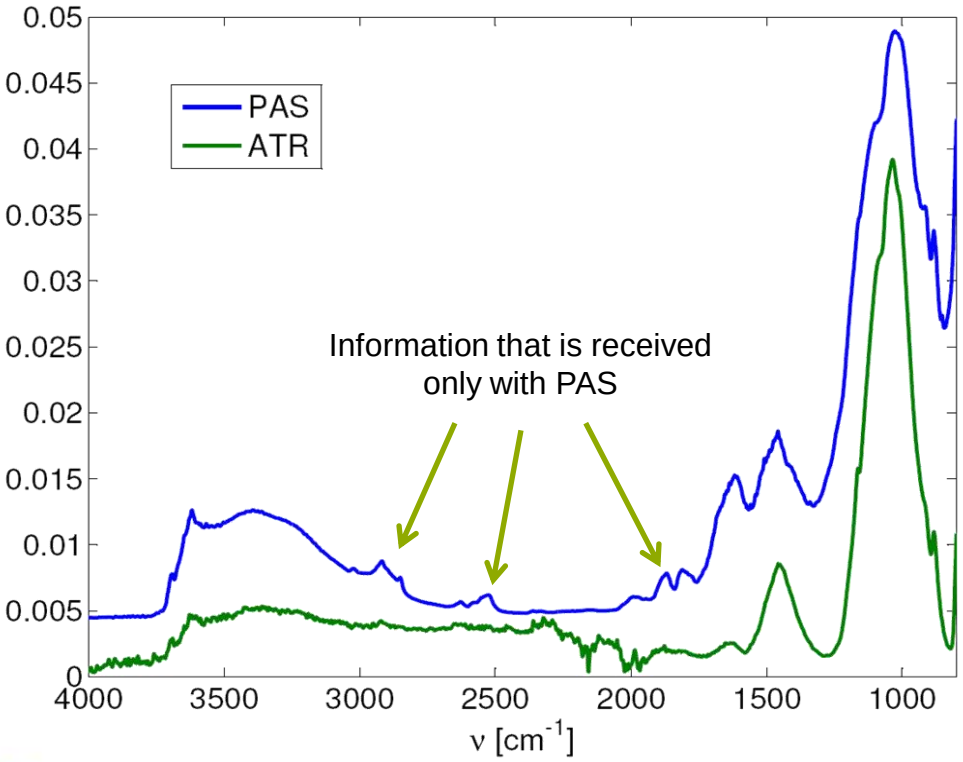
PAS



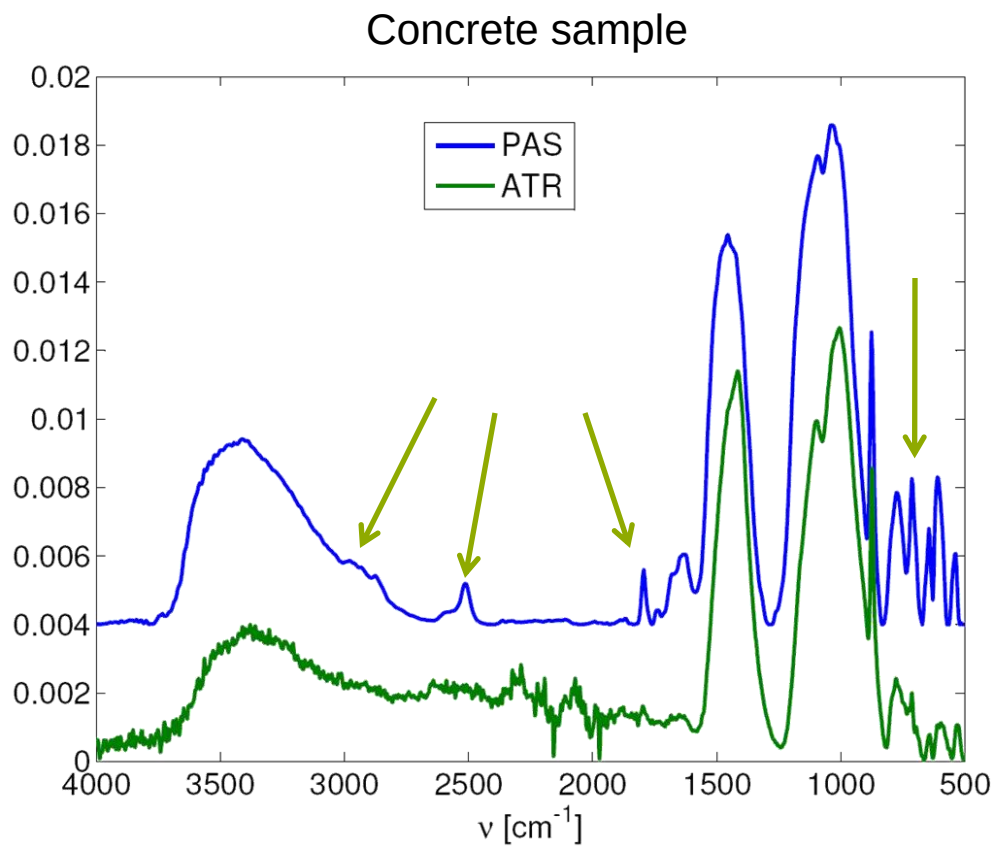
Soil samples

- A sample of soil with organic content was measured.
- Basically most information above 1600 cm^{-1} is lost with ATR.
- Information is obtained from the full spectral range with PAS.

Soil sample with organic content



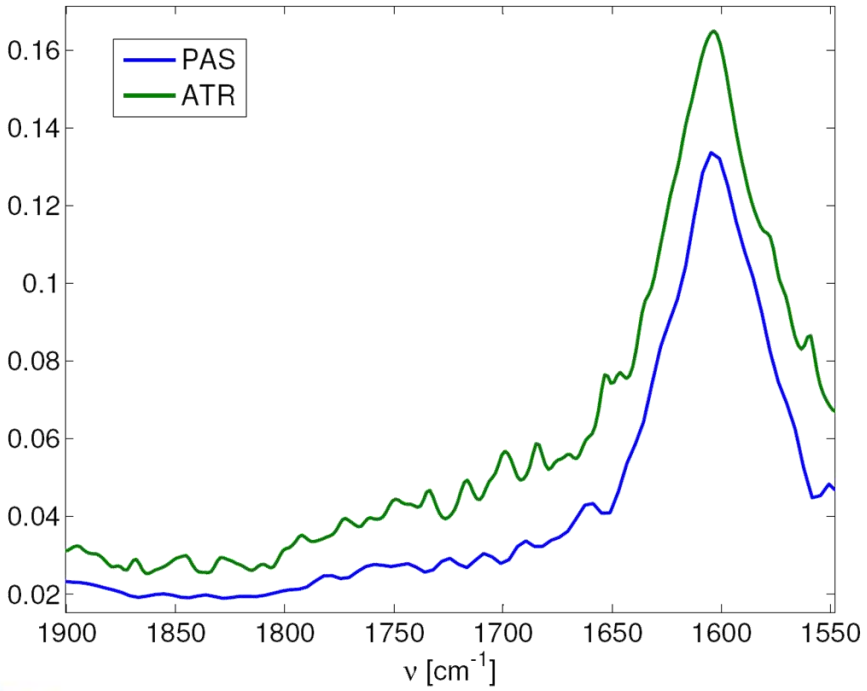
Concrete sample

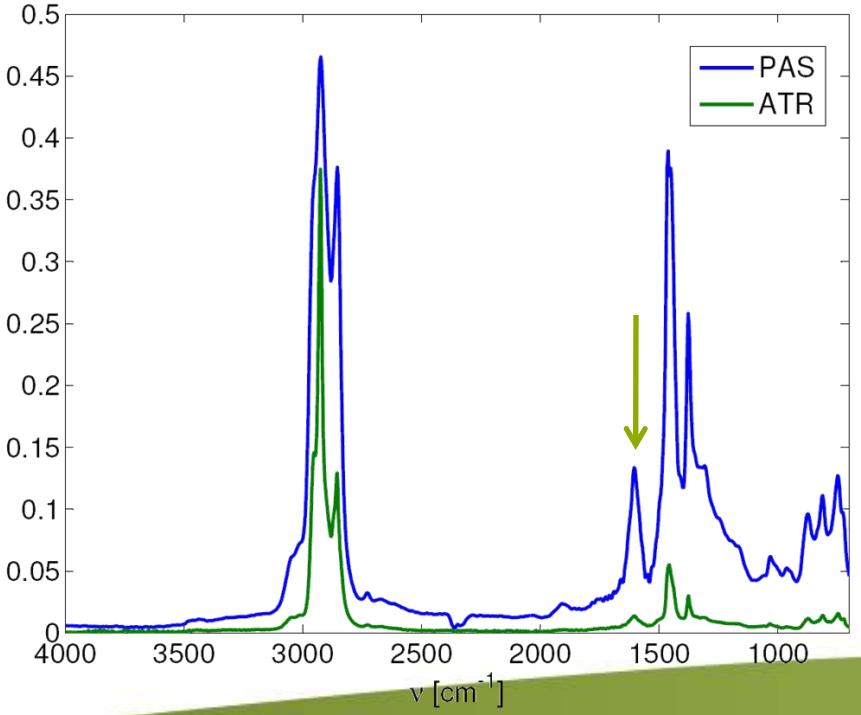


- Motivation for concrete measurements is e.g.
  - What paint has been used?
  - Is there possibly mould in the concrete?
- In this sample PAS spectrum contains clearly more information.
- With PAS it is possible to measure large area for integration or bigger pieces without breaking them.

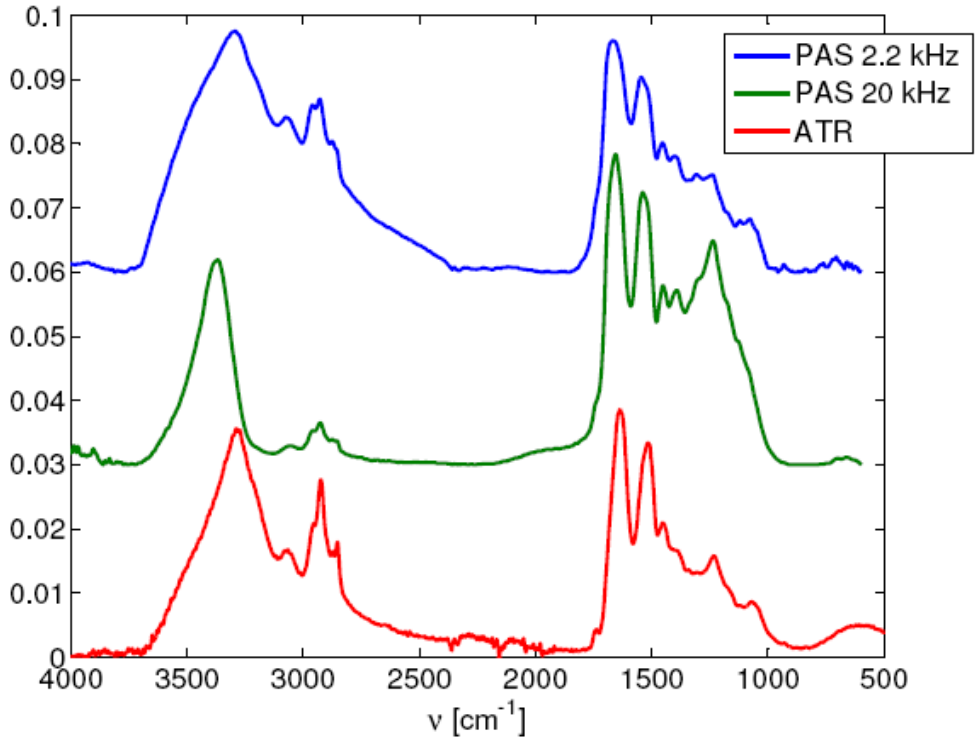
Signal-to-noise ratio comparison with oil sample

- Signal-to-noise ratio of the two accessories were compared with an oil sample, which is a good sample for both ATR and PAS.
- Good optical contact and relatively good transparency is achieved in ATR.
- SNR comparison from peak at 1600 cm^{-1} and noise between 1900 cm^{-1} and 1750 cm^{-1} was done. PAS had approximately 4 times higher SNR than ATR, but the same relation was in throughput and integration times between the Tensor 27 and Alpha FTIR interferometers resulting in approx. same SNR for both methods





Hair sample

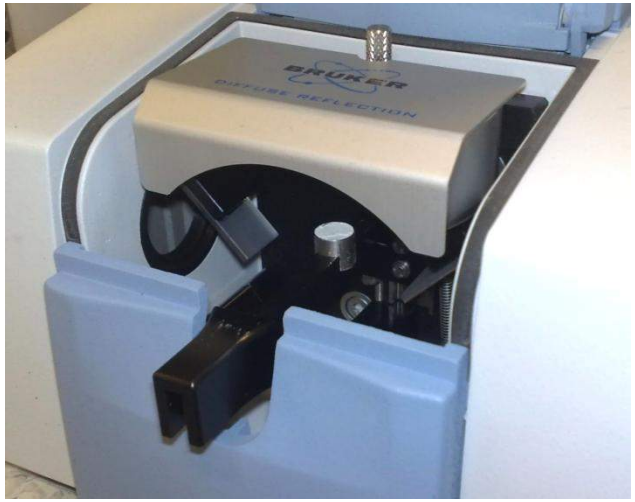


- With PAS it is possible to measure through the hair or only from the surface by changing the mirror speed (depth profiling).
- With ATR the depth can be changed only by order of two by using different ATR crystals.

Comparison – PAS and ATR

- In many cases ATR is losing information in the area above 1500 cm^{-1}, where PAS gives information from the full IR spectral range.
- This effect is stronger with hard samples, but exists with all kinds of samples.
- Depth varying information, typically from 1 to 100 µm, can be obtained with PAS. Sampling depth can not be varied in ATR, it is always less than 2 µm. It makes ATR method problematic with layered and inhomogenous samples.
- Samples with high amounts of carbon black, the PAS spectra have more information than ATR spectra.
- PAS is insensitive to the sample morphology. It is not possible to get good optical contact with single crystal samples or fragile samples with ATR, because they can not be pressed strong enough to the crystal.
- In ATR the sample space has to be always cleaned carefully by using proper solvents in order to prevent spectra for interfering by contaminants, while in PAS it is possible to discard used or contaminated sample cups.

Comparison – PAS and DRIFTS

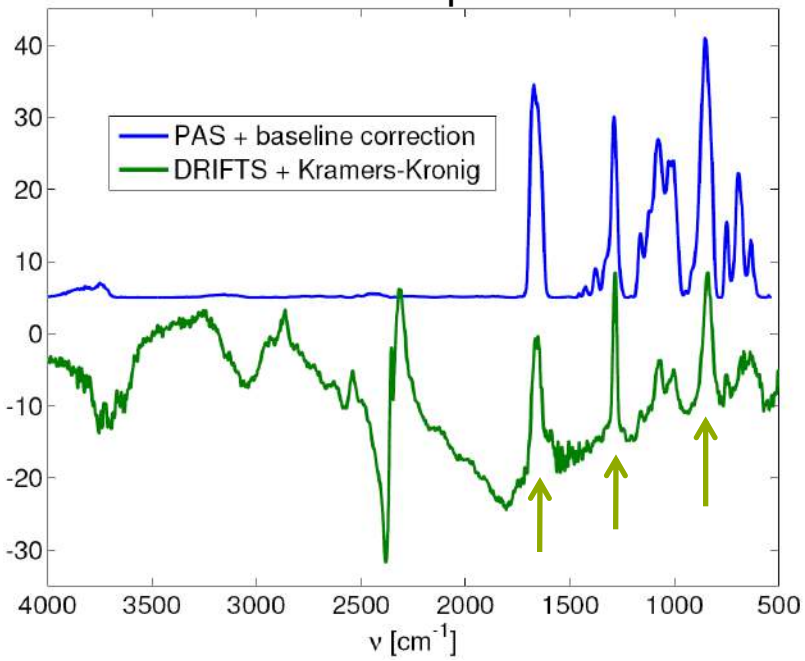


- Diffuse reflectance Fourier transform spectroscopy (DRIFTS) measures the combined reflection and transmission spectrum of the fine powder sample.
- Optimal conditions are when sample is fine powder (10 µm particle size) and mixed with KBr (1 % of sample).
- Sample loading is easy, but it is rarely possible to measure without sample preparation (grinding and mixing with KBr).
- The benefits are partially same compared to ATR than with PAS.
- The interferometers in the tests were
  - Bruker Alpha with Diffuse reflectance accessory
  - Thermo Antaris or Bruker Tensor 27 with PAS

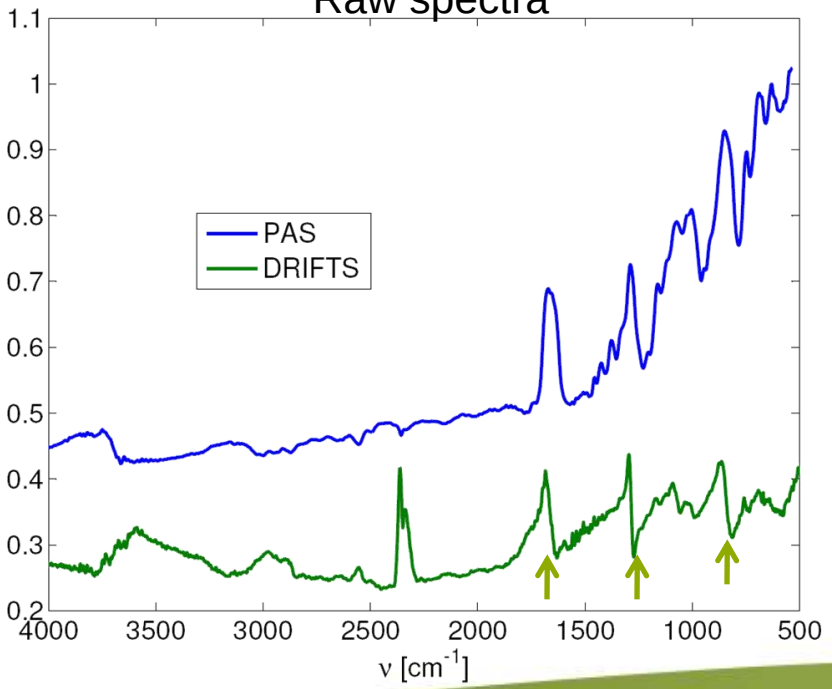
Gun powder

- Gun powder and explosives in general are samples that are rather not pressed (required in ATR) or grinded (required for DRIFTS).
- PAS does not require any sample preparation and therefore is optimal for explosives.
- Diffuse reflectance had problems with the particle size and darkness of the sample.
- Kramers-Kronig correction enhanced the line shape of the lines between 800 cm^{-1} and 1700 cm^{-1} in DRIFT spectrum.

Corrected spectra



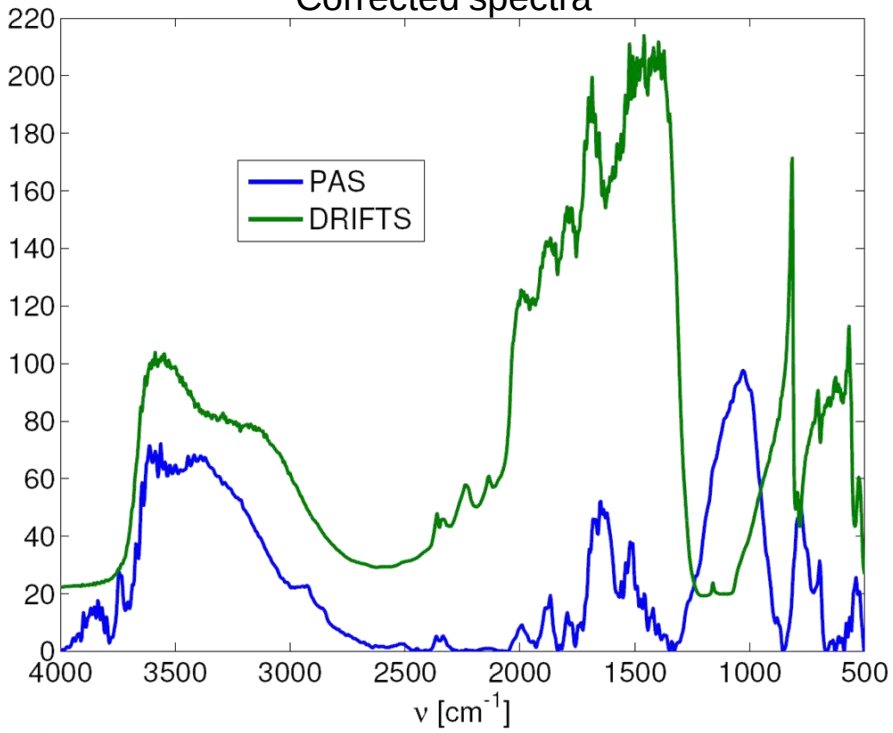
Raw spectra



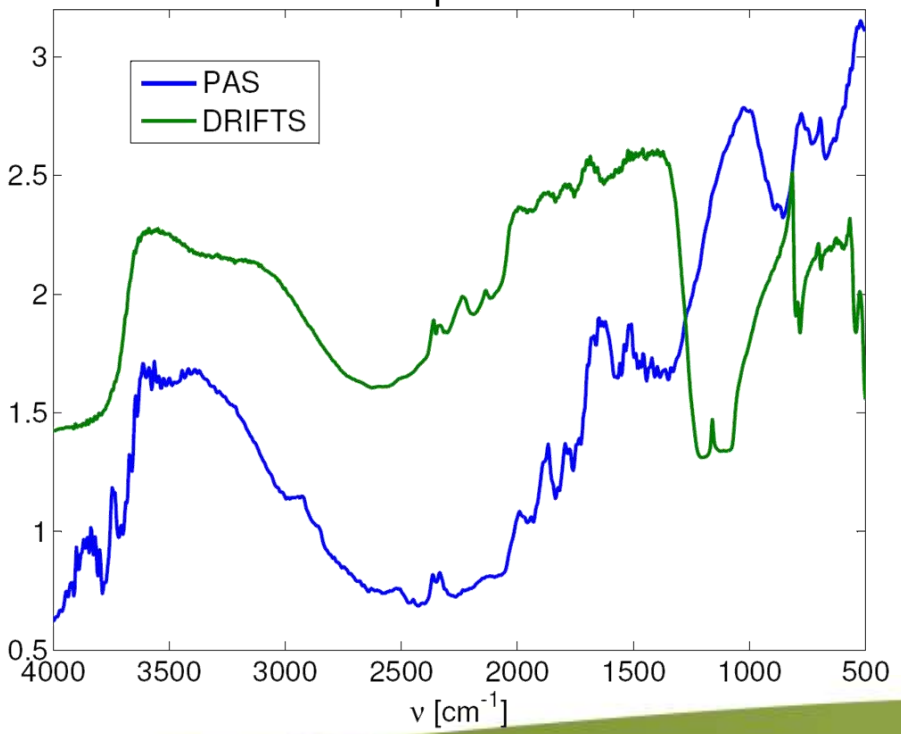
Soil sample

- This soil sample was too granular or high concentration to give a proper spectrum or to be corrected with DRIFTS.
- For DRIFT spectrum a Kubelka-Munk conversion and baseline correction for PAS is introduced.
- PAS gives proper spectrum from the soil sample without any sample preparation

Corrected spectra



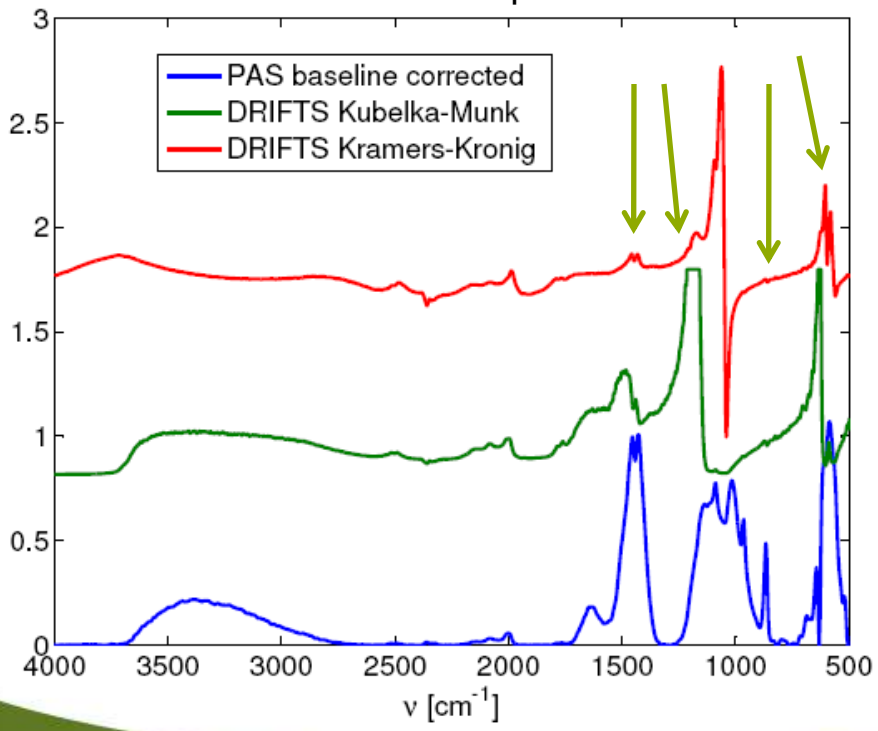
Raw spectra



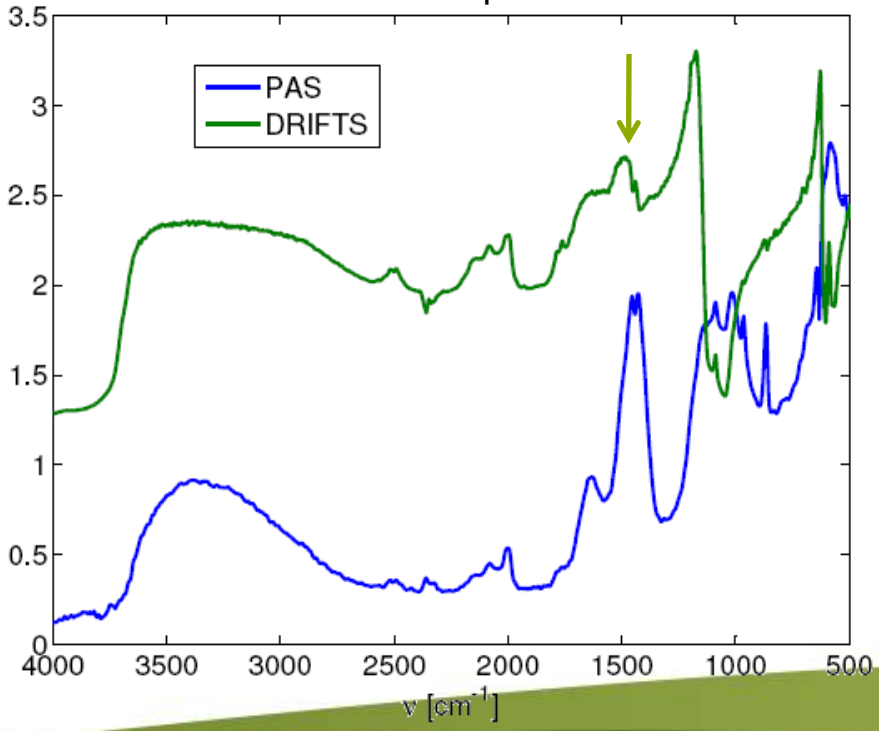
Soil (gravel)

- Kramers-Kronig correction made some lines in DRIFT spectrum visible at 1400 cm^{-1},1200 cm^{-1}, and 600 cm^{-1}, but left distortions elsewhere.
- Kubelka-Munk conversion was not possible due to saturation.
- PAS spectrum gives clearly more information e.g. at 800 cm^{-1}.

Corrected spectra

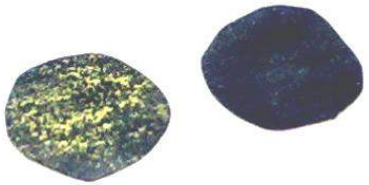


Raw spectra

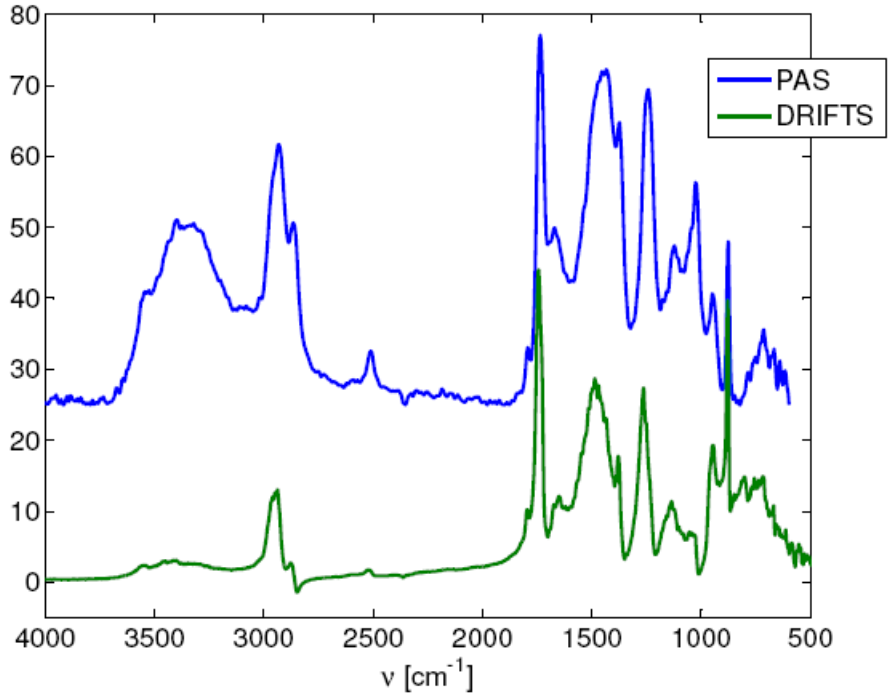


Paint on abrasive paper

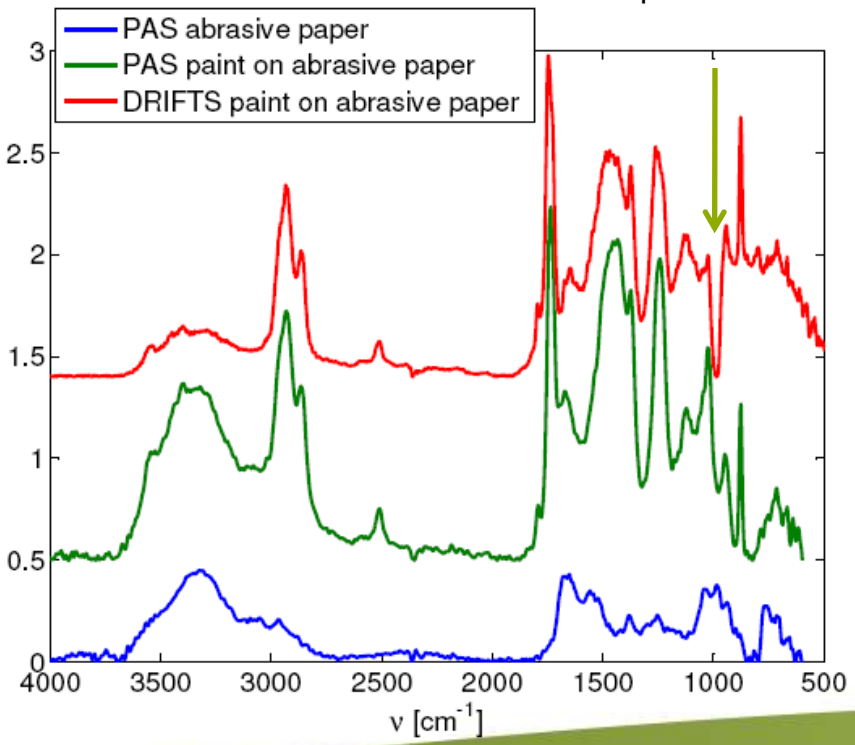
- Having paint on abrasive paper has been a common way to apply DRIFTS.
- PAS survived this task as well as DRIFTS.
- PAS sepctrum can be obtained also from the clean abrasive paper, but it did not give a proper DRIFT spectrum.



Kramers-Kronig corrected DRIFT spectrum



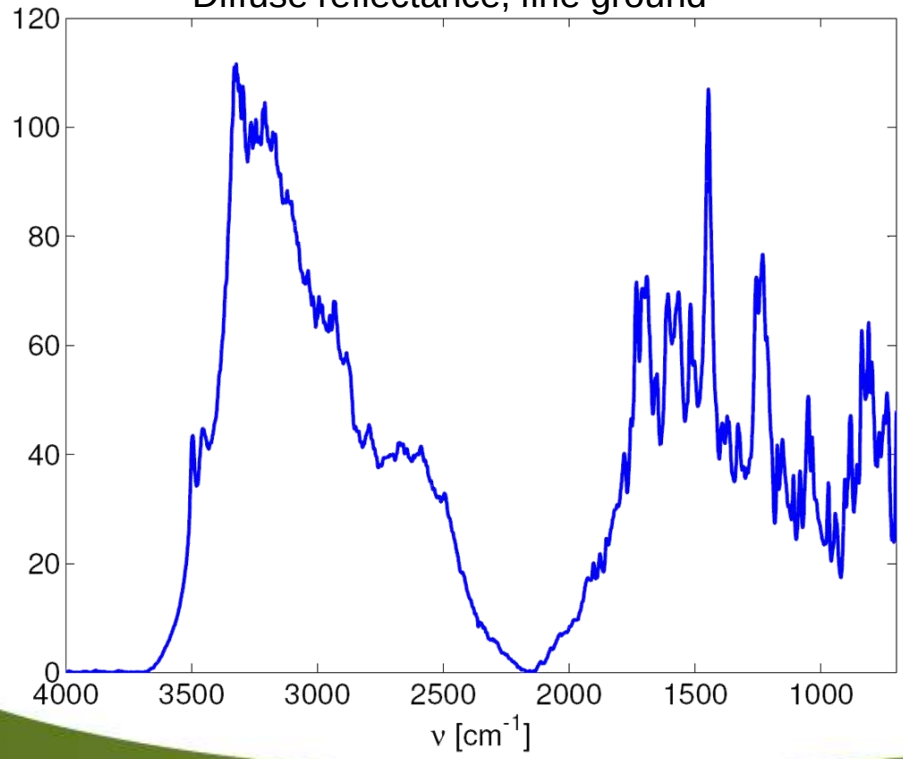
Kubelka-Munk corrected DRIFT spectrum



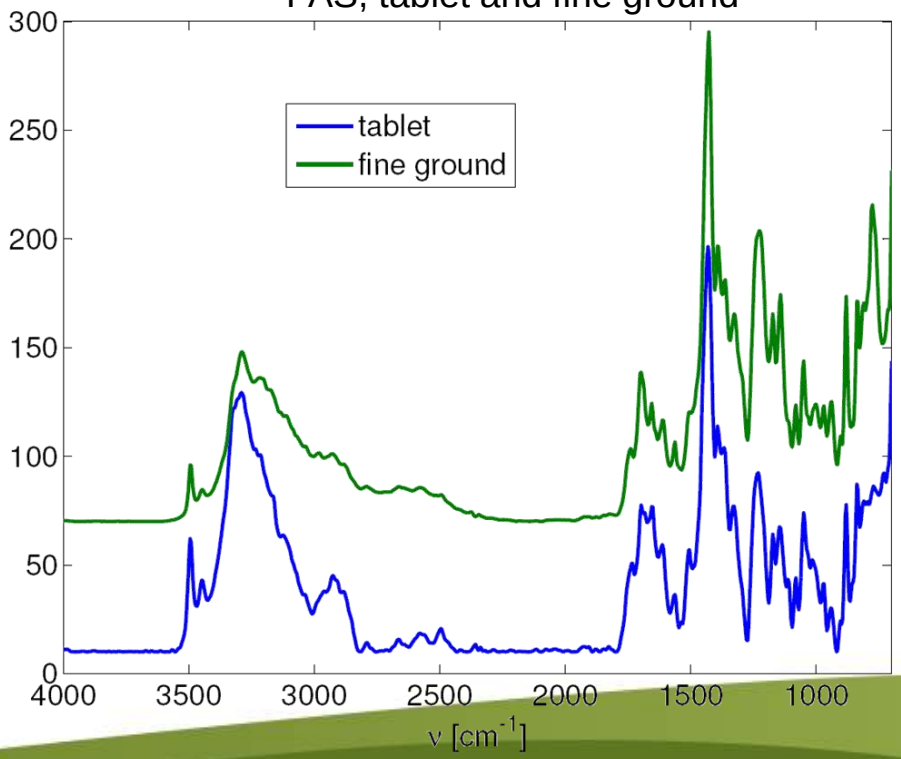
Pharmaceutical samples

- Flew medicine with pain reliever, antihistamine and nasal decongestant was used as the sample.
- With PAS it is possible to measure directly in tablet form (or broken tablet) due to the insensitivity to sample morphology and capability to variable sampling depth.

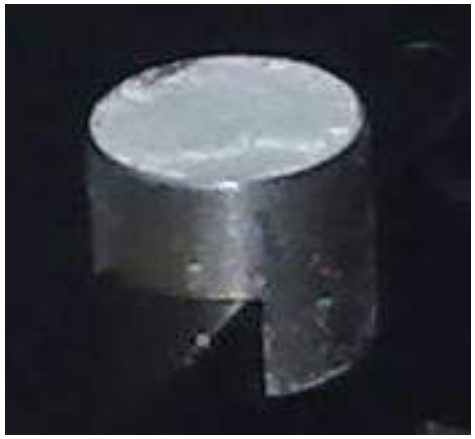
Diffuse reflectance, fine ground



PAS, tablet and fine ground



Comparison – PAS and DRIFTS



- DRIFT spectra usually requires either Kubelka-Munk or Kramers-Kronig correction. The case whether the correction should be done or not is depending strongly on the sample. PAS does not require any corrections.
- Problems with DRIFTS start to emerge as soon as the concentration/absorption is too high or the surface or sample particle is not close to optimal.
- PAS is insensitive to sample morphology and does not require sample preparation.
- In DRIFTS the line positions might be occasionally different than in PAS and transmission spectroscopy.
- Sample degrading and mixing with KBr is always required with DRIFTS, which makes the measurement tricky compared to both PAS and ATR.

Conclusions

- For some samples PAS is the only suitable method. Examples of such samples are: gun powder, fragile large samples, samples with high amount of carbon, samples requiring variable sampling depth or depth profiling.
- PAS can give all available information from any wavelength region or sample type with much less sample preparation than other accessories.
- PAS is at minimum complementing very well the performance of ATR and diffuse reflectance accessories as a basic laboratory tool.
- Photoacoustic signals are no longer noisy compared to DRIFT and ATR due to the novel patented cantilever sensor.

Thank you!