General aspects of ATR-FT-IR spectroscopy

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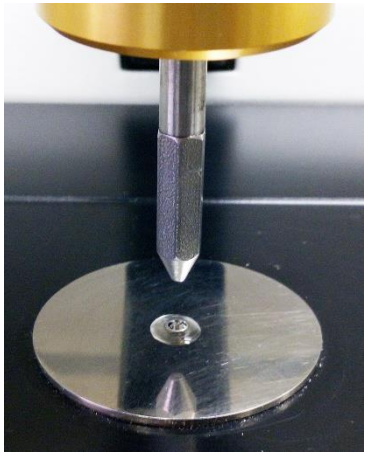
ATR - Attenuated Total Reflectance

(Internal reflection spectroscopy technique)

- Is contact technique
- Almost non-destructive
- Easy, fast and convenient
- Requires minimal or no sample preparation
- Can work with very small samples
- Spectra are recorded from sample surface that is in good contact with the ATR crystal surface
- Enables analysis of solids and liquids
- Qualitative and quantitative analysis

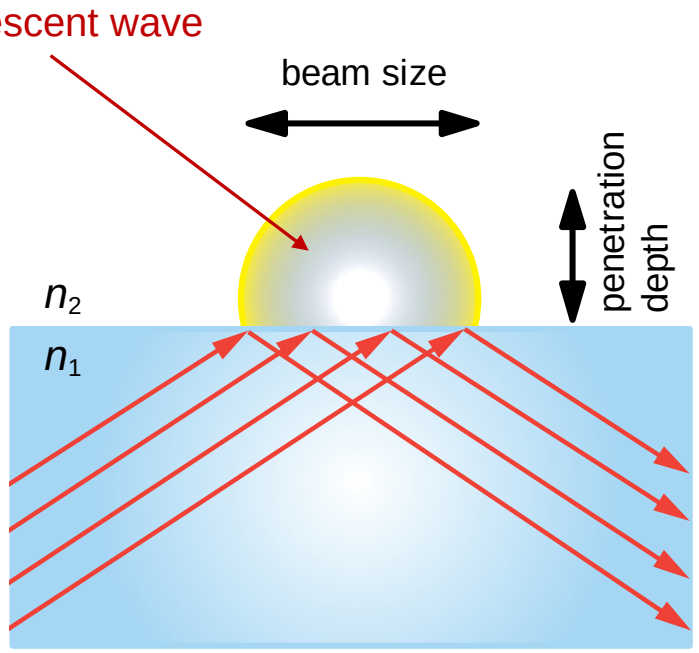
Diamond micro-ATR accessory

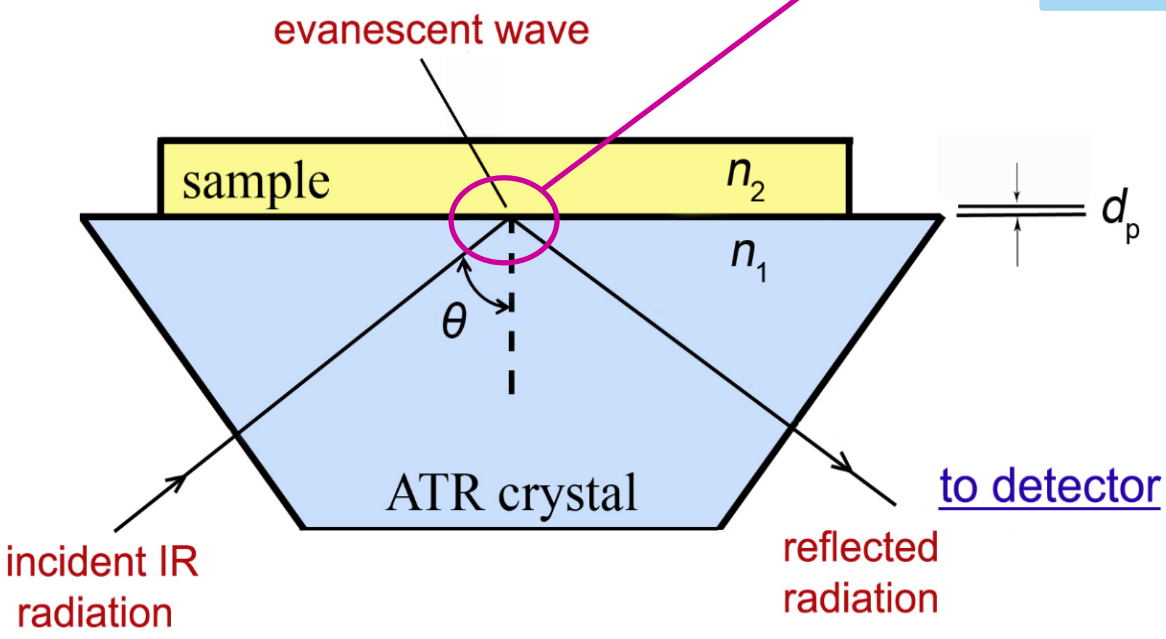


Principle of ATR

$$d_p = \frac{\lambda_1}{2\pi n_1 \sqrt{\sin^2\theta - (n_2/n_1)^2}}$$

Important:
***n*₁ > *n*₂!**



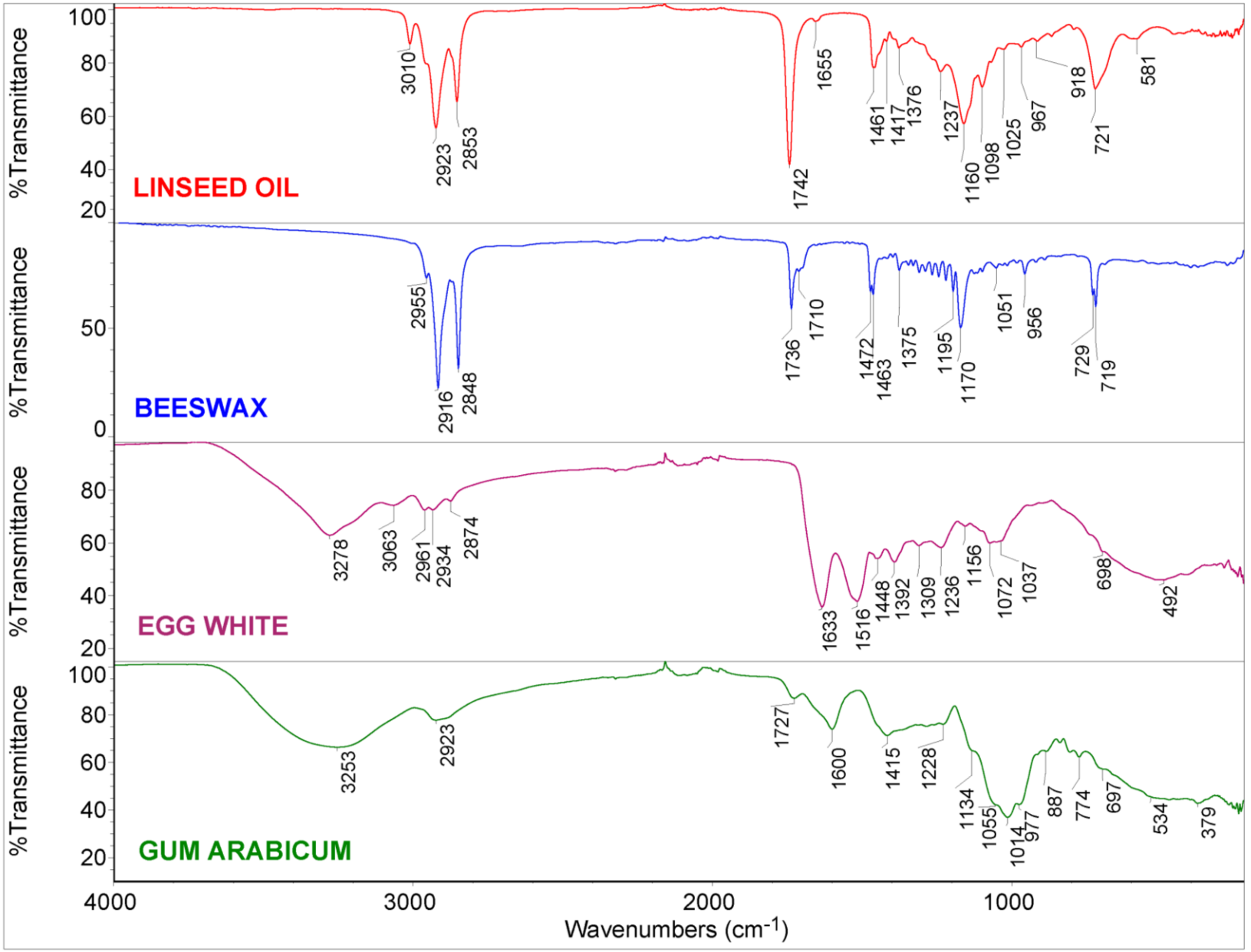


ATR crystals *n*:

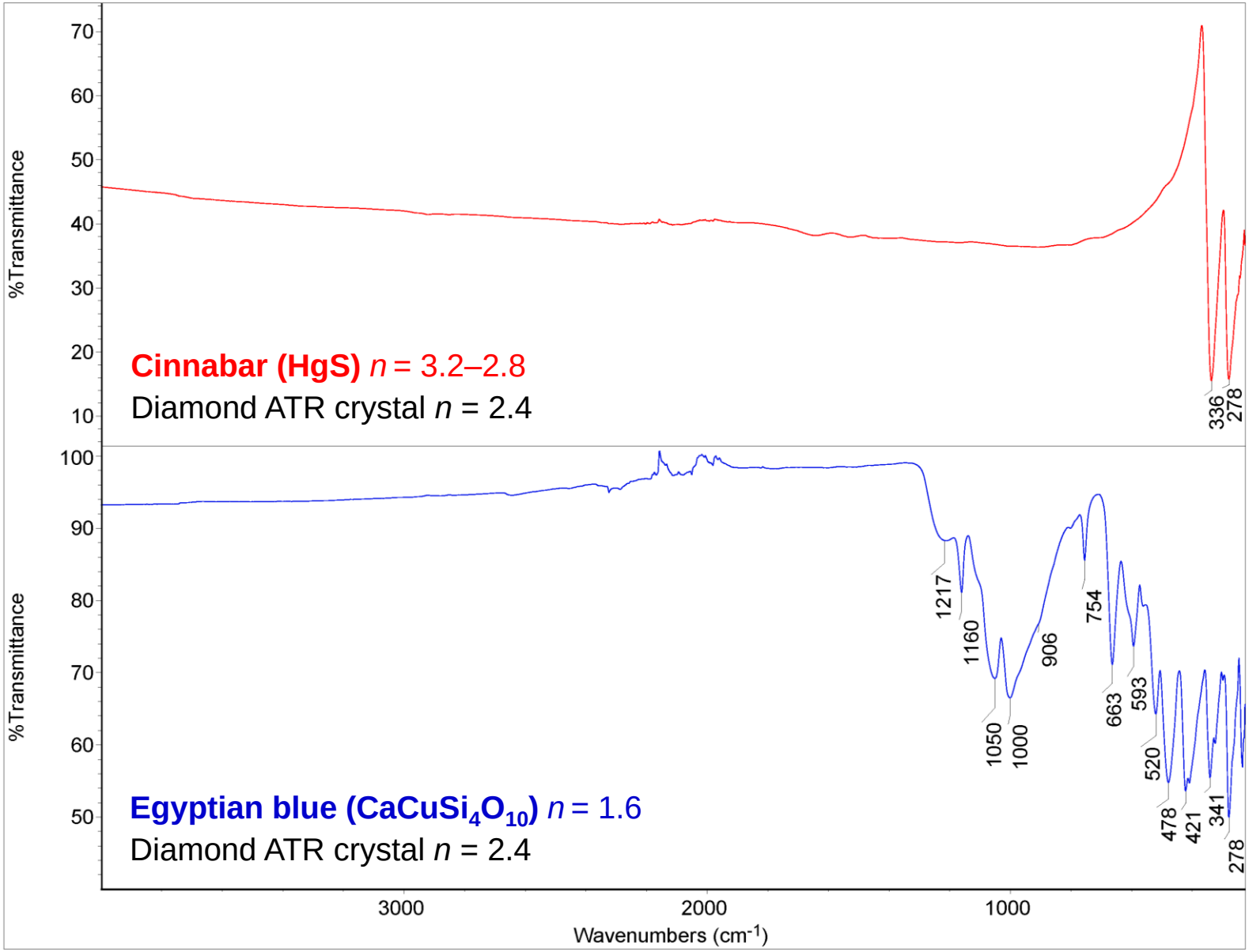
- Diamond: *n* = 2.4
- ZnSe: *n* = 2.4
- Ge: *n* = 4.0
- KRS-5: *n* = 2.37

(all *n* correspond to n_D)

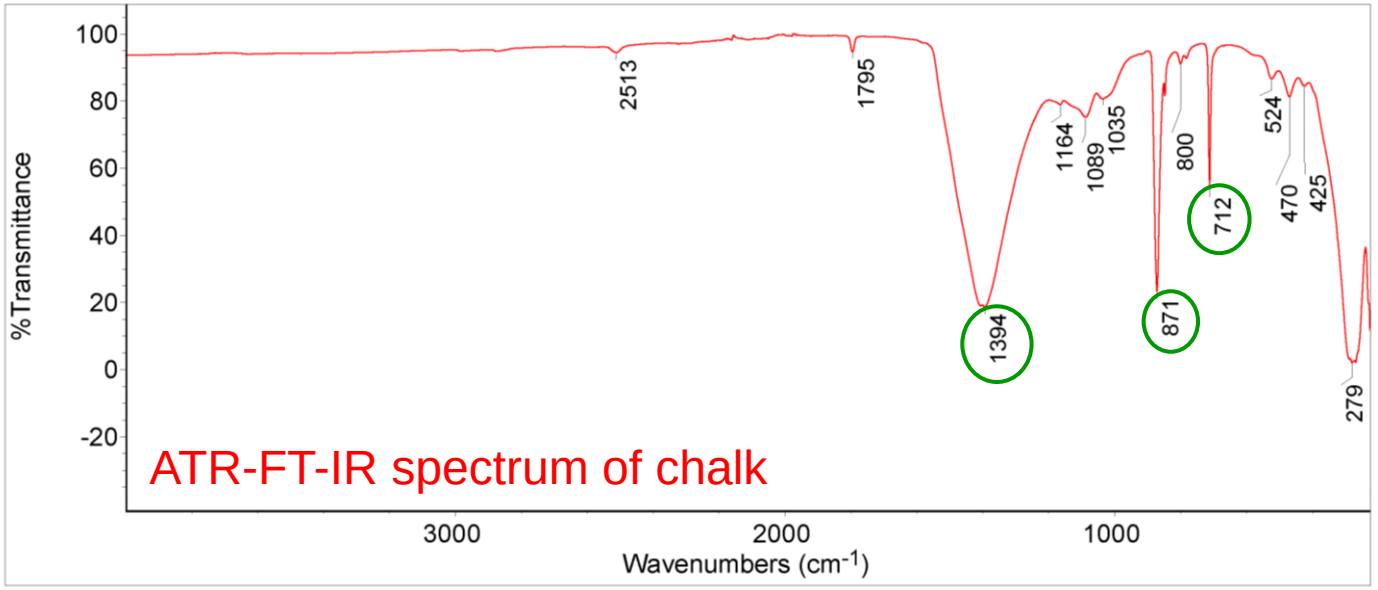
ATR-FT-IR spectra of different binders



Sometimes distorted spectra are observed

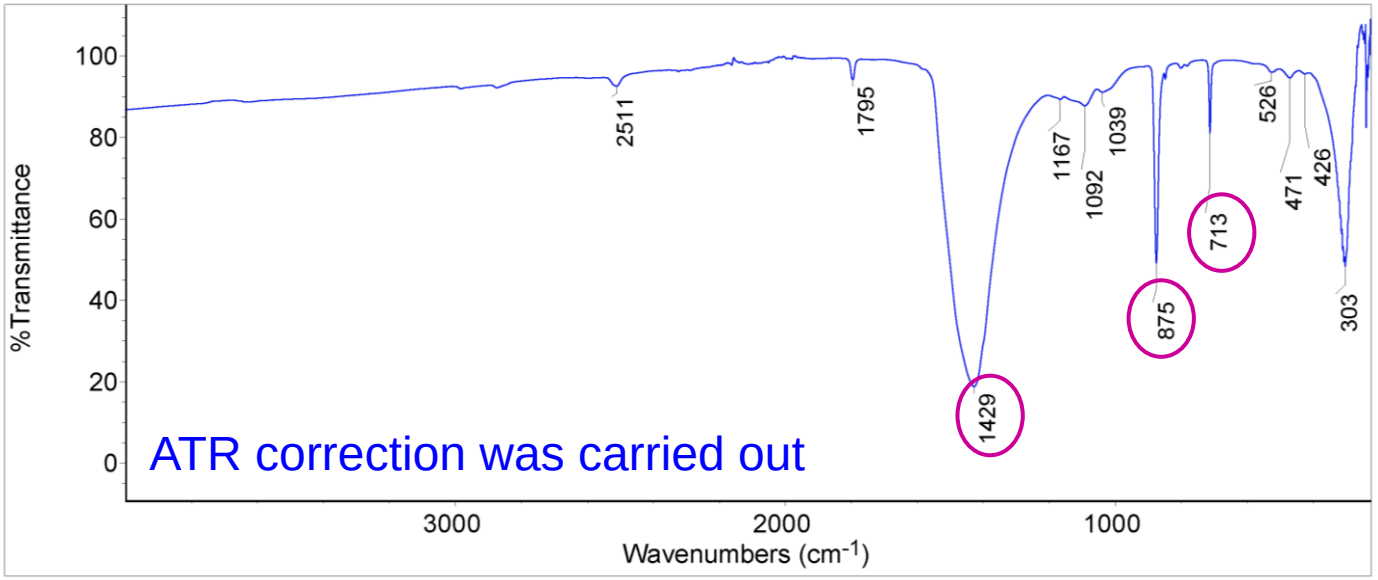


ATR and transmission mode IR spectra



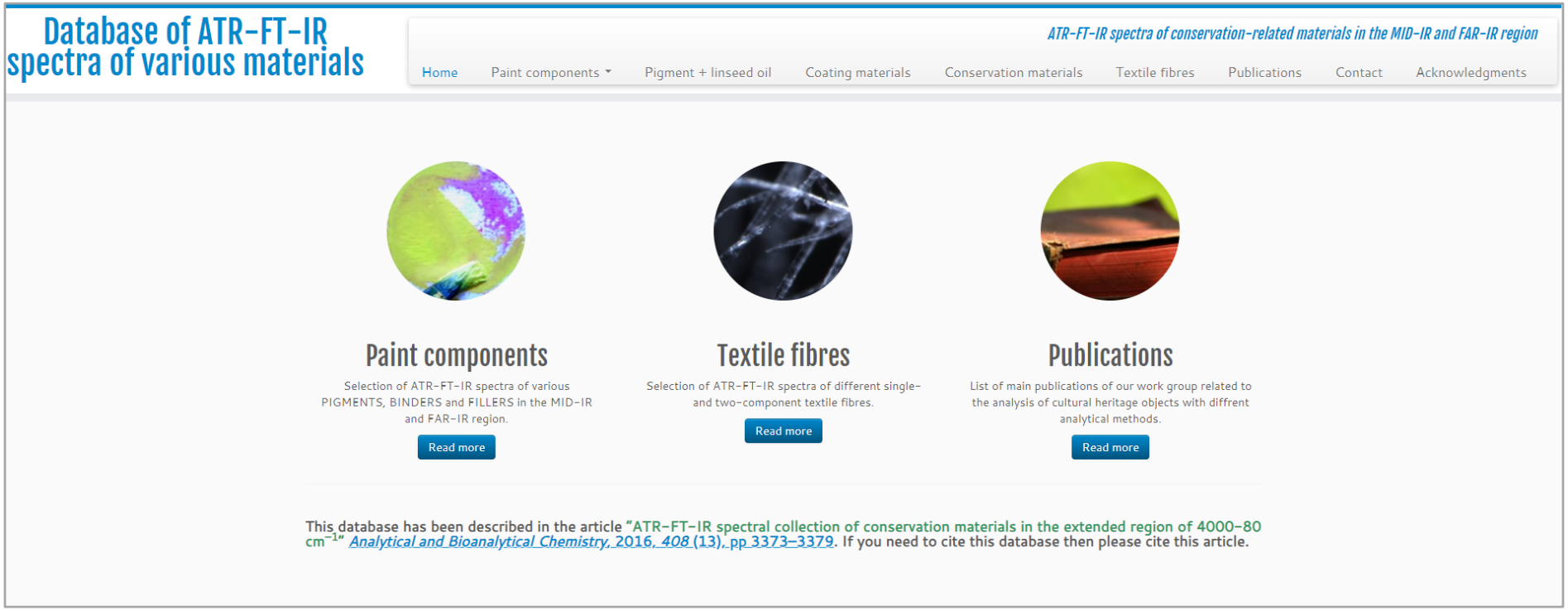
Transmission mode IR spectra (cm^{-1}):

1427 | 876 | 712



Reference IR spectra

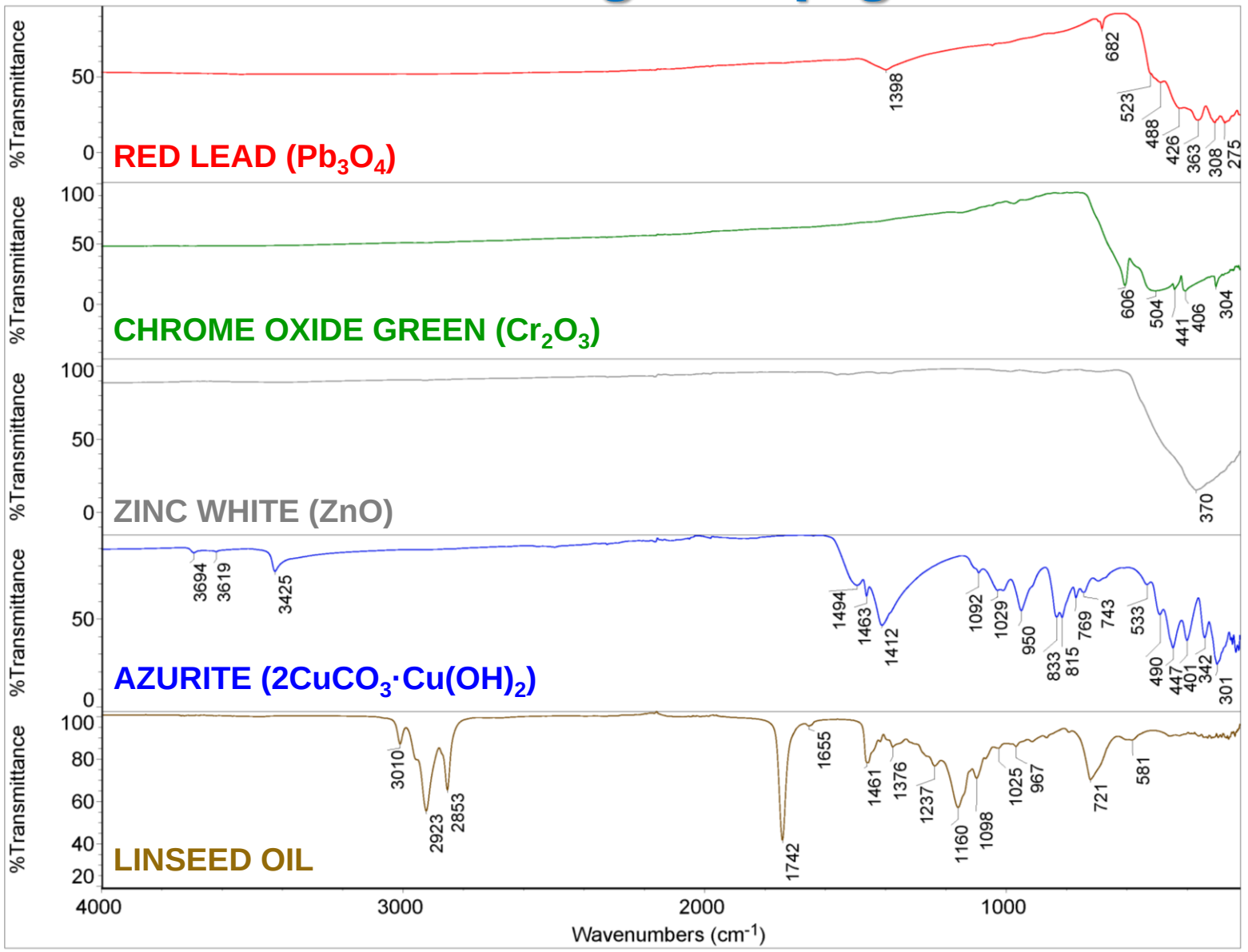
http://tera.chem.ut.ee/IR_spectra/



Some ohter IR spectral databases (Transmission and/or ATR spectra):

- IRUG - http://www.irug.org/search-spectral-database
- SDBS - http://sdbs.db.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi

Different inorganic pigments



S. Vahur, A. Teearu, I. Leito. *Spectrochimica Acta Part A*, **2010**, *75*, 1061 – 1072.

S. Vahur, U. Knuutinen, I. Leito. *Spectrochimica Acta Part A*, **2009**, *73*, 764 – 771.

Red paint sample from the coat of arms of Bengt Hinrich von Biestram (18th century) from the Dome church in Tallinn

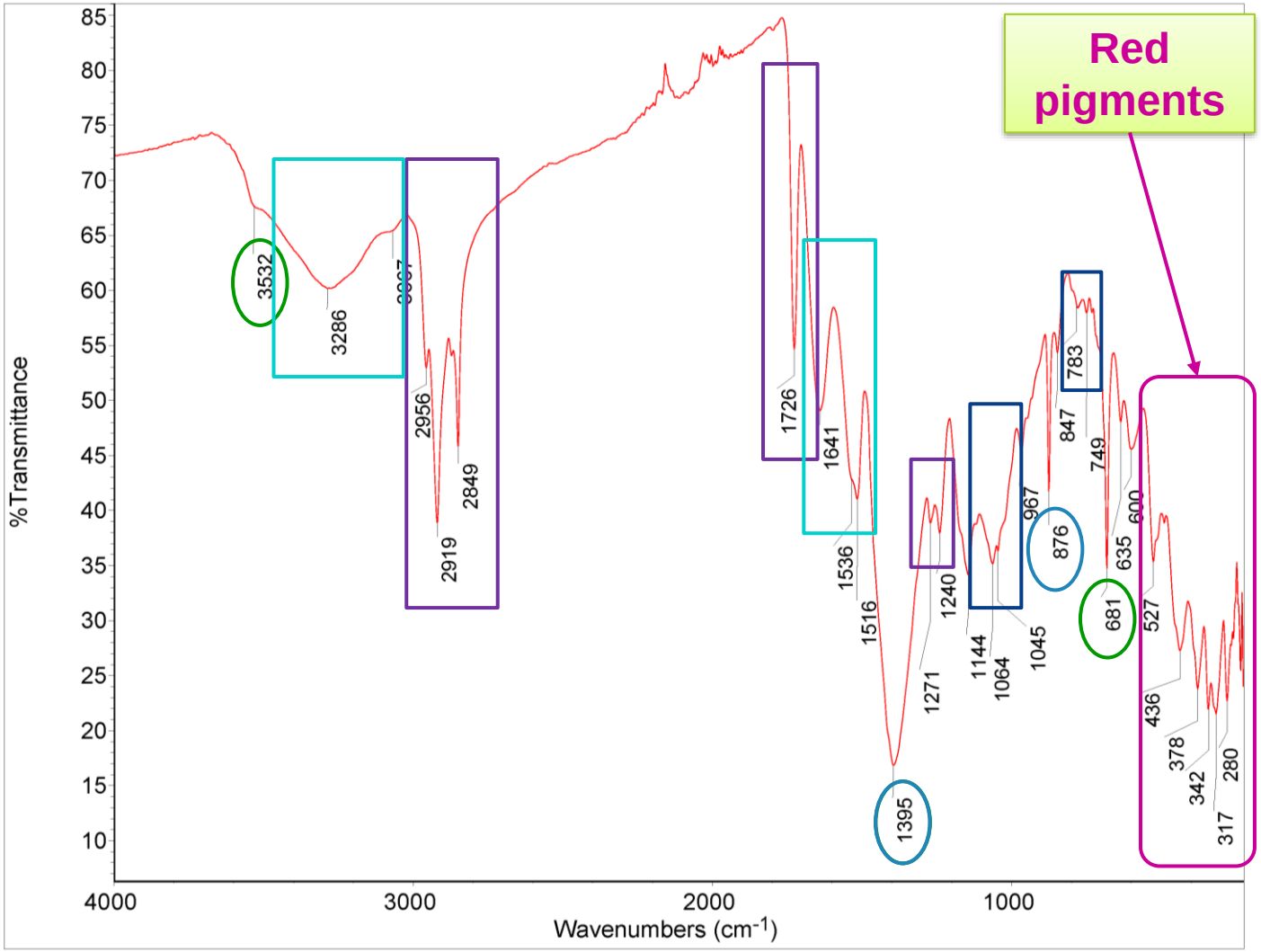


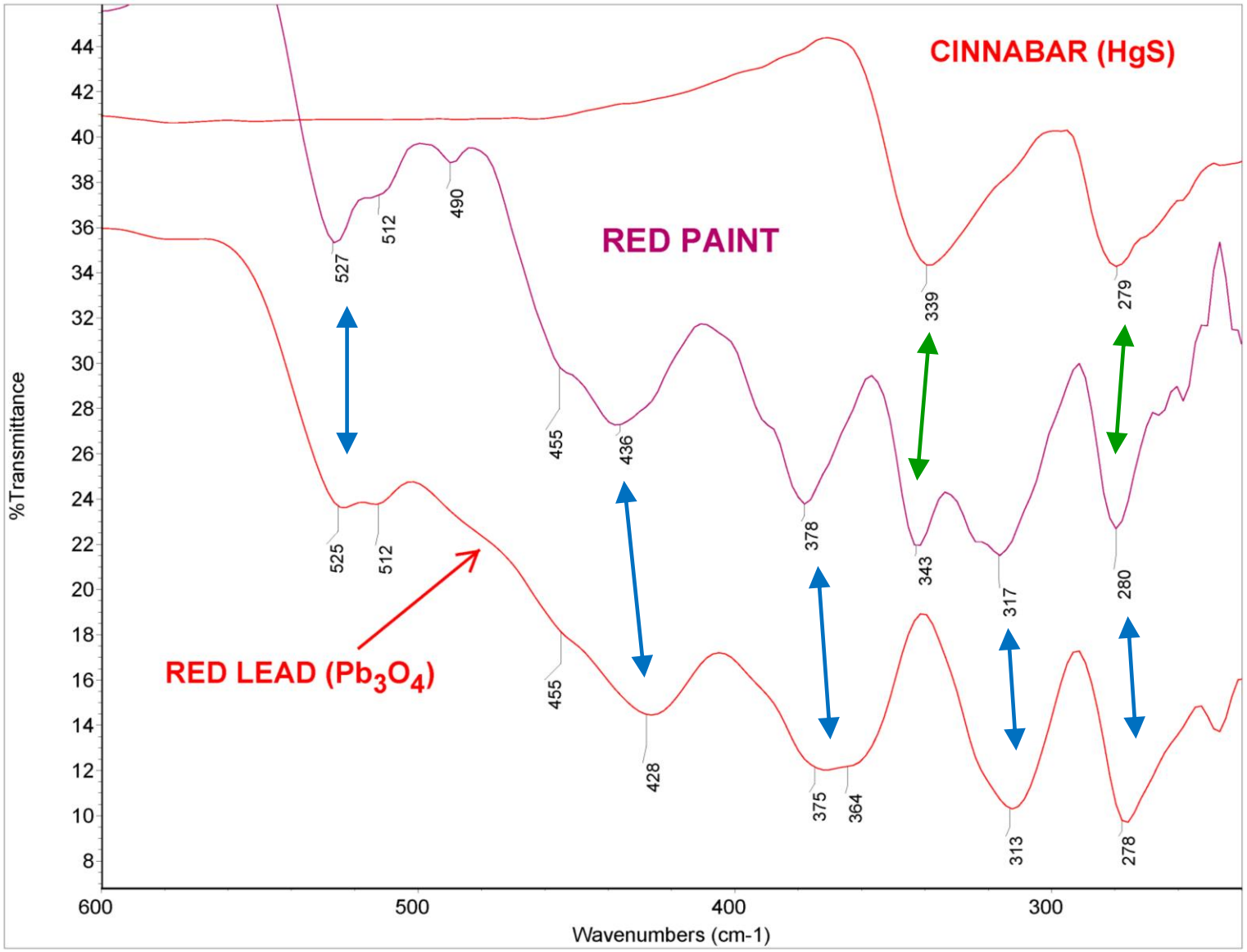
Photo: Conservation and Digitization Centre Kanut

Fillers:

- Lead white
- Chalk
- Silicates

Binders:

- Protein
- Oil or possibly acrylic resin



Red pigments: Cinnabar and Red lead

S. Vahur, U. Knuutinen, I. Leito. *Spectrochimica Acta Part A*, **2009**, *73*, 764 – 771.

Summary

- ATR is the most popular sampling technique for FT-IR spectroscopy.
- Enables to acquire high-quality IR spectra from easy and from difficult samples.
  - Refractive indices are important!
- Different materials (paints, varnishes, textiles, clays, archeological residues, glues, etc) can be analysed.
- Spectral maxima are slighly shifted compared to transmittance spectra
  - Compare against ATR spectra if possible
  - ATR correction can be applied