TECHNICAL UNIVERSITY OF LIBEREC

New Opportunities for the Development of Education at the Technical University of Liberec

Specific objective A2: Development in the field of distance learning, online learning and blended learning

NPO_TUL_MSMT-16598/2022

KNT_TNA_Characterization of nanometrials

Ing. Radek Jirkovec, Ph.D.

Funded by the European Union
NextGenerationEU

CZECH RECOVERY PLAN

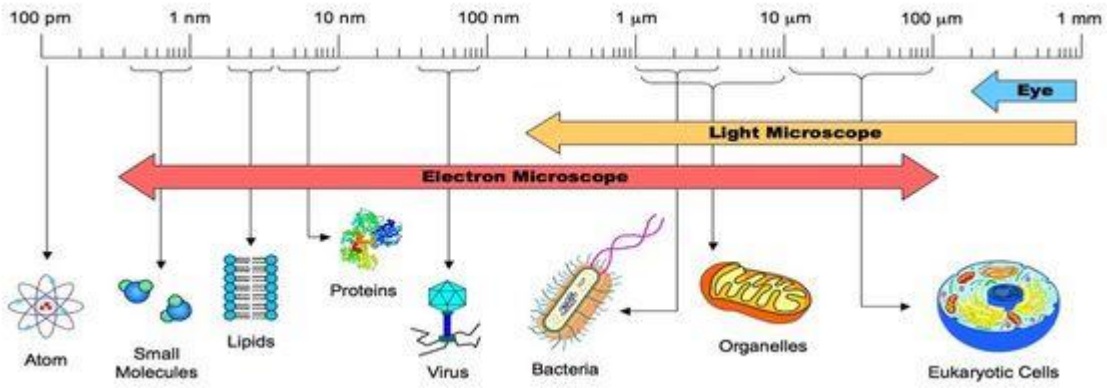
MINISTRY OF EDUCATION, YOUTH AND SPORTS

Electron microscopy

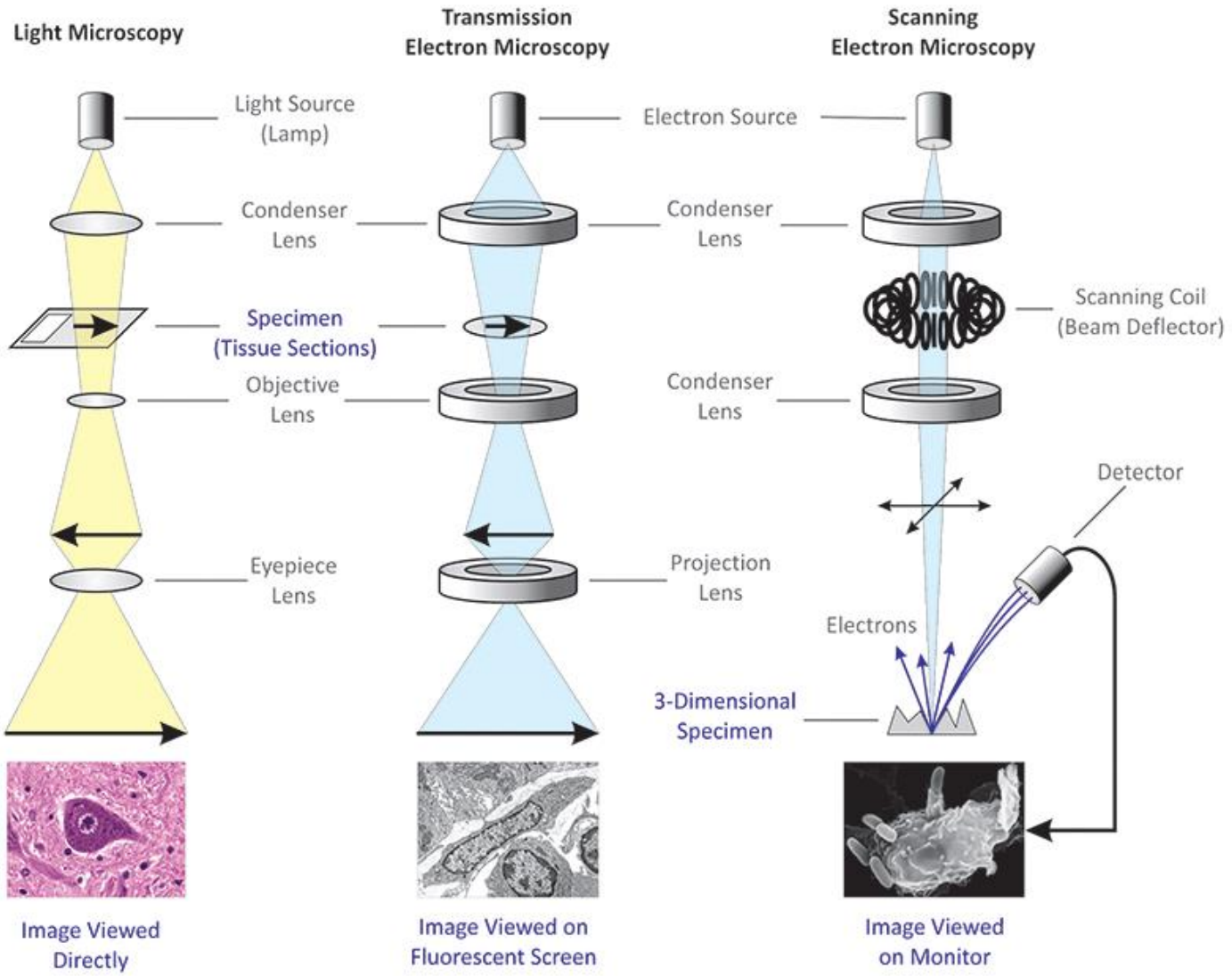
- It works with a stream of electrons in a vacuum
- Indirect electron beam observation:

TEM – transmission electron microscopy

SEM – scanning electron microscopy



The difference between light and electron microscopy

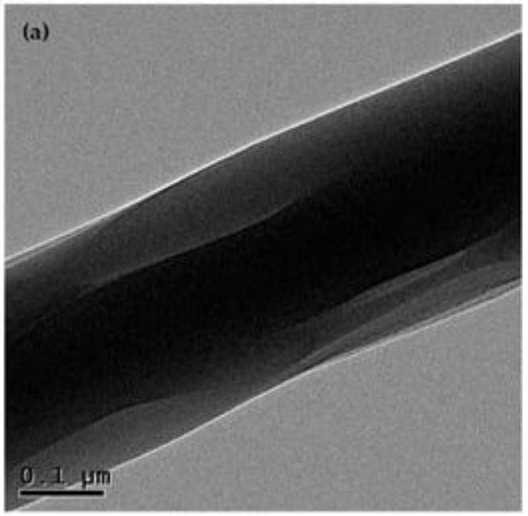


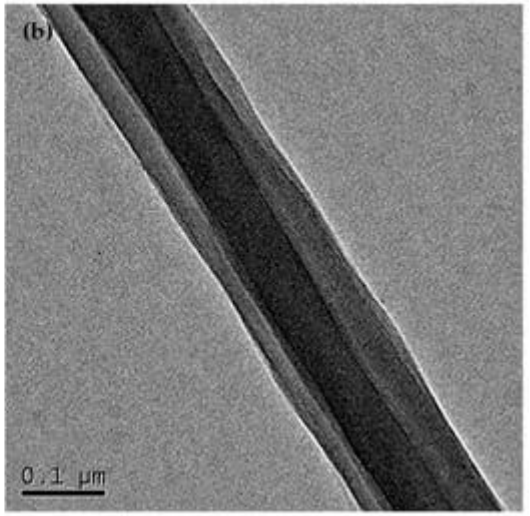
TEM

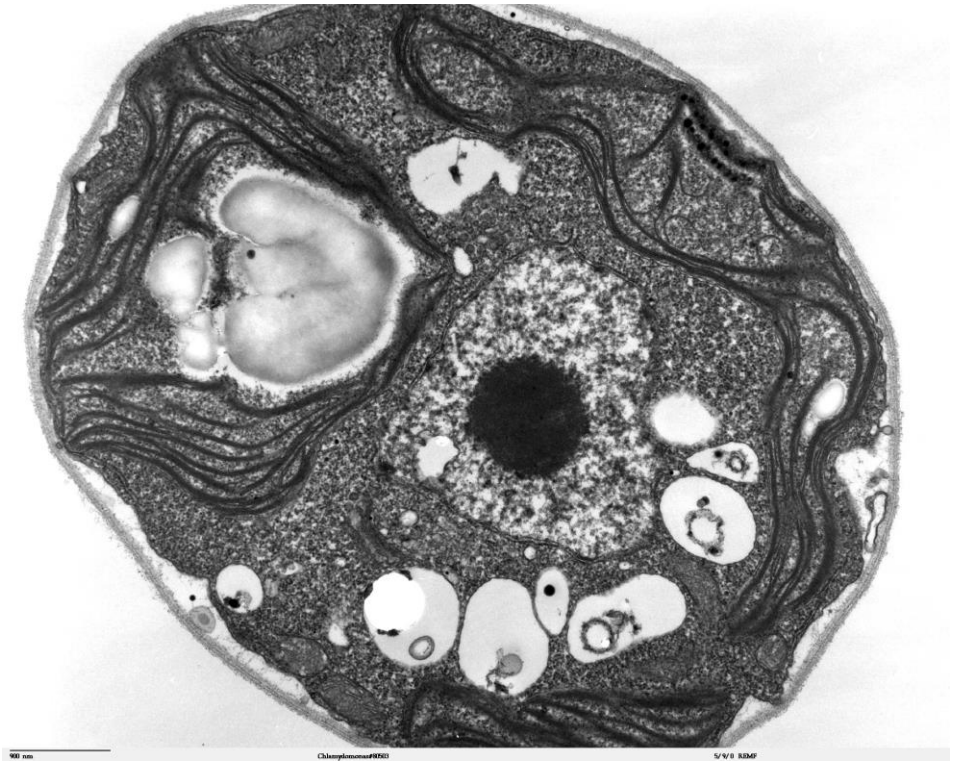
- Observation of samples up to a thickness of 100 nm at high magnification and with high resolution
- Uses a stationary electron beam
- Detection of electrons passing through the sample

- For:
  - Lateral sizes of objects
  - Morphology
  - Visualization of surface layers and modifications
  - Determination of phase composition
  - Confirmation of crystalline / amorphous character

TEM

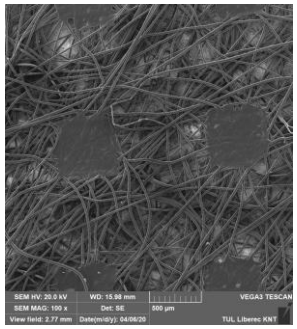




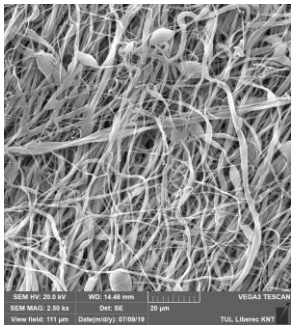


SEM

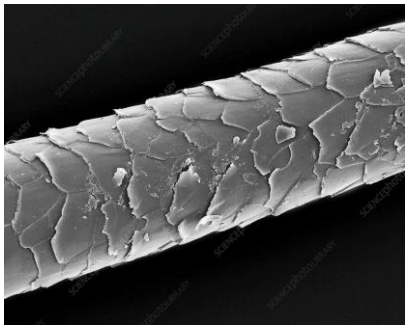
SMS



PCL



Lidský vlas



Sklo

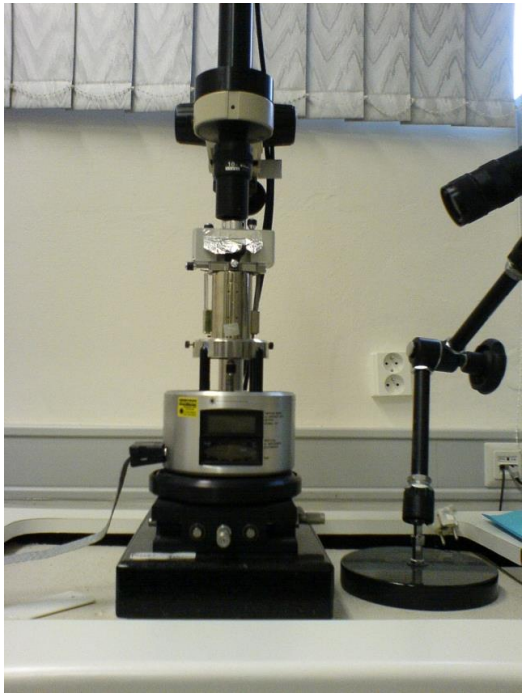
- Designed for observing the surfaces of samples
- It uses a moving electron beam
- Imaging the surface of the sample using reflected secondary electrons
- Advantage: in the interaction of accelerated electrons with the mass of the specimen, in addition to the secondary signal, X-rays, Auger electrons, cathodoluminescence are generated - they carry additional information about the specimen (elemental composition, quantitative representation of individual elements can be determined)

Comparison of TEM and SEM

- The basic difference between SEM and TEM is the location and properties of the preparation ("Massive" - SEM, "Thin" - TEM)
- SEM - electrons are primarily reflected back from the specimen
- TEM - electrons primarily pass through the specimen

Atomic force microscopy - AFM

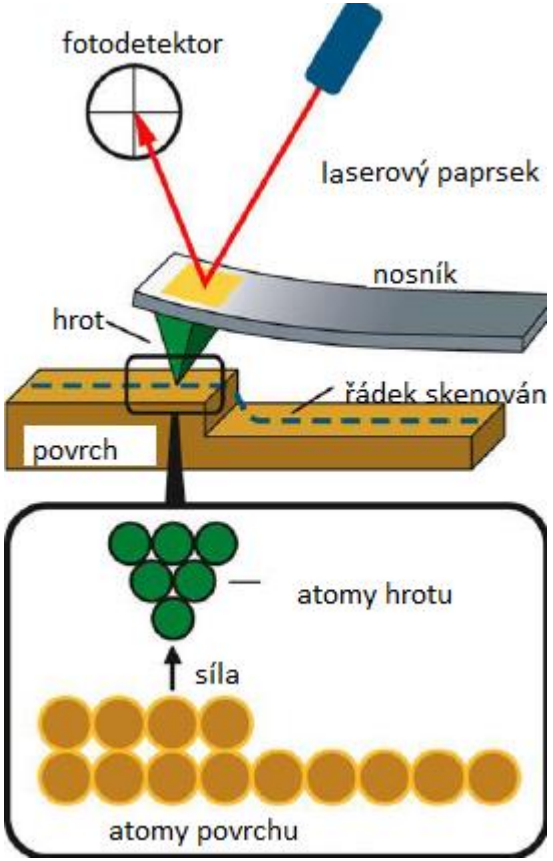
- Three-dimensional imaging of surfaces
- Very high resolution (hundreds of micrometers to nanometers)



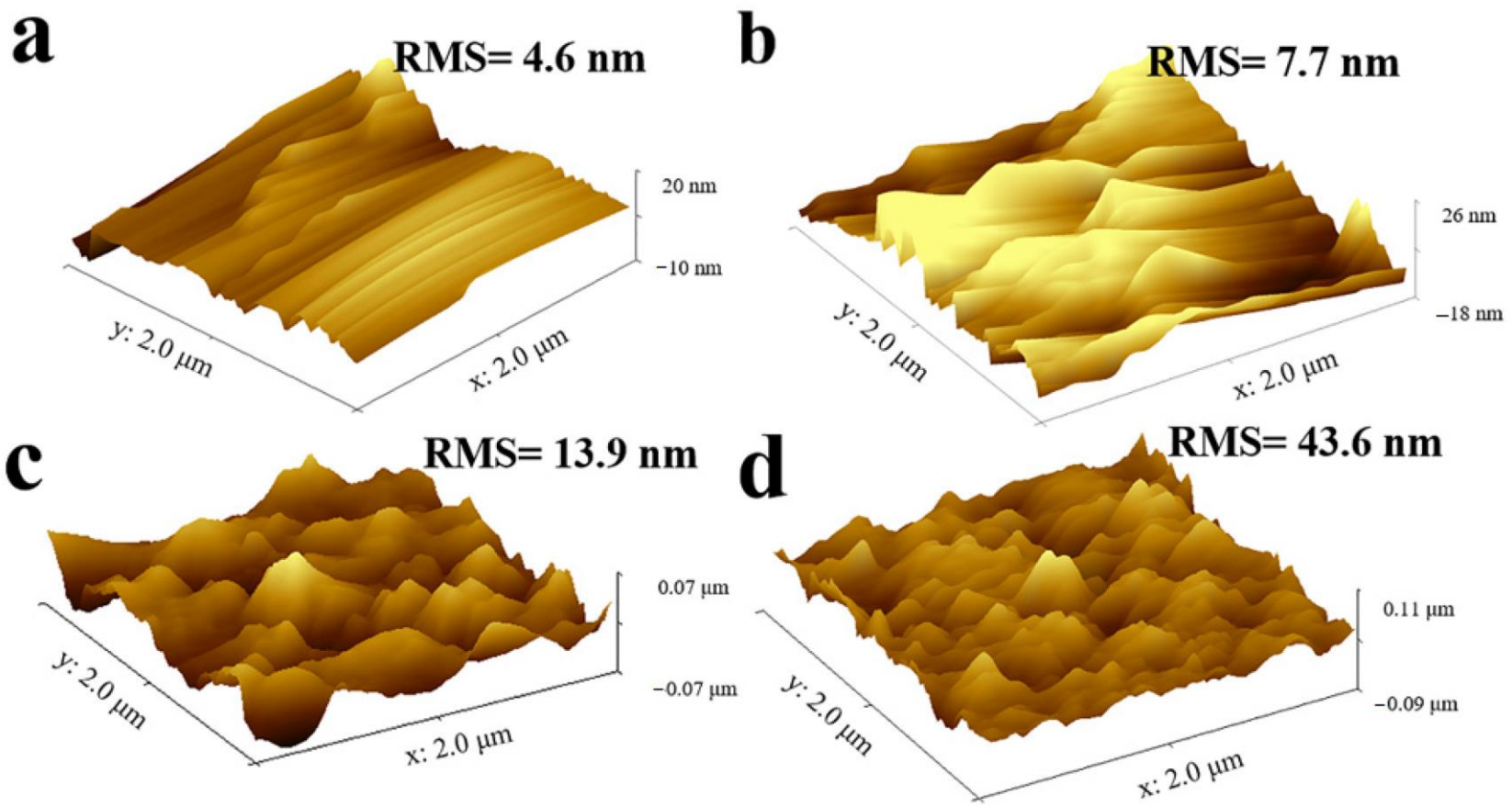
- Use:
  - display
  - creation of structures

Principle of AFM

- Detection of probe tip movement as it passes over the sample
- Maps the distribution of atomic forces on the sample surface
- The forces are caused by the close approach of the tip to the surface → the emergence of an attractive / repulsive force → causes the tip arm to bend
- Arm fluctuations are monitored by laser
- Advantage - possibility to study conductive and non-conductive samples



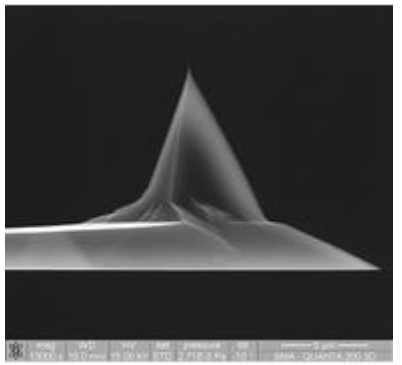
AFM

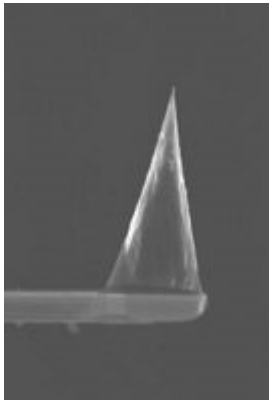


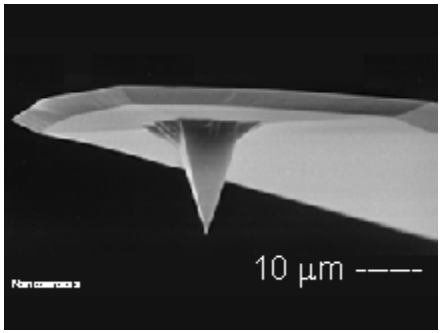
Atomic force microscopy (AFM) images of the fabrics: (**a**) pristine fabric, (**b**) PDMS-coated fabric, (**c**) PDMS/STA-coated fabric, and (**d**) PDMS/STA/SiO_2-coated fabric.

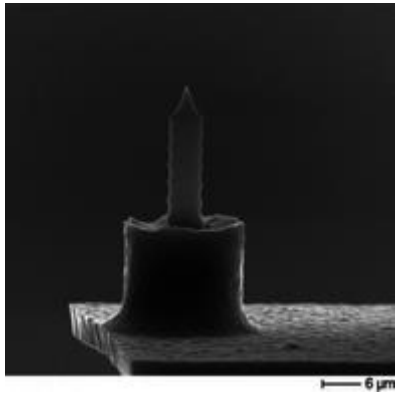
Principle of AFM

- The main element - the arm with the tip
- Tip length: several µm
- Tip radius: 10 - 50 µm
- Tip: silicon, silicon nitride
- Arm: important flexibility









AFM properties

- Scanning of small samples
- Electrically non-conductive samples can also be studied
- Displays the surface, not the volume structure
- Does not require sample adjustment
- Scanning is slow (min.)
- Large dispersion of usable environments (air, gas, solutions, magnetic field)

Differential scanning calorimetry - DSC

- Basic method of thermal analysis
- Investigation of thermal properties of material
- It is used to determine melting point, glass transition and crystallization
- Thermal processes are studied as a function of time or temperature during a defined temperature process
- Standard temperature range of the device: -100 - 600 °C

Principle of DSC

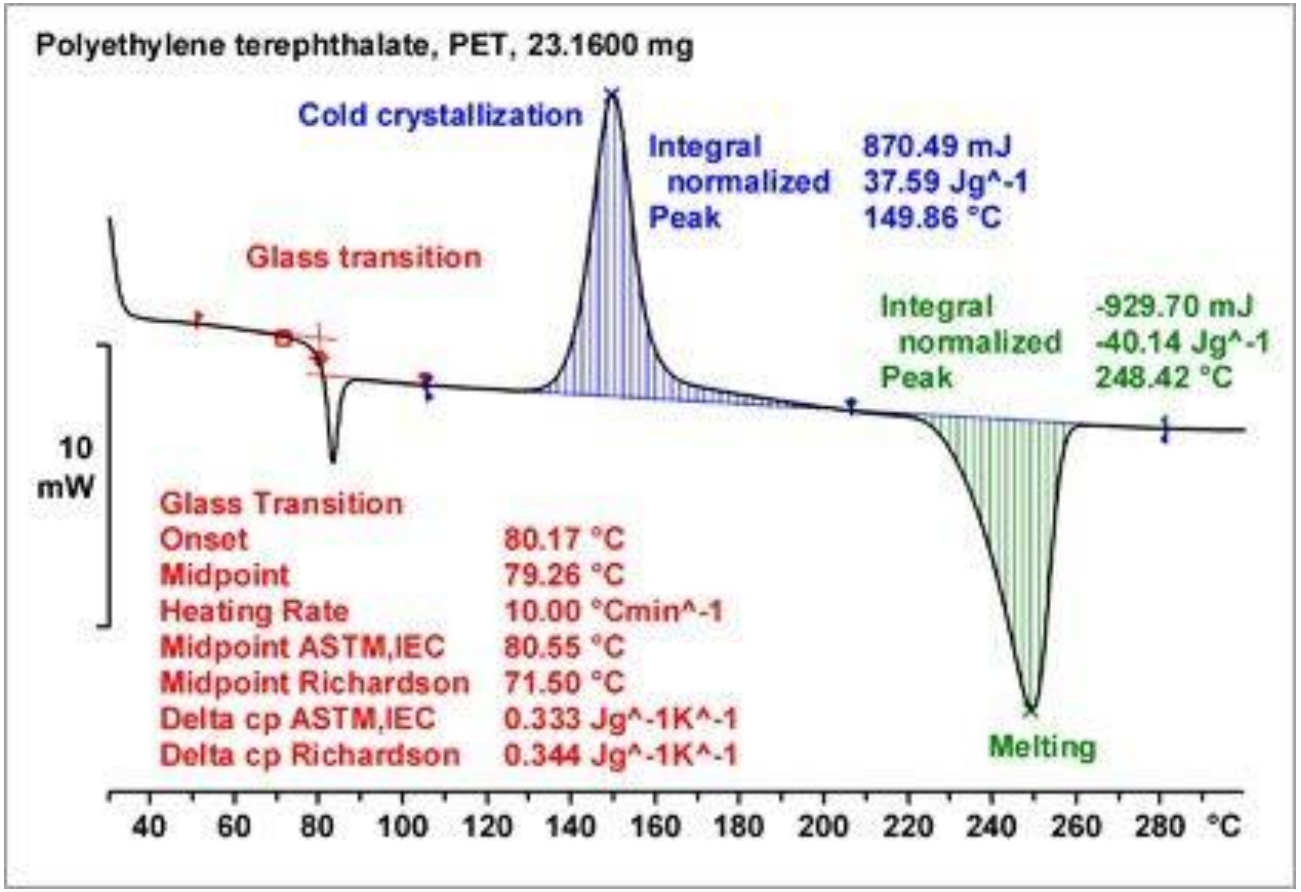
- DSC with power compensation
- Maintaining a zero temperature difference between the measured and the reference sample
- 2 separate measuring cells and 2 heat sources
- We measure the electrical power required to maintain a constant temperature of both samples

- DSC with heat flux
- We measure the temperature difference of the measured and comparative sample
- Both samples are in a common cell and are connected by a thermal bridge
- If we know the thermal resistance between the furnace, the measured sample and the reference sample, the heat flow from or to the sample is proportional to the temperature difference

Principle of DSC measurement

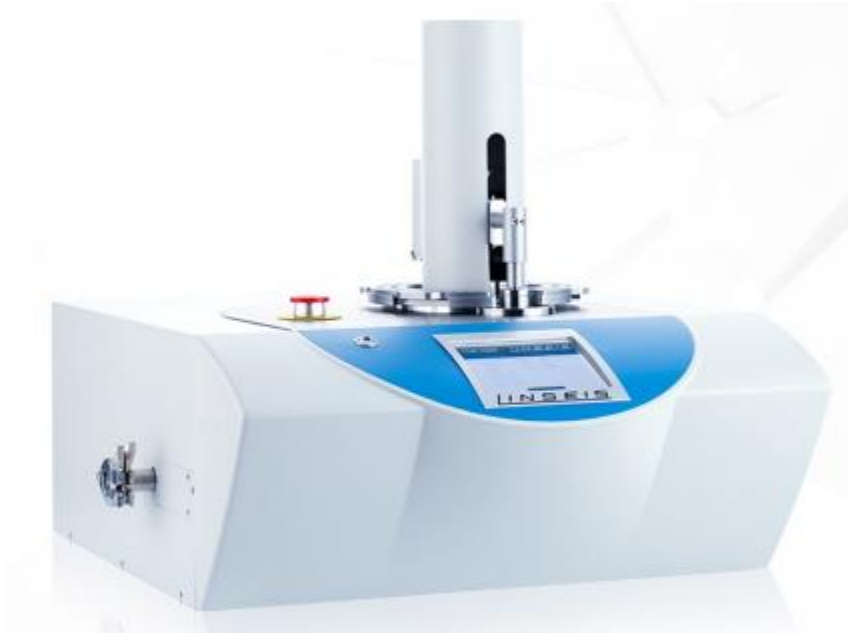
- The measured sample in the crucible is placed on a thermocouple in a calorimetric cell together with a reference sample which is placed on another thermocouple
- We choose: weight, temperature program, furnace atmosphere (N, H, Ar, O,…)
- Exothermic process - the heating of the measured sample slows down
- Endothermic process - the heating of the studied sample is accelerated
- Higher heating rate increases sensitivity, but reduces the possibility of event resolution

DSC


Polyethylene terephthalate, PET, 23.1600 mg
Cold crystallization
Integral 870.49 mJ
normalized 37.59 Jg^-1
Peak 149.86 °C
Glass transition
Integral -929.70 mJ
normalized -40.14 Jg^-1
Peak 248.42 °C
10 mW
Glass Transition
Onset 80.17 °C
Midpoint 79.26 °C
Heating Rate 10.00 °Cmin^-1
Midpoint ASTM,IEC 80.55 °C
Midpoint Richardson 71.50 °C
Delta cp ASTM,IEC 0.333 Jg^-1K^-1
Delta cp Richardson 0.344 Jg^-1K^-1
Melting
40 60 80 100 120 140 160 180 200 220 240 260 280 °C

Thermogravimetric analysis - TGA

- Basic method of thermal analysis - dynamic analytical method
- It studies changes in weight as a function of temperature
- Determination of material

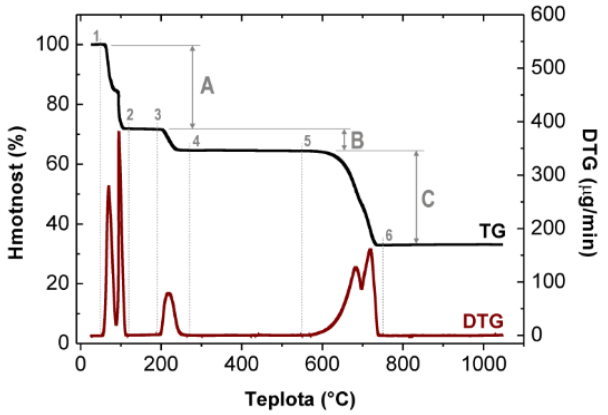


TGA measurement principle

- The sample in the crucible is placed on the thermal scales in the oven of the thermal analyzer
- We choose: sample weight, temperature program, furnace atmosphere and flow
- Thermogravimetric curve:
- Determination of partial and total weight loss of thermal decomposition
- Determination of decomposition temperature of substances
- Study of reaction kinetics of individual processes of thermal decomposition

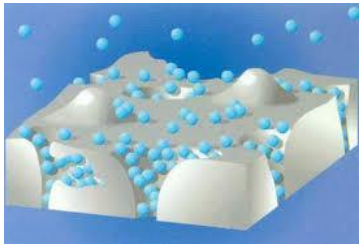
TG curve

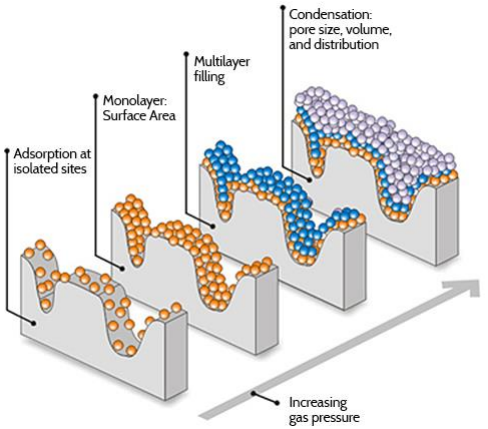
- Loss of crystal-bound molecules of water and other solvents
- Sublimation
- Drying
- Evaporation of volatile components
- Desorption and absorption of gases
- Oxidation of metals
- Thermal decomposition in an inert atmosphere
- Heterogeneous chemical reaction



Determination of specific surface area by BET method

- Adsorption - the accumulation of particles (atoms, molecules) of a gas, liquid or solid on the surface (phase interface) by the effect of interfacial attractive forces
- Physisorption - gas or liquid molecules are bound to the surface of a solid by physical forces (van der Wals)





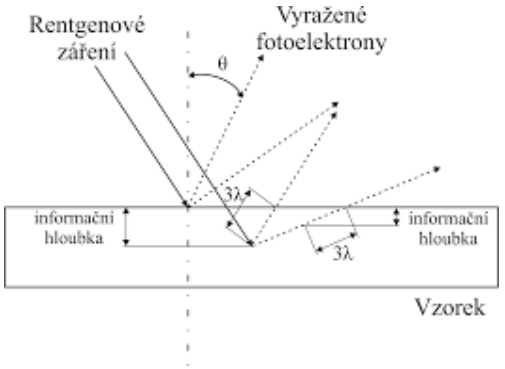
Principle of BET

- Determination of the dependence of the adsorbed amount of gas on the equilibrium pressure
- After heating in vacuo, small portions of gas are gradually added
- The amount of gas adsorbed on the surface is measured
- When creating a molecular monolayer, the specific surface area can be calculated - knowledge of the area occupied by one molecule and the number of adsorbed molecules
- Further adsorption - formation of multilayers
- After complete filling of the pores, the total pore volume can be determined (knowledge of adsorbate density)
- Hysteresis evaluation - determination of pore shape

X-ray photoelectron spectroscopy XPS

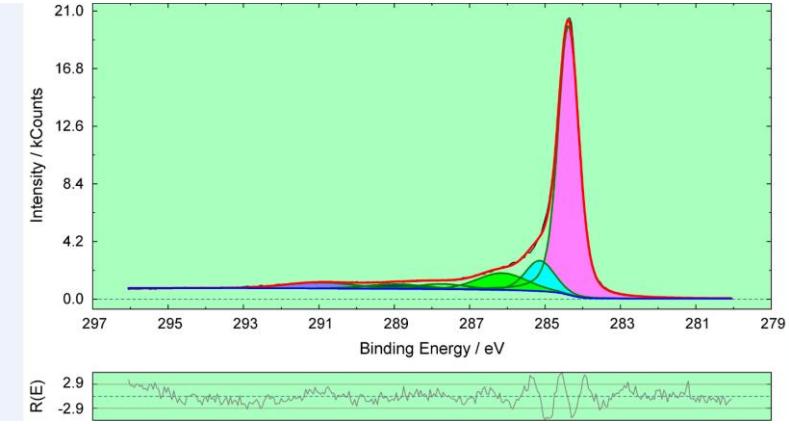
- It examines the chemical composition and surface condition of solids
- Relatively simple technique with easy evaluation of results
- The method is non-destructive (the sample can be used repeatedly)

Principle of XPS



- The examined sample is irradiated with X-rays, causing the emission of photoelectrons from the surface of the sample
- Photoelectrons undergo both elastic and inelastic collisions with atoms in the sample
  - Inelastic collision - the photoelectron continues to fly in the original direction, but loses its energy
  - Elastic collision - energy does not change, the direction of flight changes
- The photoelectrons that leave the sample are detected in the appropriate direction by the analyzer - they measure the intensity of the photoelectrons depending on their kinetic energy

XPS



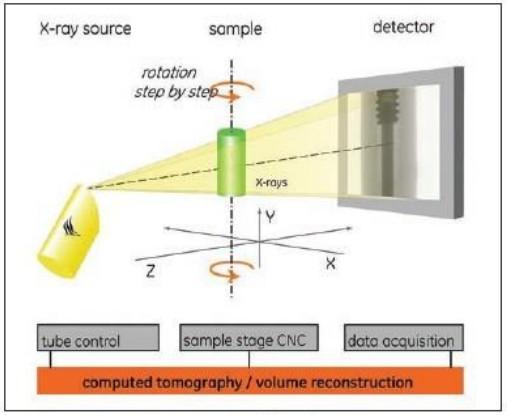
- The result is a photoelectron spectrum - the dependence of intensity on energy (kinetic / binding)
- Spectral lines (peaks) - identification of elements in the sample
- It is possible to determine chemical compounds in which the binding energy of the photoelectron changes
- Quantitative analysis - relative concentrations of elements and compounds in the sample

XPS

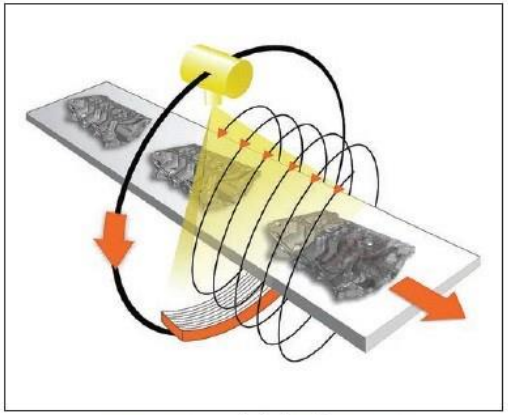
- All elements except H and He can be measured
- Photoelectrons are released only if they are embossed at a depth of up to about 10 nm
- Problem when measuring non-conductive samples - charging
- Industrial applications - polymer surface modification, catalysis, corrosion, adhesion,…

Computed tomography - CT

- Measurement of X-ray absorption by a measured object using many projections and computer image processing
- The industry mainly uses cone beam scanning
- In medical practice - helical scanning



Obr. 1 CT – kuželový svazek

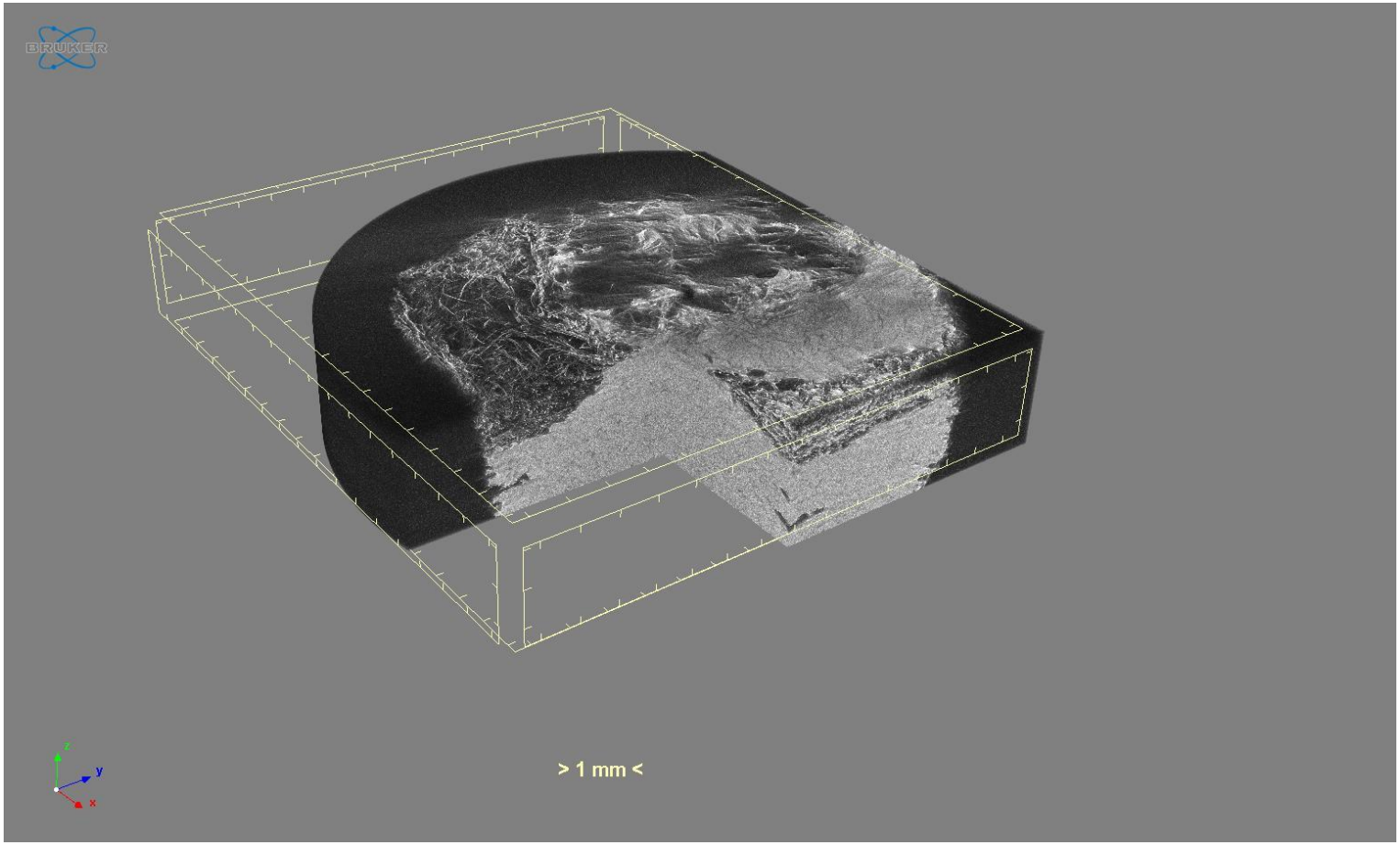


Obr. 2 CT – snímání po šroubovici

Principle of CT

- The X-ray machine emits a narrowly collimated beam of radiation in the shape of a fan, which passes through the examined object and is registered by a set of detectors that convert the passed quantum of X-rays into an electrical signal, which is digitized and further processed.
- Within 1 cycle (360°), the system obtains 400 - 700 projection measurements of the absorption of a given object from different angles
- Computed tomography is a method presenting an image of a specific layer of the examined object with a predefined thickness, which is given by the collimation of the primary beam.

CT



Thank you for your attention!

TEST

- Explain the difference between scanning and transmission electron microscopy.
- What is the purpose of atomic force microscopy (AFM)?
- Draw and describe the curve from the DSC measurement.
- Describe the principle of computed tomography (CT)?