



FKITMCMXIX

Sveučilište u Zagrebu
Fakultet kemijskog
inženjerstva i tehnologije



Thermal analysis methods

Workshop, postgraduate course of study
Kemijsko inženjerstvo i primijenjena kemija

Prof. dr. sc. Jelena Macan

Plan of the workshop

- Introduction to thermal analysis, the methods
- Break
- Experimental parameters
- Break
- Examples of curve analysis, applications, kinetics

What is thermal analysis (TA)?

How a property is connected to temperature while the sample is heated/cooled in controlled manner.

Proučavanje veze svojstva tvari i njezine **temperature** dok se uzorak **kontrolirano** zagrijava ili hladi.

(definicija ICTAC-a, *International Confederation for Thermal Analysis and Calorimetry*)

TA Methods

- **TGA:** Termogravimetrijska analiza / Thermogravimetric analysis
- **DSC:** Diferencijalna/razlikovna pretražna kalorimetrija / Differential scanning calorimetry
- **DTA:** Diferencijalna/razlikovna toplinska analiza / Differential thermal analysis
- **TMA:** Termomehanička analiza / Thermomechanical analysis
- **DMA:** Dinamička mehanička analiza / Dynamical mechanical analysis
- **EGA:** Analiza oslobođenih plinova / Evolved gas analysis

TA Methods

Vezane tehnike / Coupled techniques:

- DSC-TGA
- TGA-EGA
- TMA-DTA

TA Methods

- I još... / Also...

TD: (termo)dilatometrija / dilatometry

DEA: dielektrična toplinska analiza / dielectric thermal analysis

TSC: toplinski potaknuta struja / thermally stimulated current

TOA: termooptometrijska analiza / thermooptometric analysis

TL: luminiscencija / thermoluminescence

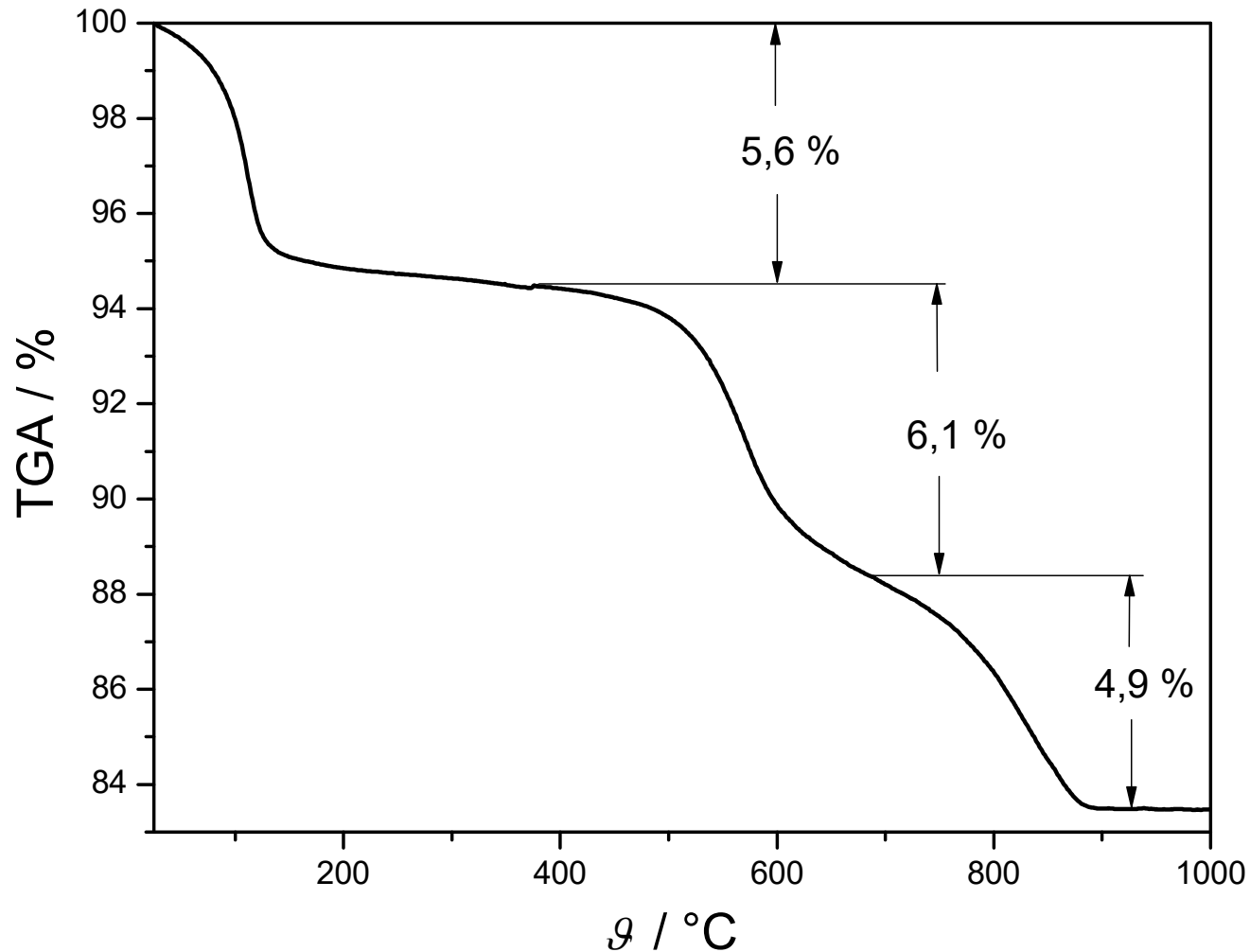
- Spectrometry, microscopy, acoustic methods...

Which methods do you know?

- From the literature...
- Are available where you work...
- You worked with them yourselves...

Think – which methods would be useful to you?

TGA



Step ID: together with DSC or DTA, EGA

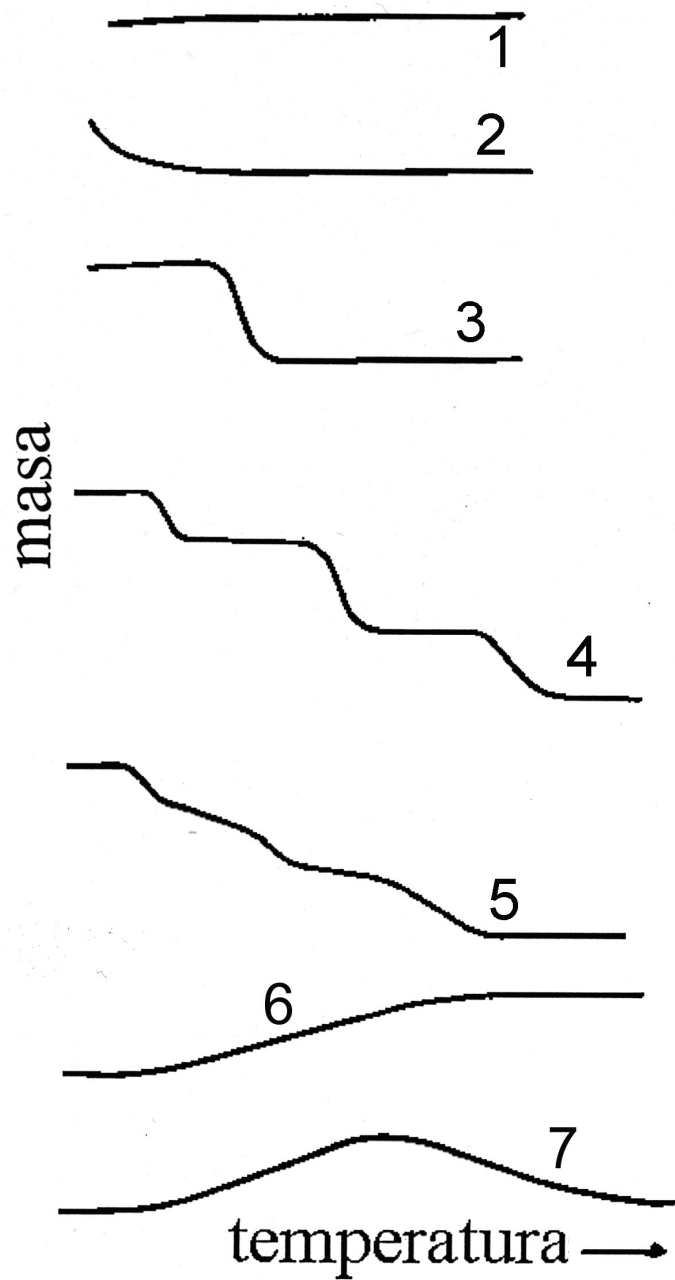
TGA – applications

Reakcije čvrsto/plinovito / Solid-gas reactions:

- Toplinska razgradnja u inertnoj ili reaktivnoj atmosferi / Thermal degradation
- Oksidacija metala (porast mase) / Oxidation

Sastav / Composition:

- Udio hlapive komponente (vlage, aditiva) / volatiles
- Udio gorive komponente / combustibles
- Udio anorganske komponente (pepela) / ash



Typical TGA curves:

(1) no change

(2) desorption, drying

(3) one step degradation

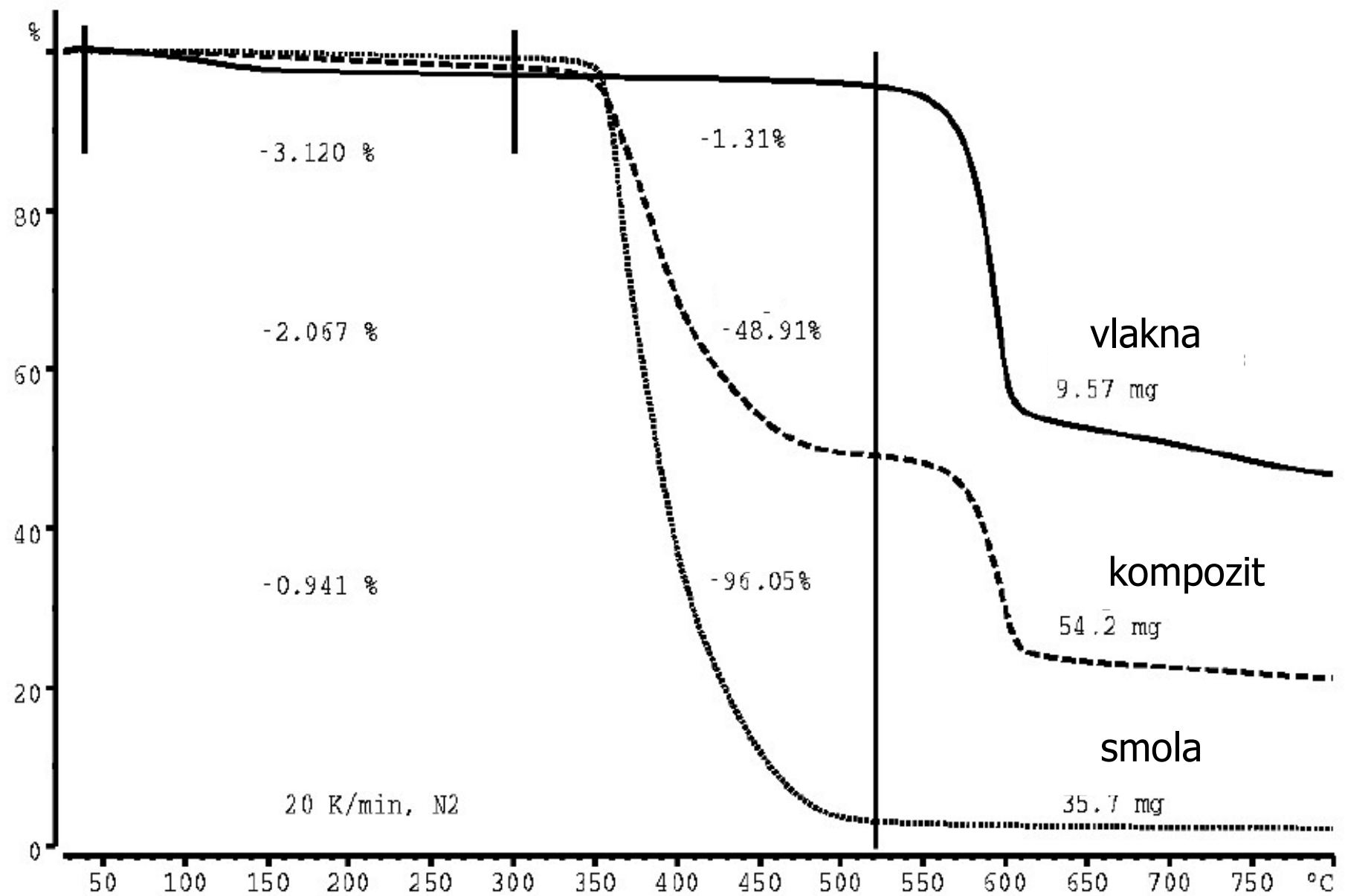
(4) several step degradation

(5) same as (4) but without intermediates or fast heating

(6) reaction with atmosphere

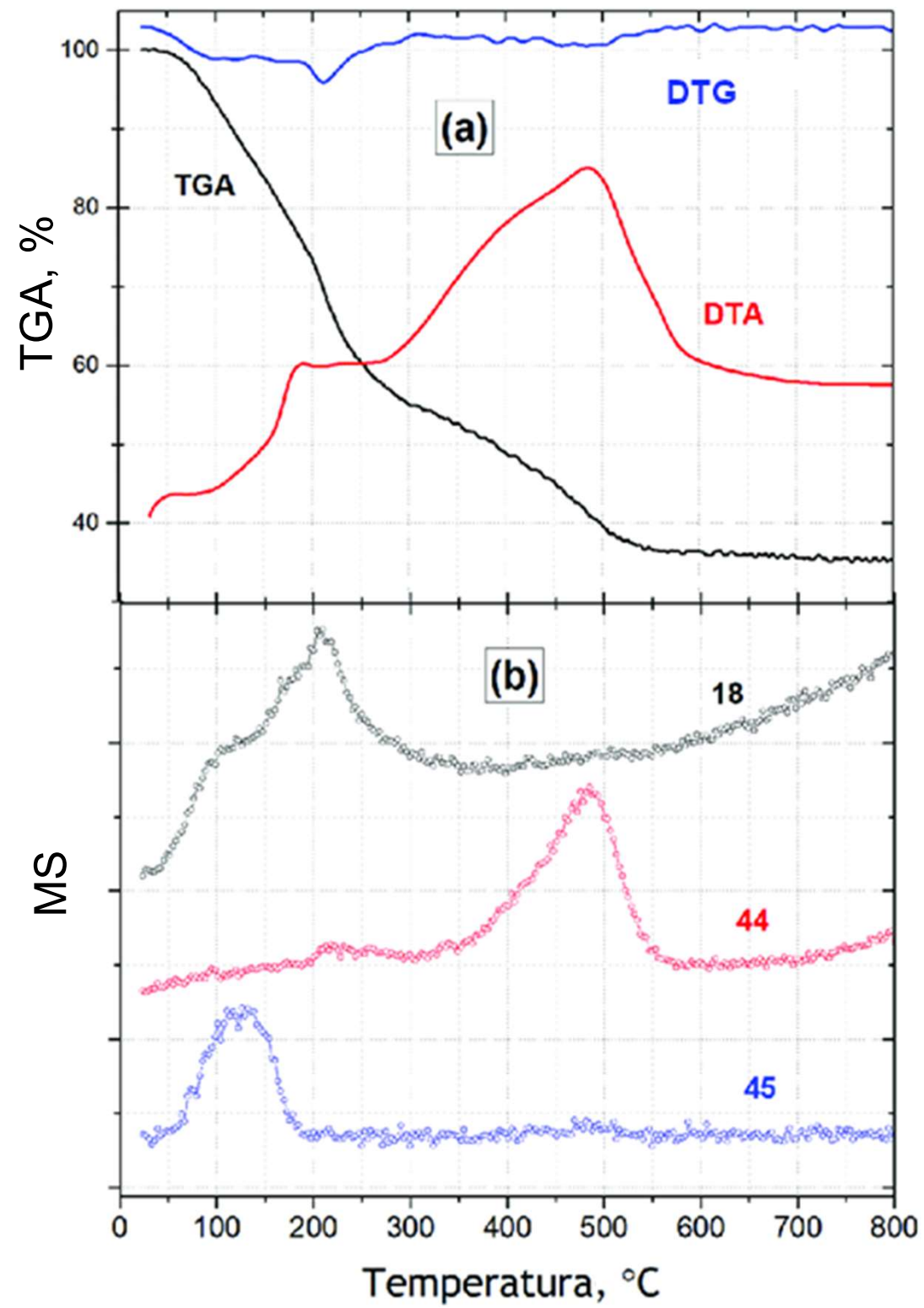
(7) same as (6) but the products degrade at higher temperature

TGA



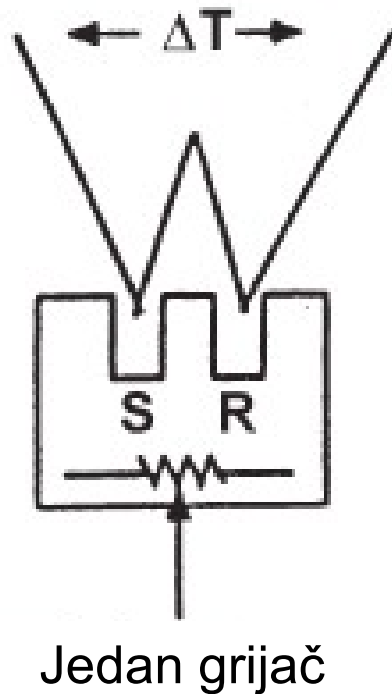
EGA

- Povezivanje TGA s FTIR, MS ili GC koji služe kao detektori i analizatori oslobođenih plinova / detection and analysis of evolved gases
- Točno definiranje reakcija/pojaava na TGA krivulji (pomaže i analiza ostatka!) / ID of TGA effects
- Instrumenti povezani vrućom kapilarom: metalnom ili od kvarcnog stakla / hot capillary
- Integrirana krivulja količine plina: Gram-Schmidt integrated curve



	FTIR	MS	GC/MS
Istovremeno	Da	Da	Ne
Granica detekcije	normalna	visoka	vrlo visoka
Uzorak	svi oslobođeni plinovi	rascijepljeni plinovi	uhvaćeni plinovi
Identifikacija: plinovi male <i>M</i>	Da (osim IR inertnih plinova)	Da	zahtjeva skupljač plina
velike <i>M</i>	Da	problematično (ionizacija)	Da (velika točnost)
Noseći plin	bez ograničenja	helij	bez ograničenja
Poveznica	kapilara	kapilara uz vakuum	posebni mehanizam
Općenita ocjena	lako povezivanje, dobro za identificiranje	pogodno za praćenje određenog poznatog nastalog plina	najbolja za identifikaciju mješavine, dobra za mikroanalizu

DTA



Mjerni i referentni uzorak
Measured and reference sample



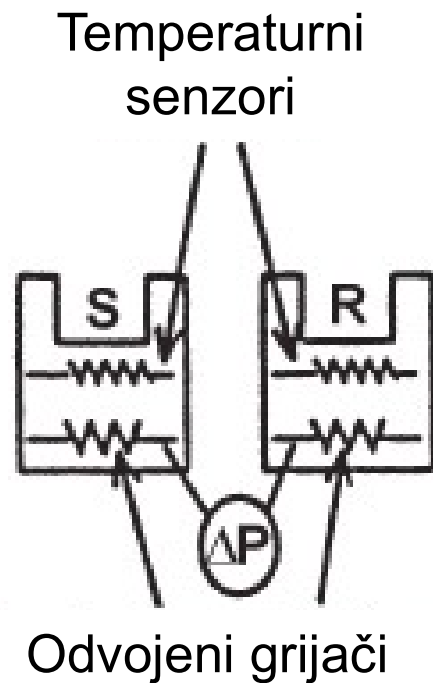
Razlika temperature, bliski kontakt termopara
s uzorkom

Temperature difference, close contact with the
sample



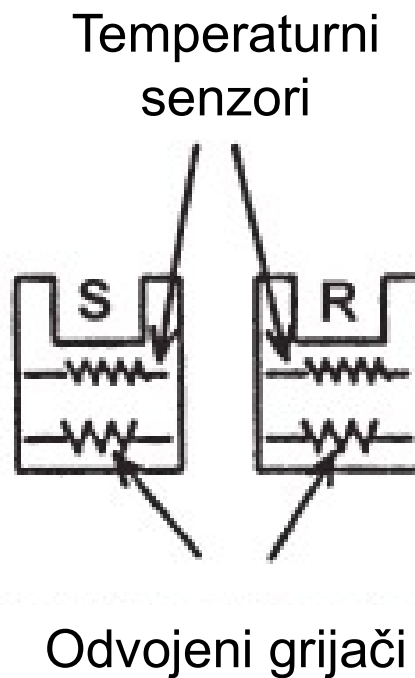
DTA-TGA

DSC



Kompenzacija
snage

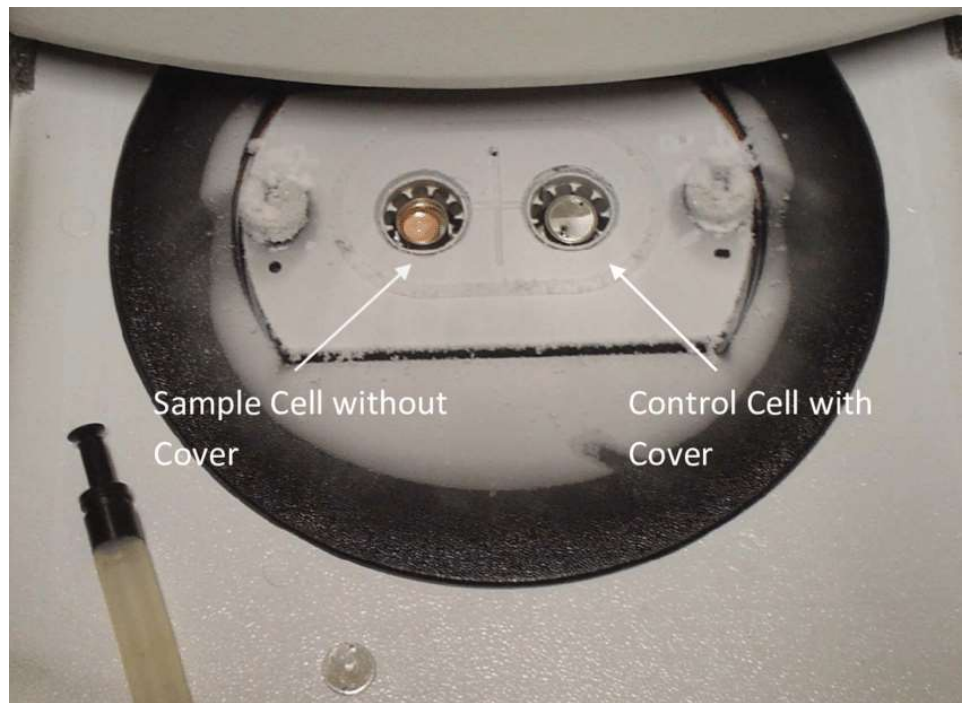
Power compensation

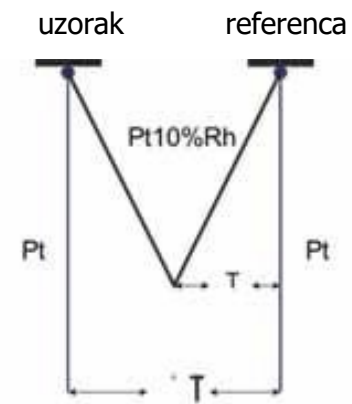
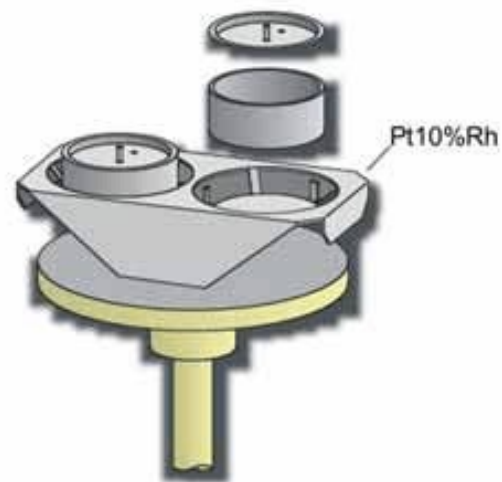


Toplinski
tok

Heat flux

Mjerni i
referentni
uzorak





DSC-TGA

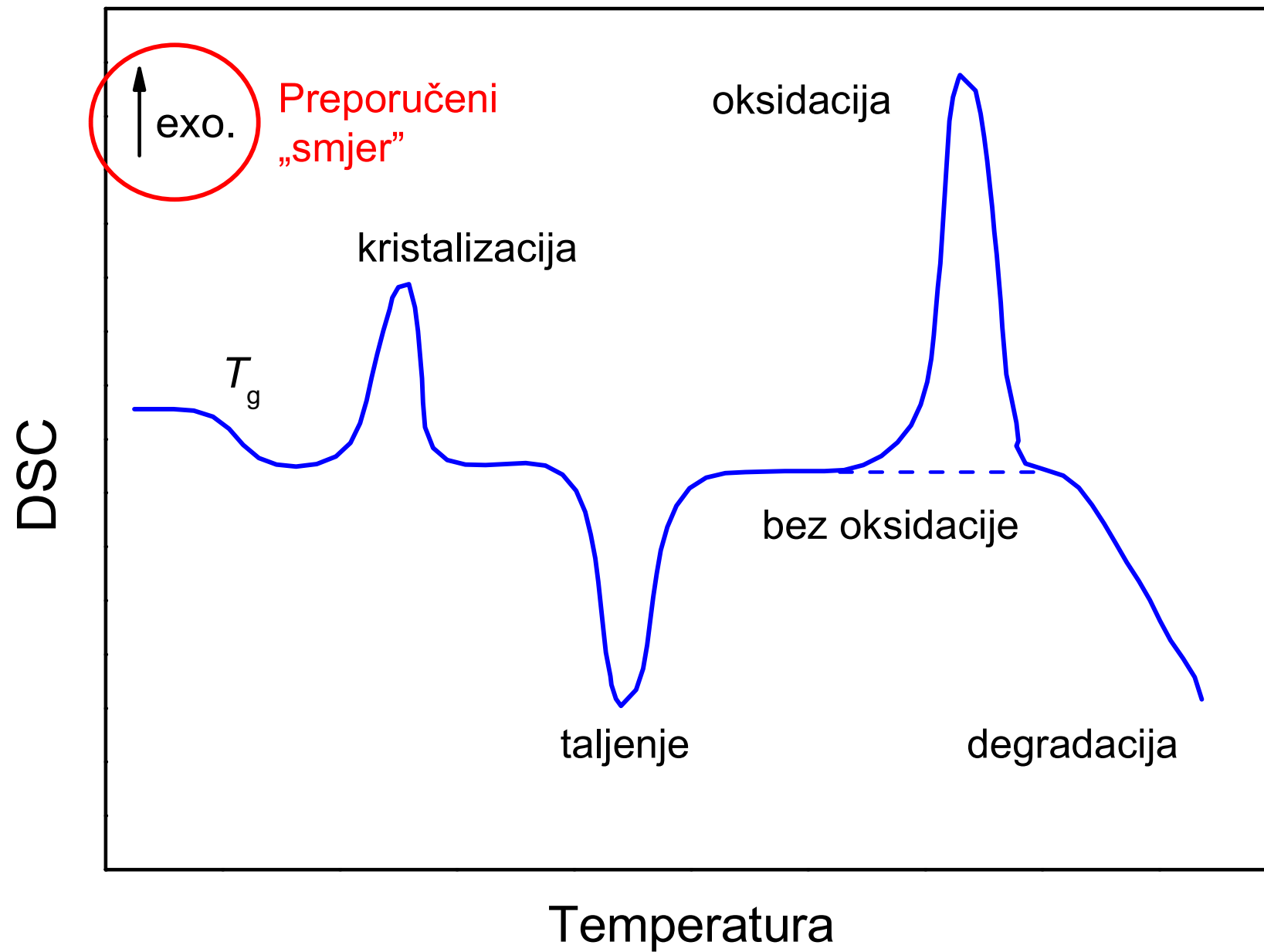
DTA ili DSC?

DTA

- Robusnija / More robust
- Više temperature (danas i DSC) / Higher temperatures
- Bliski kontakt termopara i uzorka / Close contact

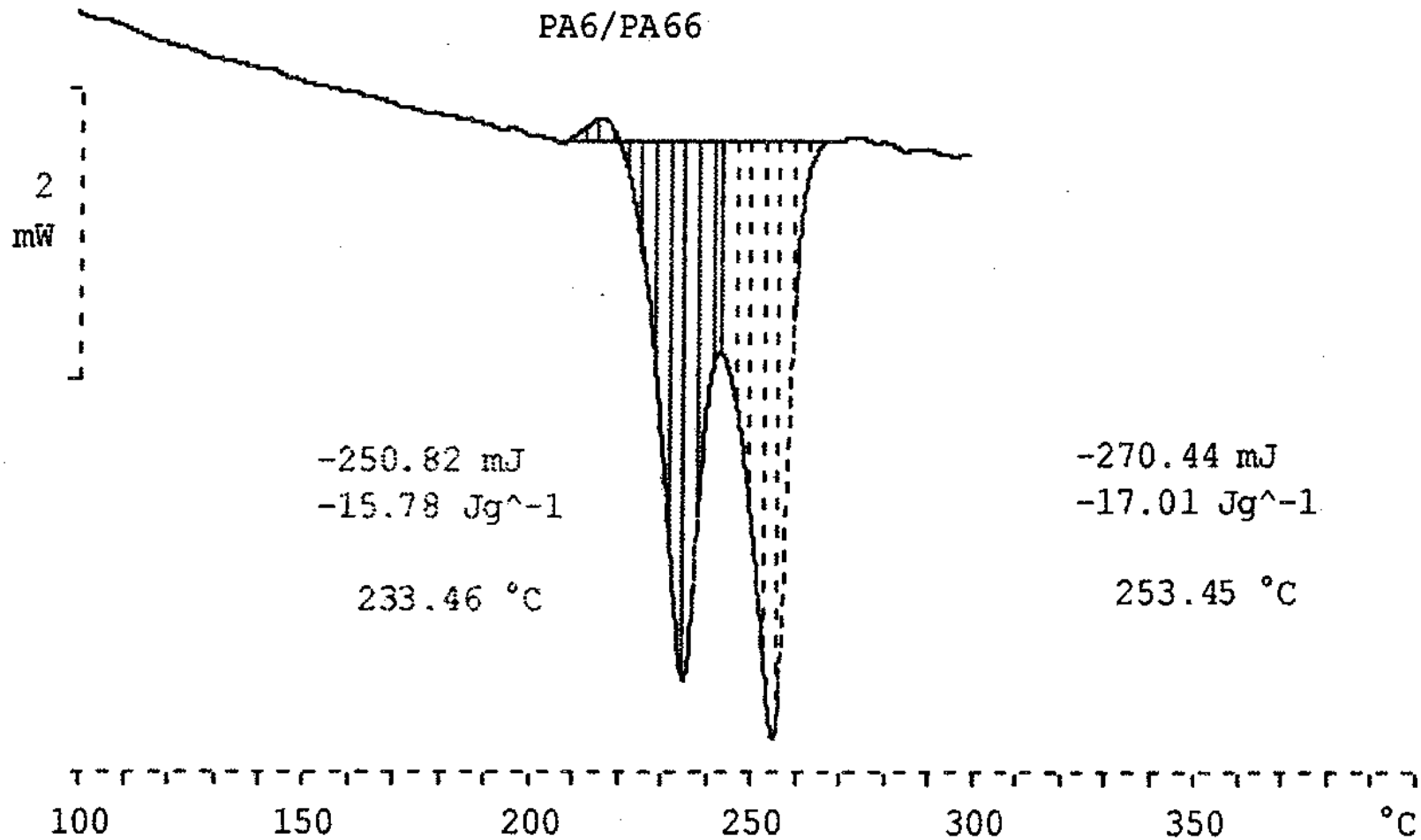
DSC

- Osjetljivija, manji utjecaj postavki / More sensitive
- Prikladnija $< 500\text{ }^{\circ}\text{C}$ / Better at $< 500\text{ }^{\circ}\text{C}$
- Izravno mjerenje entalpija i C_p / direct enthalpies and capacities



DSC and DTA applications

- Kemijske reakcije i druge fizikalno-kemijske promjene / Physical and chemical changes
- Staklišće, toplinski kapacitet / glass transition, capacity
- Talište (onset vs. maksimum), čistoća uzorka, kristalnost i kristaliziranje / melting point, purity, cristalinity



Udjeli u polimernoj mješavini /
Polymer blend composition
(mješljivost/miscibility: T_g !)

Quantitative DSC

Površina ispod maksimuma:

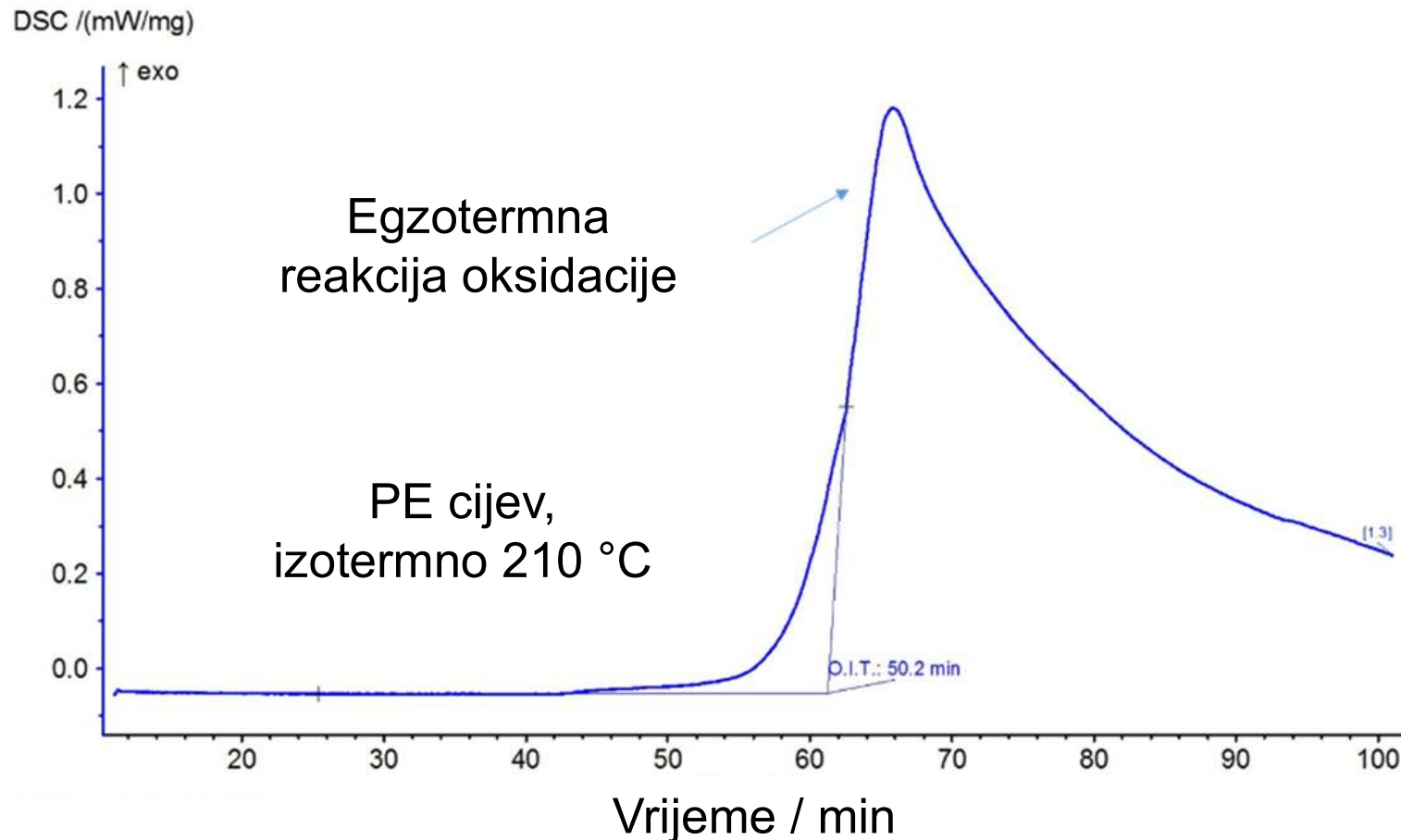
$$A = \frac{n \Delta H_m}{g \lambda}$$

λ – toplinska provodnost! (praškasti, porozni... atmosfera oko uzorka!)

g – faktor oblika maksimuma

DSC: OIT

- Oxidation induction time (from time atmosphere switches to oxidative)



Photocalorimetry in DSC

- Exposing the sample to light of certain wavelength & duration, photoinduced reactions (polymerization etc.)
- Suscebility of food and pharmaceuticals to light (also pre-treatment of samples prior to classical DSC measurement)
- Both crucibles exposed to the same intensity of light by splitting the same source

Thin / tiny samples methods

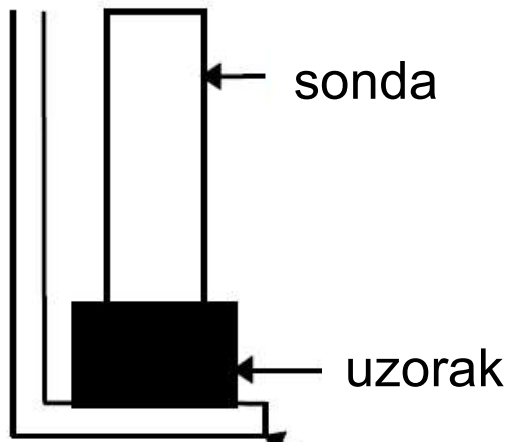
- DSC for samples $< 1 \mu\text{g}$, very fast heating/cooling rates: characterization of metastable states
 - Samples straight to sensor – single-use sensors!
- Influence of surface and sample size on properties, kinetics etc.

Examples of DSC and TGA analysis

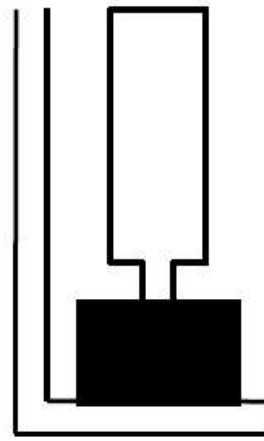


primjeri

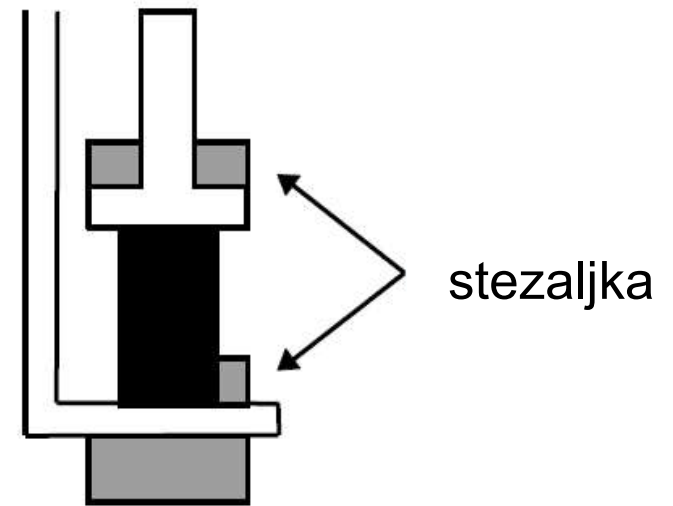
TMA



a) širenje/tlačenje



b) prodiranje



c) istezanje

Constant strain on sample:
compressive, extension, bending, torsion
(must be defined) and measuring deformation

TMA – applications

- Toplinsko širenje i stezanje / expansion and shrinking
 - Bubrenje u otapalima / swelling
 - Mekšanje i staklišće /softening and glass transition
 - Toplinska postojanost / Thermal stability
 - Puzanje i relaksacija u materijalu /Creep and relaxation
- ...anything that includes changes in dimension.

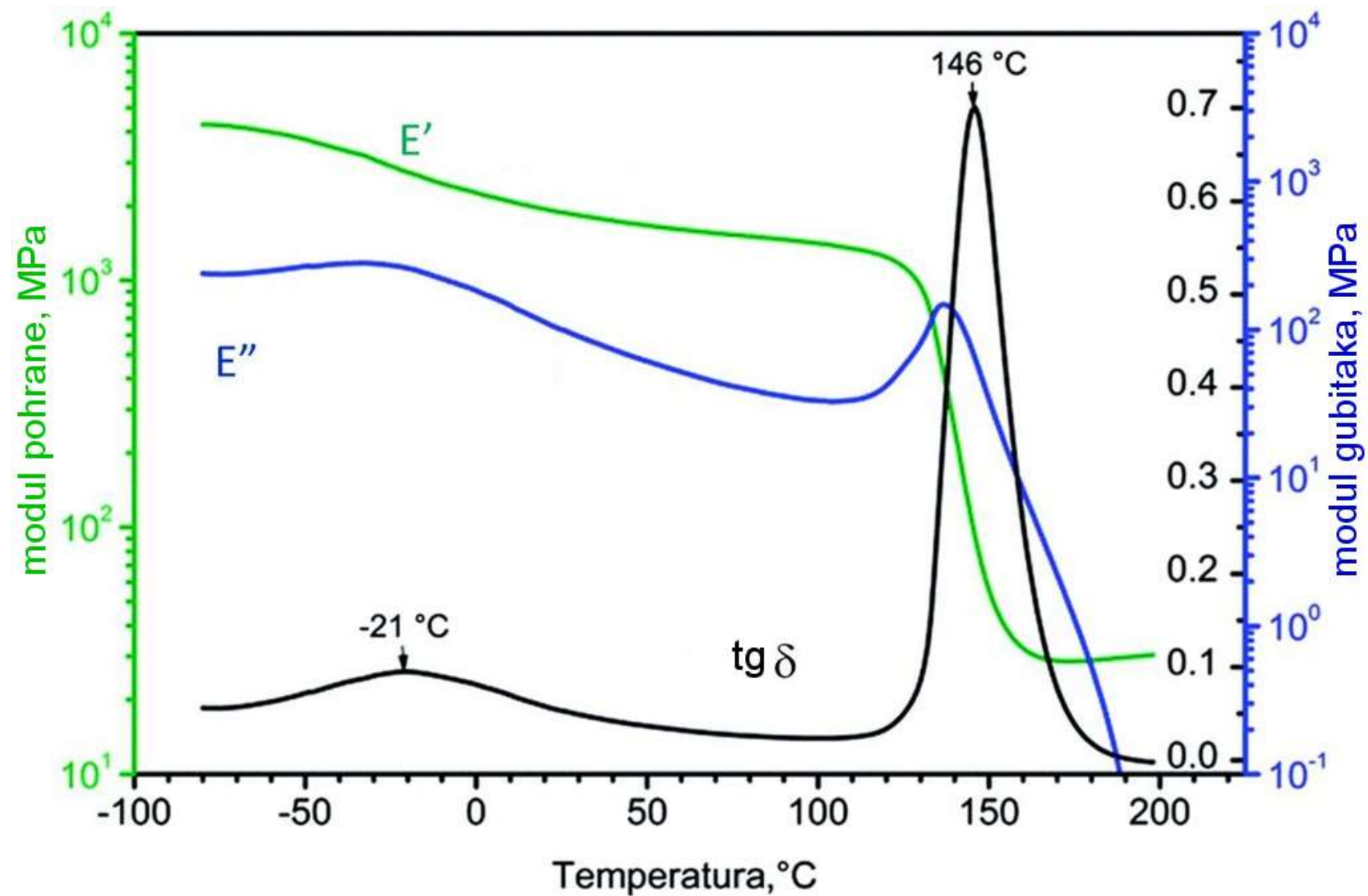
DMA

Oscillating (sinusoidal) excitation – viscoelastic properties:

- Modul pohrane / storage modulus, E' (in phase, elastic)
- Modul gubitaka / loss modulus, E'' (out of phase, viscous)
- Tangens gubitaka / loss tangent, $\tan \delta = E''/E'$

$$\sigma = \sigma_0 \sin(\omega t + \delta)$$

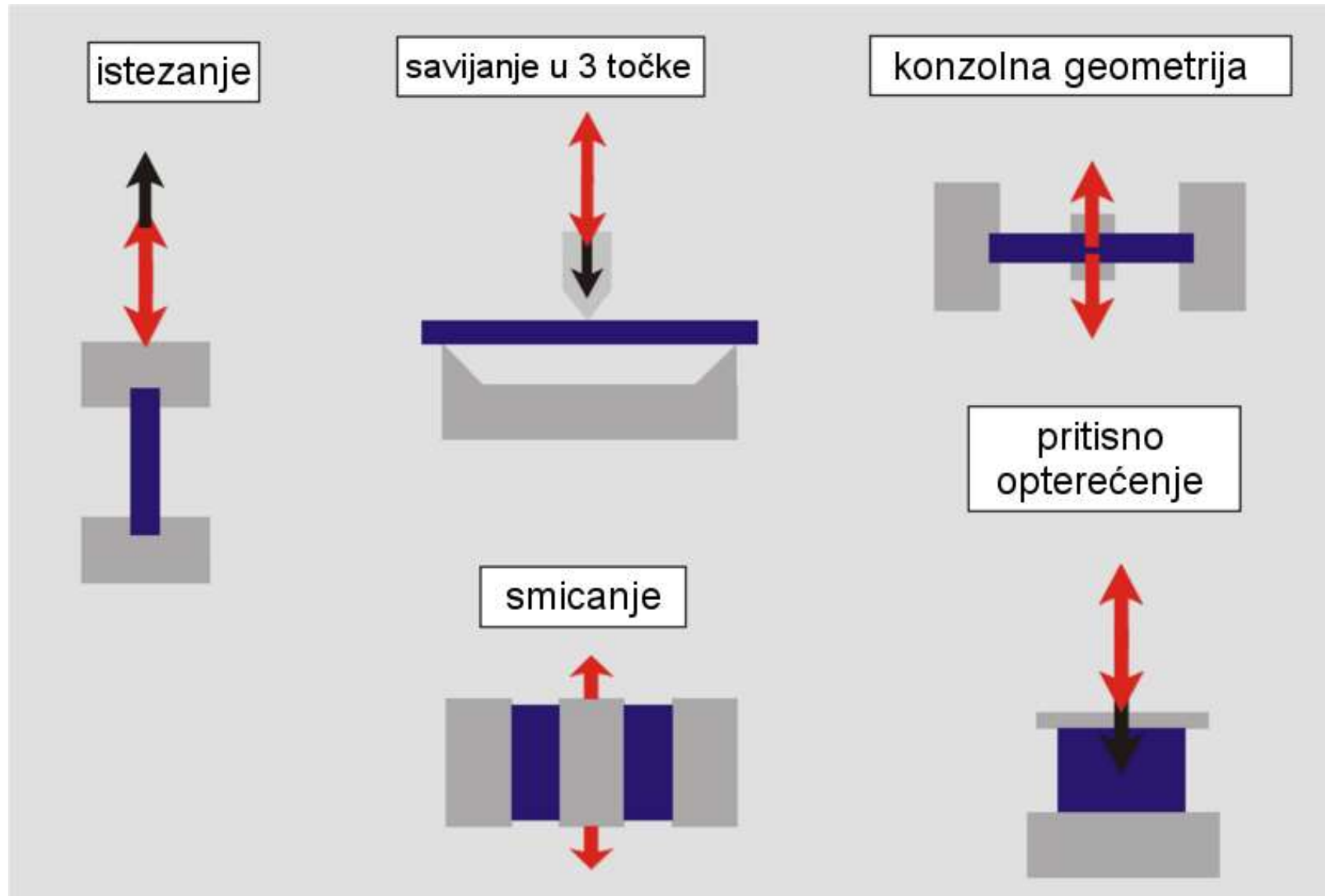
DMA



DMA

- Osim pri stalnoj (niskoj) frekvenciji, može i snimanje pri stalnoj temperaturi uz variranje frekvencije / constant or varying frequency
- Kutna frekvencija / Angle frequency:
$$\omega = 2\pi f$$
- Most often tensile and shear stress

DMA



DMA – applications

- Moduli
 - Staklišta / Glass transition
 - Međumolekulne interakcije polimera / Intermolecular interactions
 - Starenje i toplinska razgradnja / Aging and thermal degradation
 - Prigušno ponašanje / Damping
 - Otpornost na trošenje / Wear resistance
- Prvenstveno za polimere. / Polymers mostly.

TMA or DMA

- Noviji TMA također mogu raditi pod dinamičkim opterećenjem, analogno DMA (*dynamic load* TMA)
- TMA je osjetljiviji na male pomake, DMA može nametnuti jaču deformaciju uzorku
- Instrumenti optimirani za svoj glavni način rada, ali mogu zadovoljiti i u alternativnom

(Thermo)dilatometry

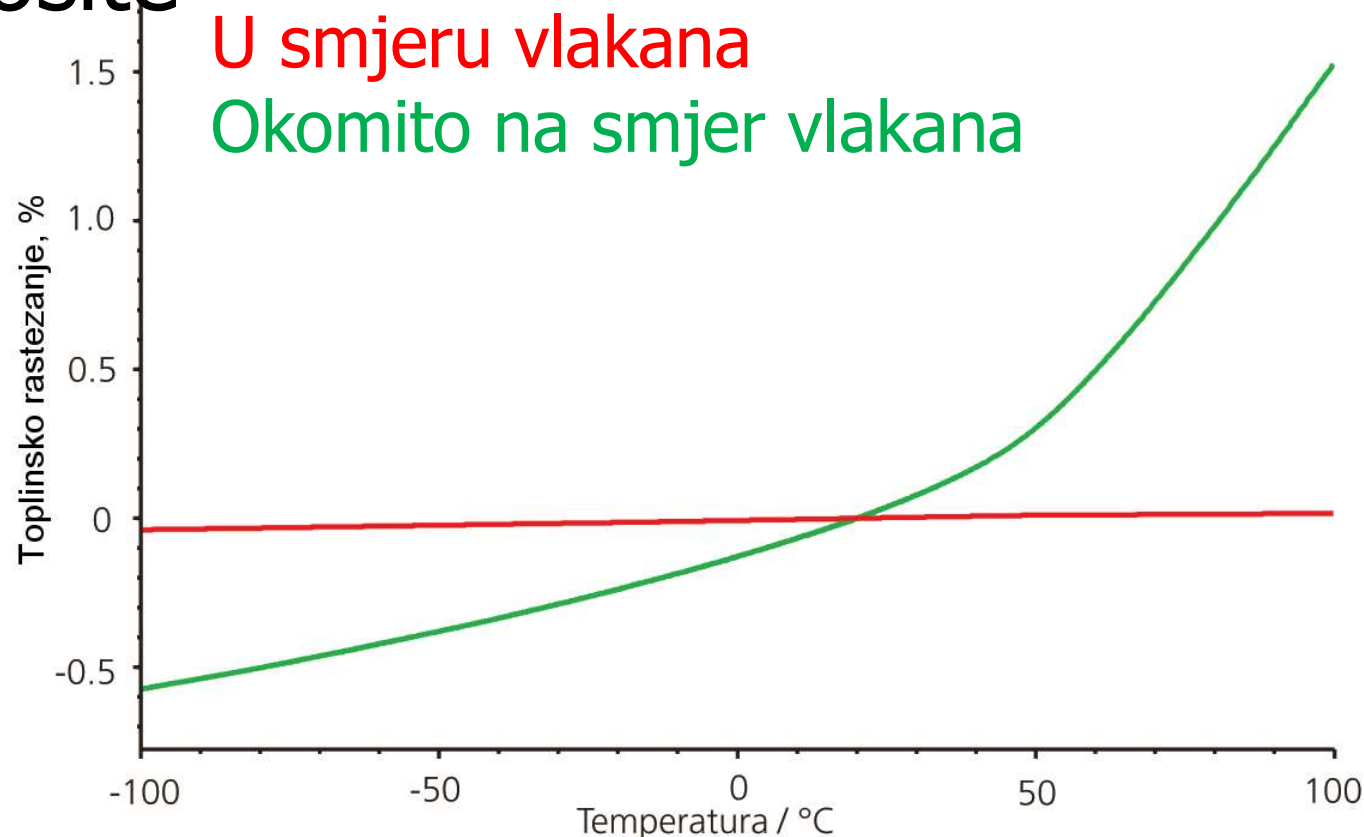
- Promjena volumena ili (češće) duljine uzorka zagrijavanjem / changes in volume or length
- Koeficijent toplinskog rastezanja / Thermal expansion

$$\alpha(T)_{p=\text{konst}} = \frac{1}{L_0} \cdot \frac{\partial L}{\partial T}$$

- Baždarenje materijalom poznatog α pod jednakim uvjetima da se odredi rastezanje nosača / Calibration with known α

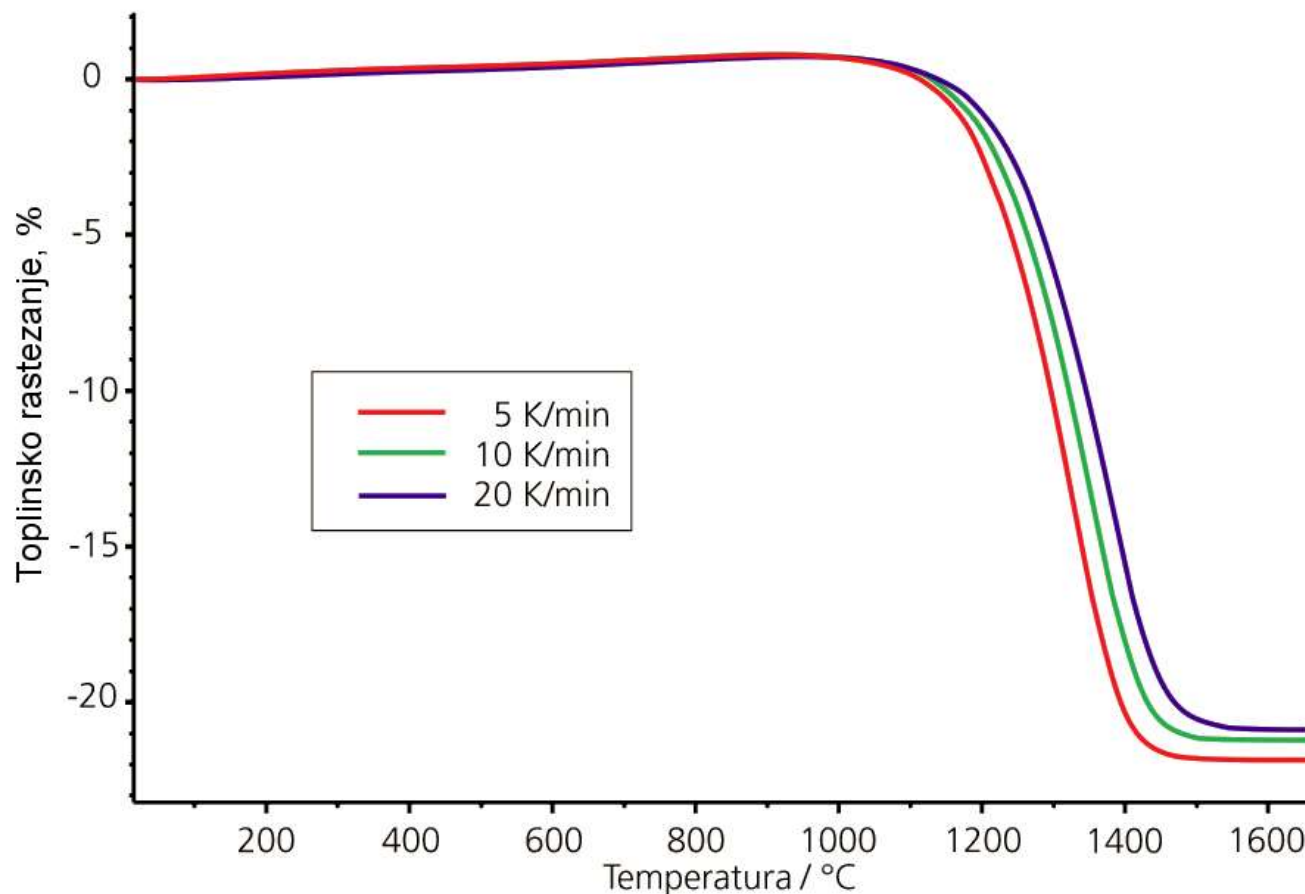
(Thermo)dilatometry

Toplinsko rastezanje vlaknima ojačanog polimernog kompozita / fiber reinforced composite



(Thermo)dilatometry

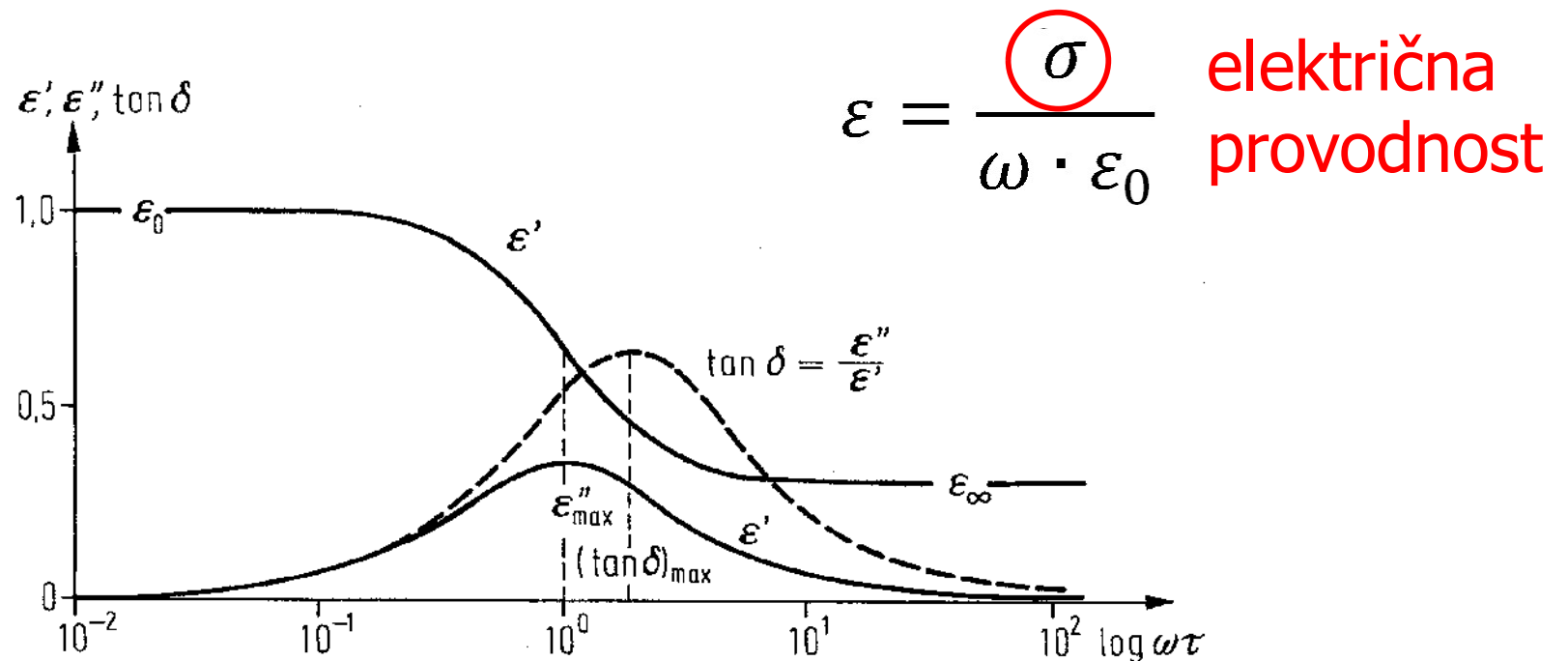
Određivane uvjeta sinteriranja
(zgušnjavanja) keramike / ceramic sintering



DEA

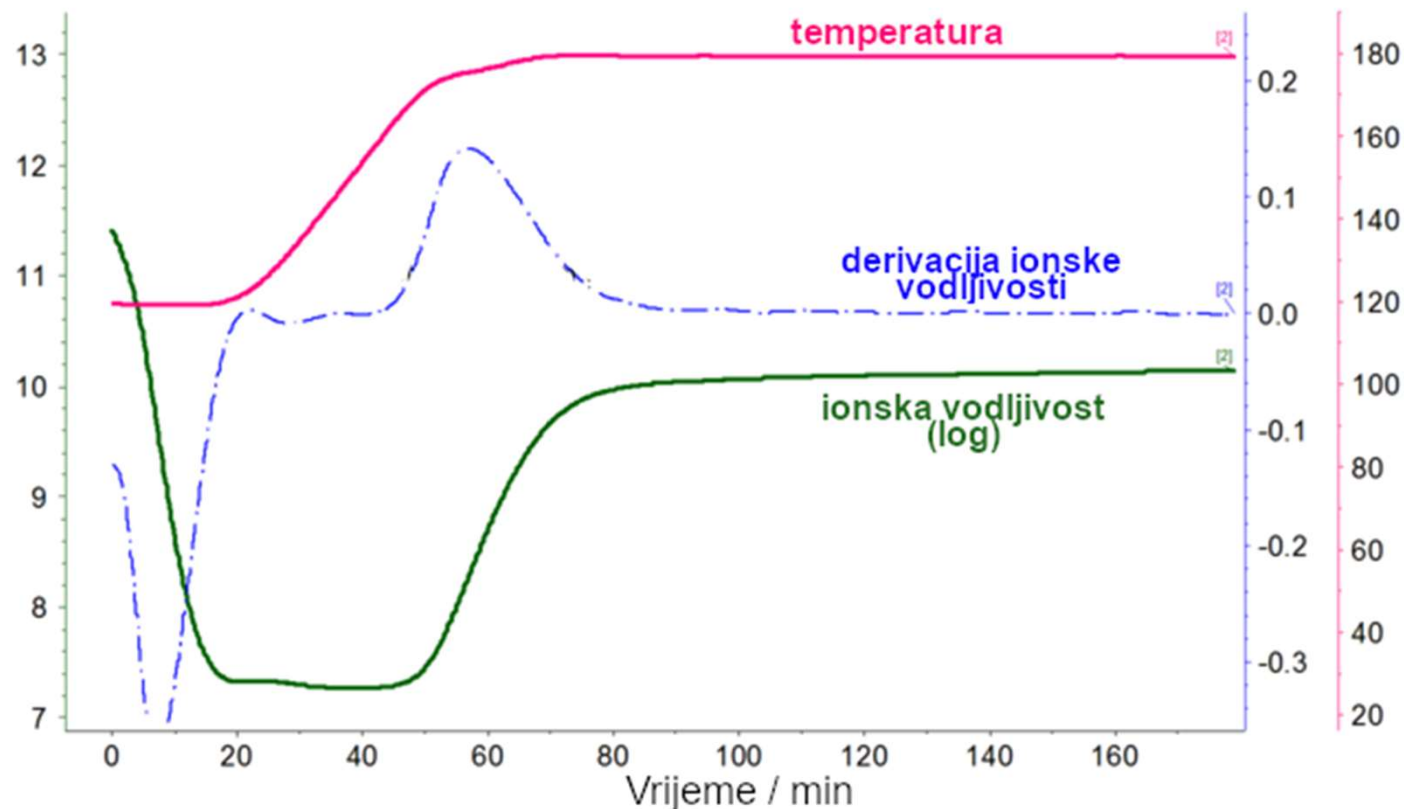
DEA – dielectric thermal analysis

- Dobrim dijelom pandan DMA / Parallel to DMA
- Changes in dielectricity in oscillating electric field



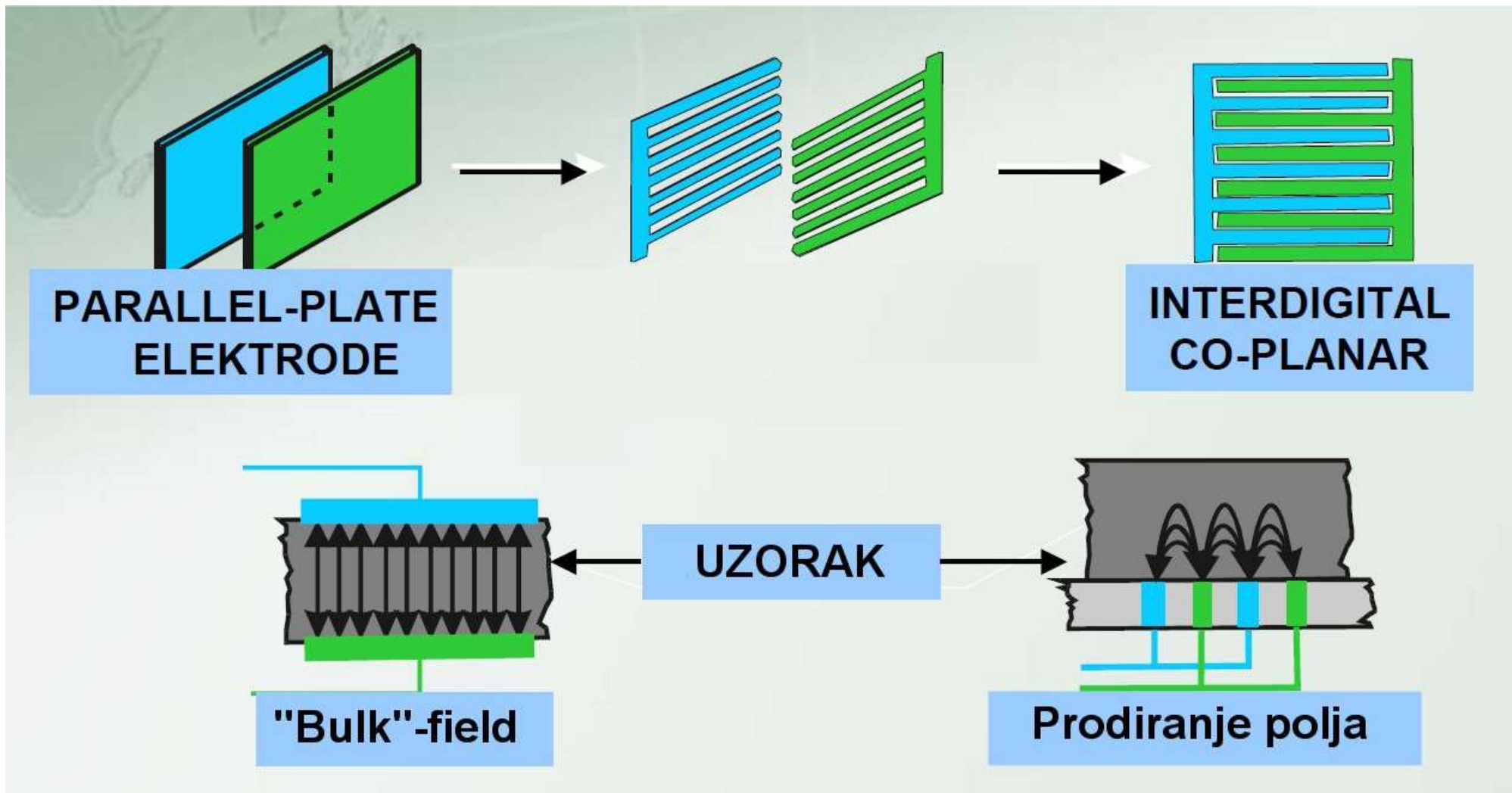
DEA

- Measuring of „ionic viscosity” ($1/\sigma$) while crosslinking, wider range than rheometers



DEA

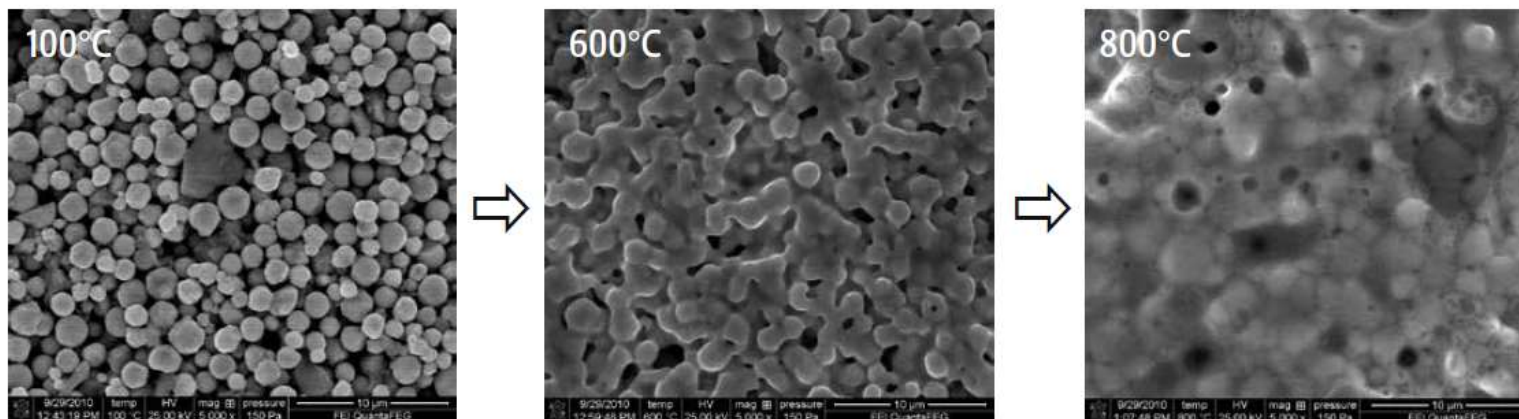
- Izvedbe geometrije elektroda



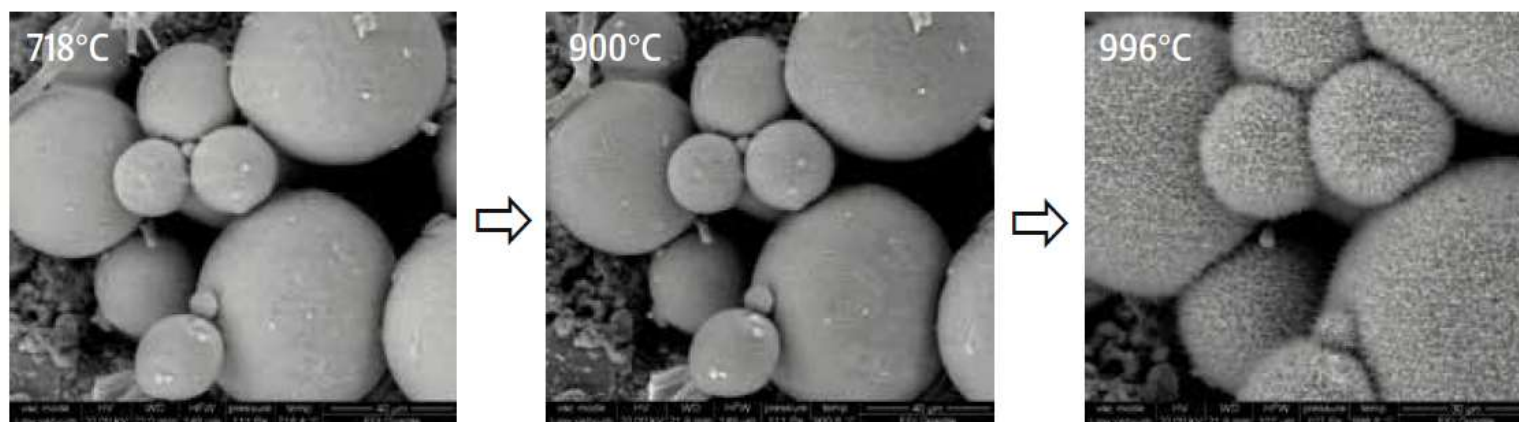
Thermooptometry

- Thermophotometry – emitted light
- Thermorefractometry – refraction index
- Thermoluminescence
- Thermomicroscopy – e.g. in combination with DSC

Heated stages in light and electron microscopy

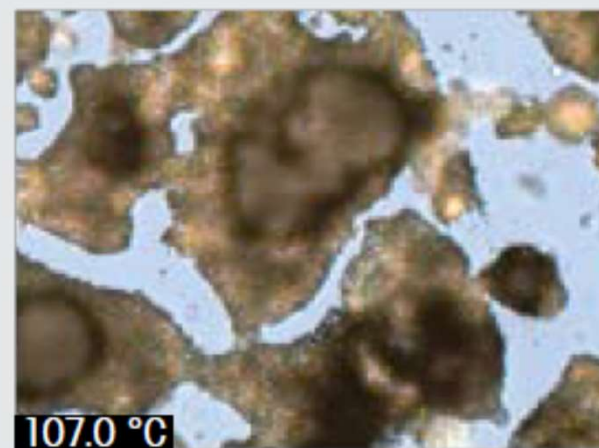
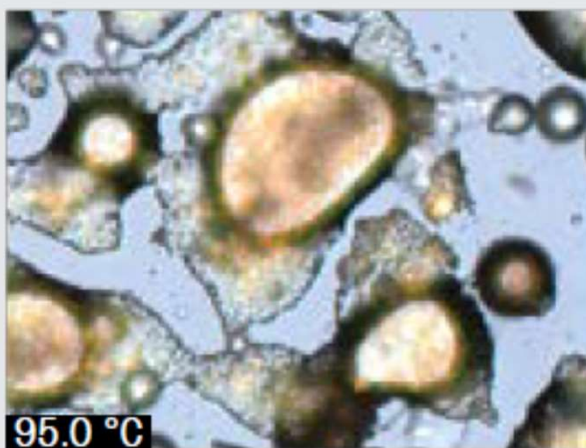
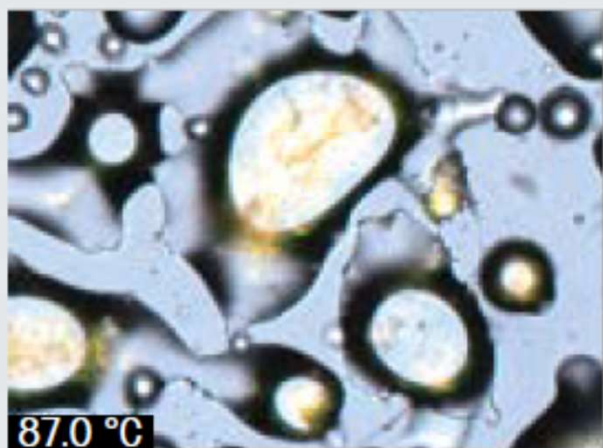
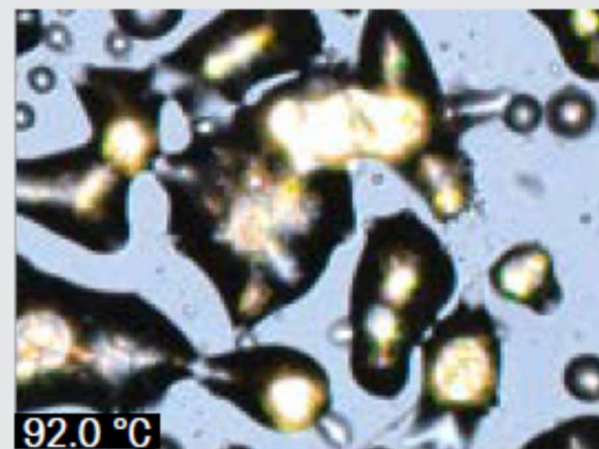
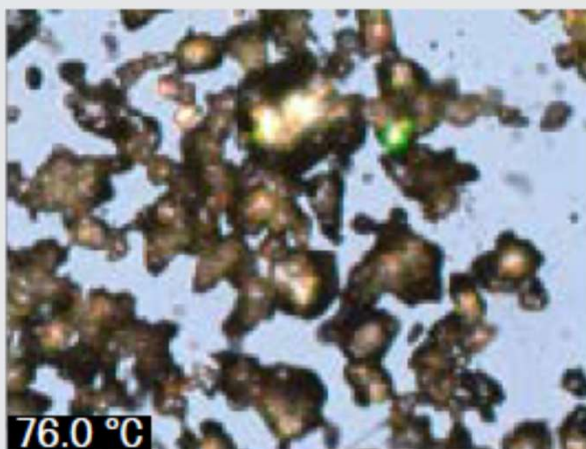
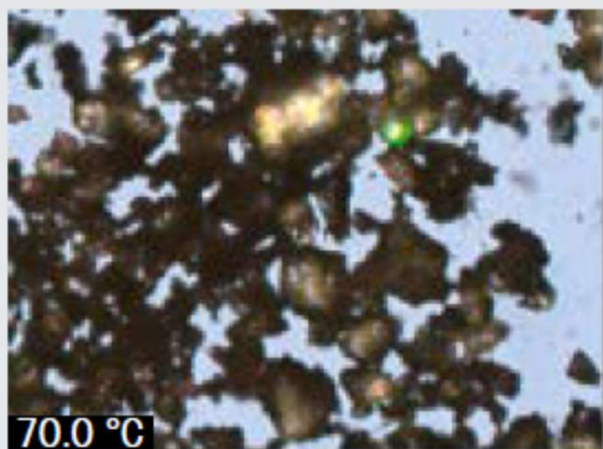


Taljenje srebrne paste



Metalne čestice – promjena površinske morfologije

Zagrijavanje uzoraka u pretražnom
elektronskom mikroskopu / Heating in SEM



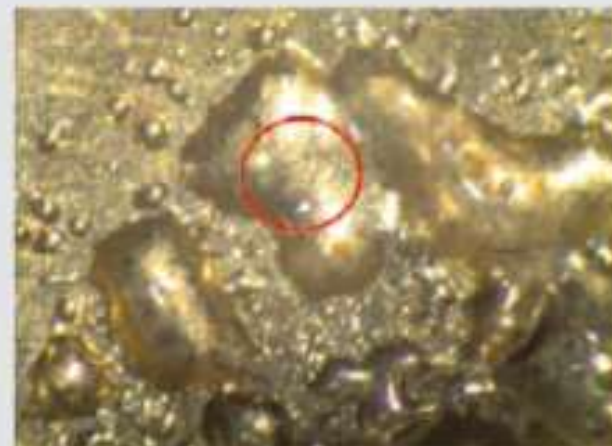
Zagrijavanje farmaceutika u mikroskopu /
Pharmaceuticals heated in microscope



30 °C Čvrsti kristali



89 °C Taljenje



95 °C Pred kraj taljenja



104 °C Kristalizacija i
isparavanje



120 °C Kristalizacija
pri kraju



185 °C Početak taljenja
anhidrida

Zagrijavanje farmaceutika, termomikroskopija

Thermooptometry in DSC

- Microscopy: lakša interpretacija i identificiranje artefakata **uslijed pomicanja lončića** (pucanje uzorka, stezanje polimera) / artefact interpretation
- chemiluminiscence: obično kao pomoć u detektiranju oksidativne degradacije organskih tvari (OIT) / aiding in OIT

Simultaneous methods

- DSC-TGA
- TMA-DTA
- TGA-EGA
- DSC-optické
- DEA-reometar
- DEA-DMA

Thermo-physical properties

- Razvoj novih instrumenata koji služe određivanju osnovnih toplinskih svojstava materijala (prijenos topline):
 - toplinska provodnost/conductivity, λ
 - toplinska difuznost/diffusivity, a

$$a = \frac{\lambda}{\rho \cdot c_p}$$

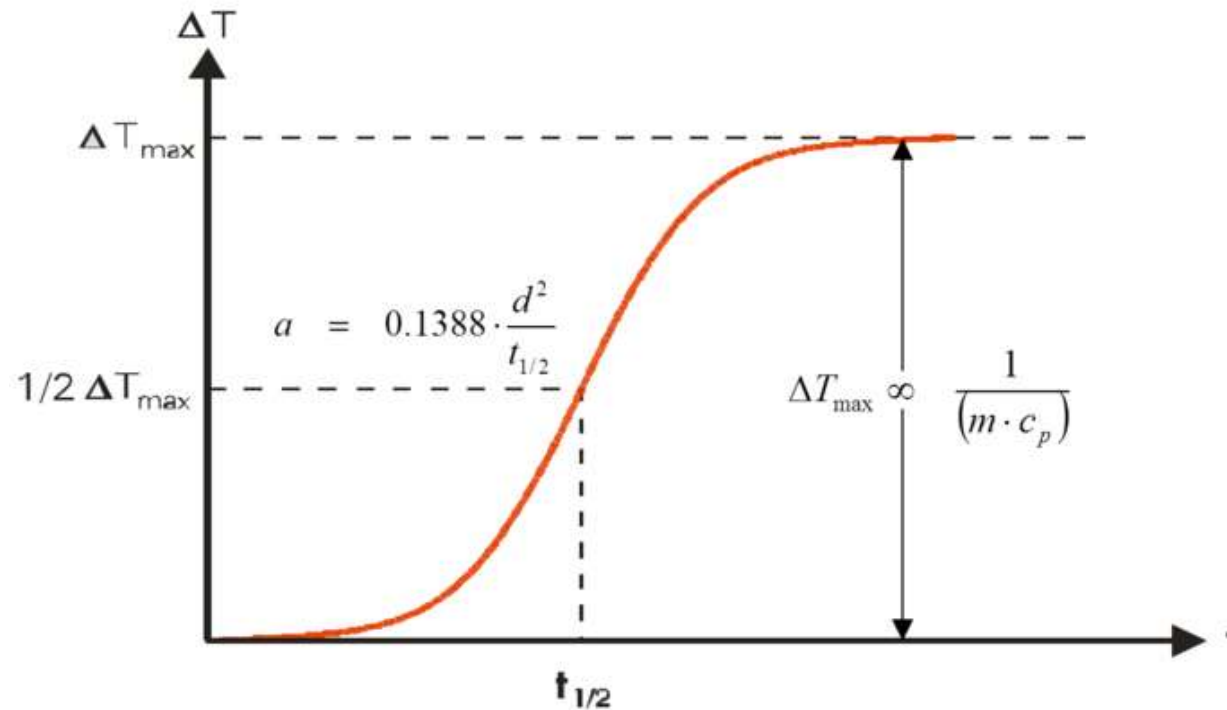
LFA

- *Laser Flash Method*: laserskim pulsom se uzorak zagrijava s jedne strane, IR detektor mjeri prolaz topline s druge strane



LFA

- daje a , λ se može izračunati iz poznatih ρ i c_p



- mjerenje do 900 °C / up to 900 °C

LFA

- Radi jednolike apsorpcije energije naparivanje uzorka npr. grafitom ili zlatom, u svakom slučaju nije dobro da bude zrcalno sjajan! / graphite or gold coating for equal energy absorption
- Uz prilagodnu detektora i za male (mikro) uzorke i tanke filmove! / also for micro samples and thin films
- Za tanje ili slabo vodljive uzorke, da se izbjegne pregrijavanje: PLH (*Periodic Laser Heating*), moduliranje pulsa ulazne energije. / for thinner or less conductive samples

LFA variant – HSXD

- Umjesto lasera, izvor je ksenonska lampa (*High Speed Xenon Discharge*, HSXD)
- Znatno jeftinije i jednostavnije od lasera a rezultati adekvatni. / cheaper and simpler than laser, adequate results

**Which methods do you
find interesting?**

~ intermission~

Experimental conditions

Odabir i utjecaj parametara
mjerjenja

Experimental conditions

- **U**zorak / sample
- **L**ončić / crucible
- **B**rzina (zagrijavanja/hlađenja) / rate
- **A**tmosfera / atmosphere
- **M**asa (i raspodjela) / mass + distribution

Kontrolirano mijenjanje parametara može
pomoći u interpretaciji rezultata! /
Parameter change can help interpretation

Sample

- Koja atmosfera? / Which atmosphere?
- Koji lončić? / Which crucible?
- Raspon temperatura / Temp range
- Očekivane pojave / what is expected
- Količina uzorka / Sample quantity

Sample preparation

Za svaku instrumentalnu metodu:

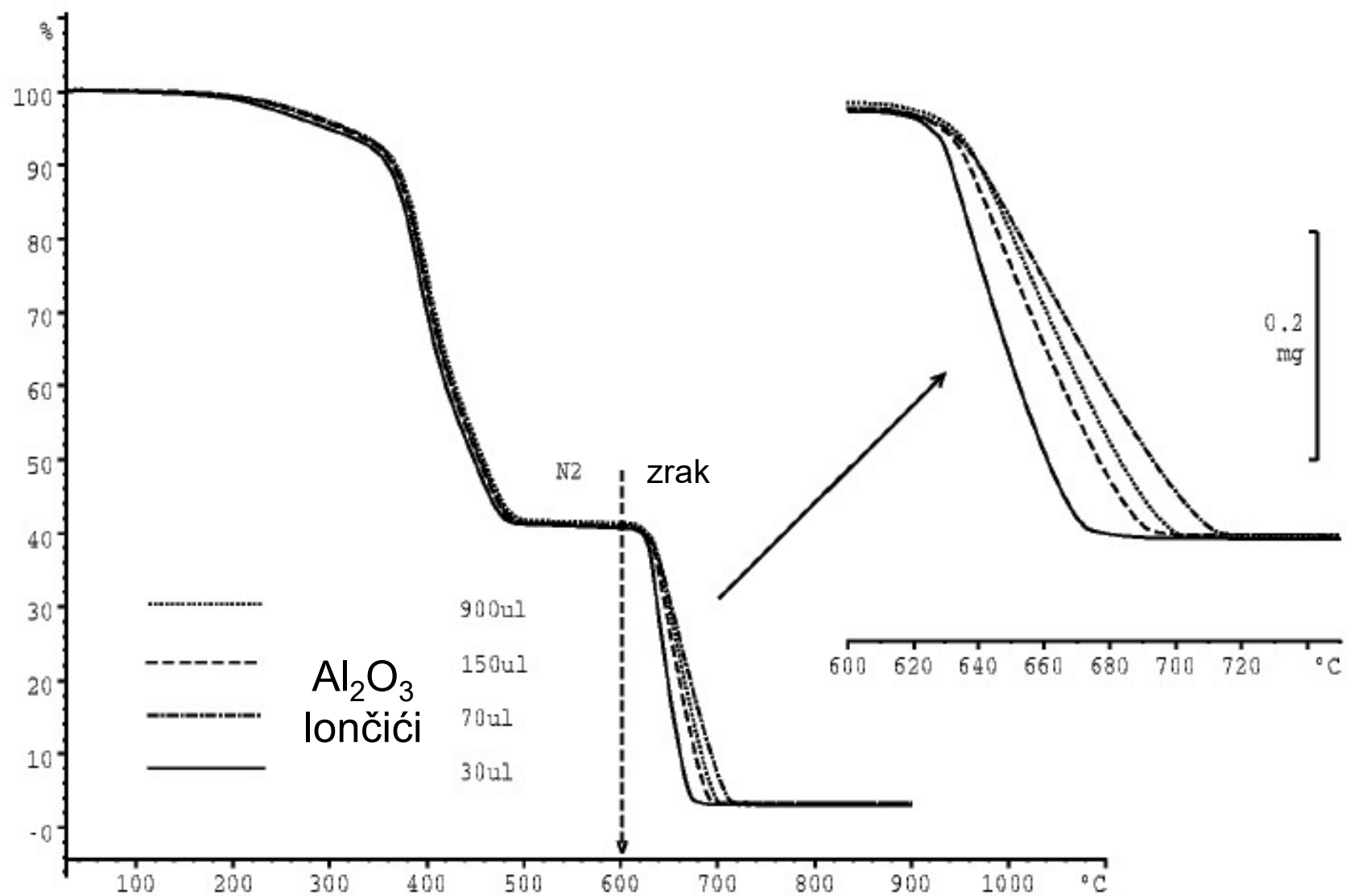
- Najvažnija / The most important
- Prividno jednostavna / Deceptively simple
- Ne može se naučiti teorijski / Can't be taught theoretically

Crucible

- Samo za neke metode! / Not all methods!
- Utjecaj oblika i C_p kompenzira se kalibracijom / calibration for shape and C_p





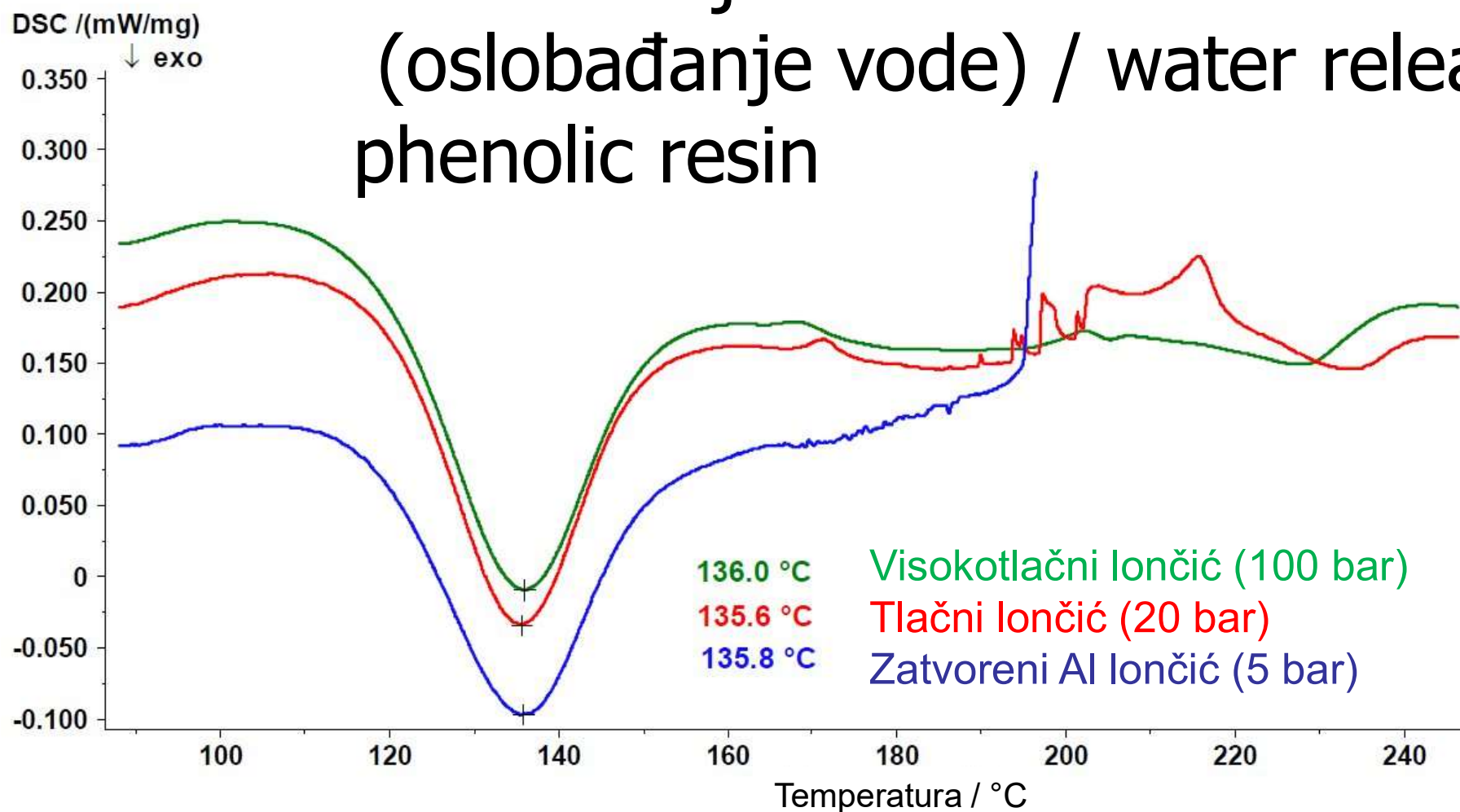


Crucible

- Atmosphere contact:
 - otvoreni / open
 - probušeni poklopac / hole in lid
 - 50 μm otvor (samo-generirana atmosfera) / self-generated atmosphere
 - hermetički zatvoren / hermetical
- Hermetički samo $< 200\text{ }^{\circ}\text{C}$ ($p \sim T!$)

Crucible

Očvrščivanje fenolne smole
(oslobađanje vode) / water release
phenolic resin



Crucible

- Ponekad i TGA bez lončića, radi boljeg dodira s atmosferom (reaktivnim plinom):
 - platforma za uzorak (bez bočnih stijenki)
 - mrežasti držač uzorka da plin može strujati kroz njega!

TGA without crucible – a platform or a grid

Crucible

Izbor materijala / Material choice:

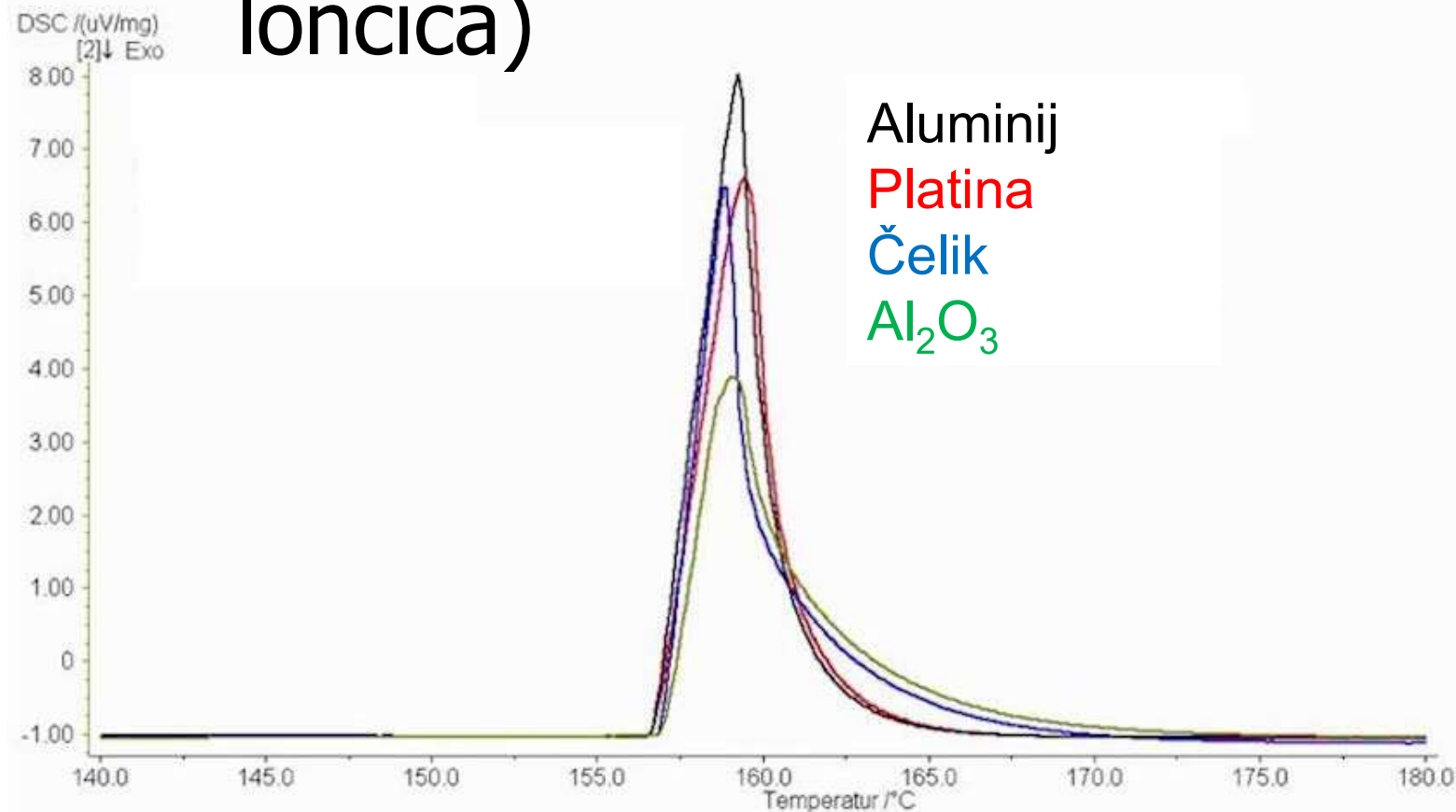
- Inertan! / Inert!
- Katalitička aktivnost: Cu za OIT / Catalytic activity
- Temperaturni raspon / Temp range:

$$T_m(\text{Al}) = 660\text{ }^{\circ}\text{C}$$

- Često jednokratni (čišćenje teško) / often single-use (tough to clean)

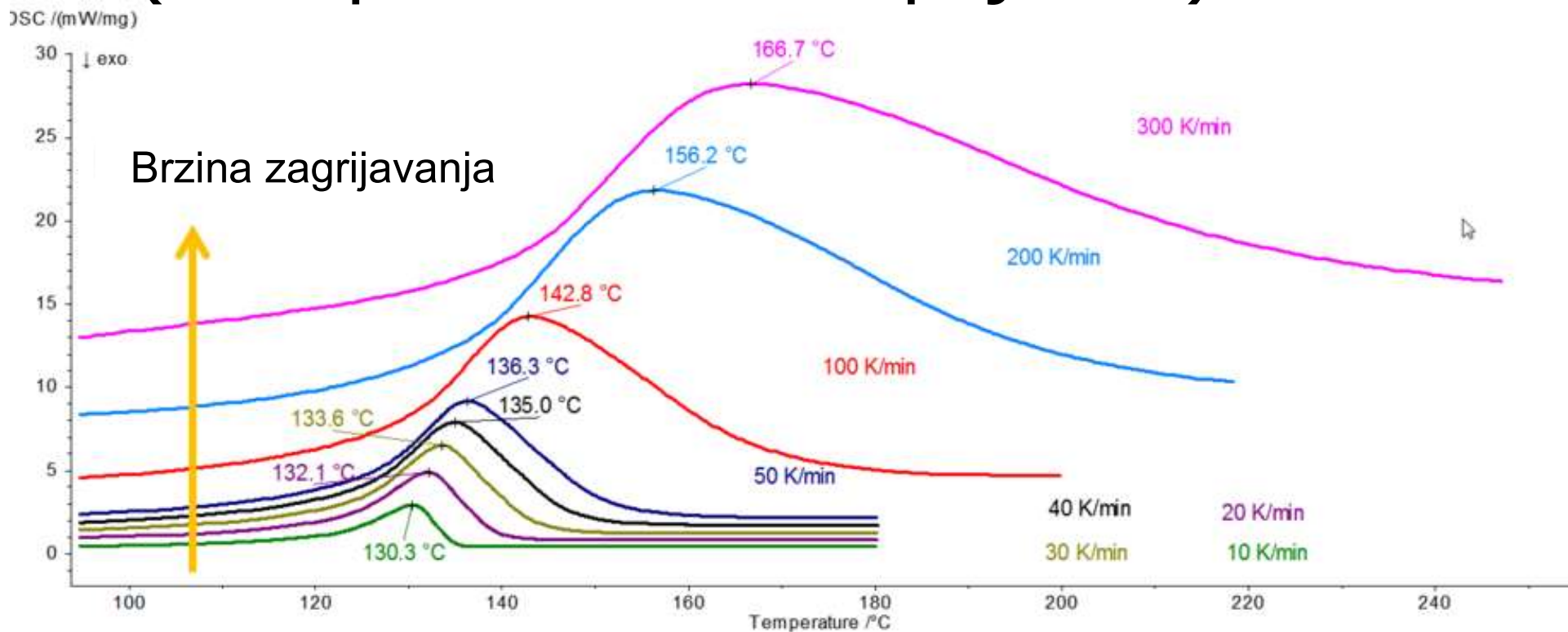
Crucible

Utjecaj na DSC maksimum (toplinska provodnost, toplinski kapacitet i masa lončića)

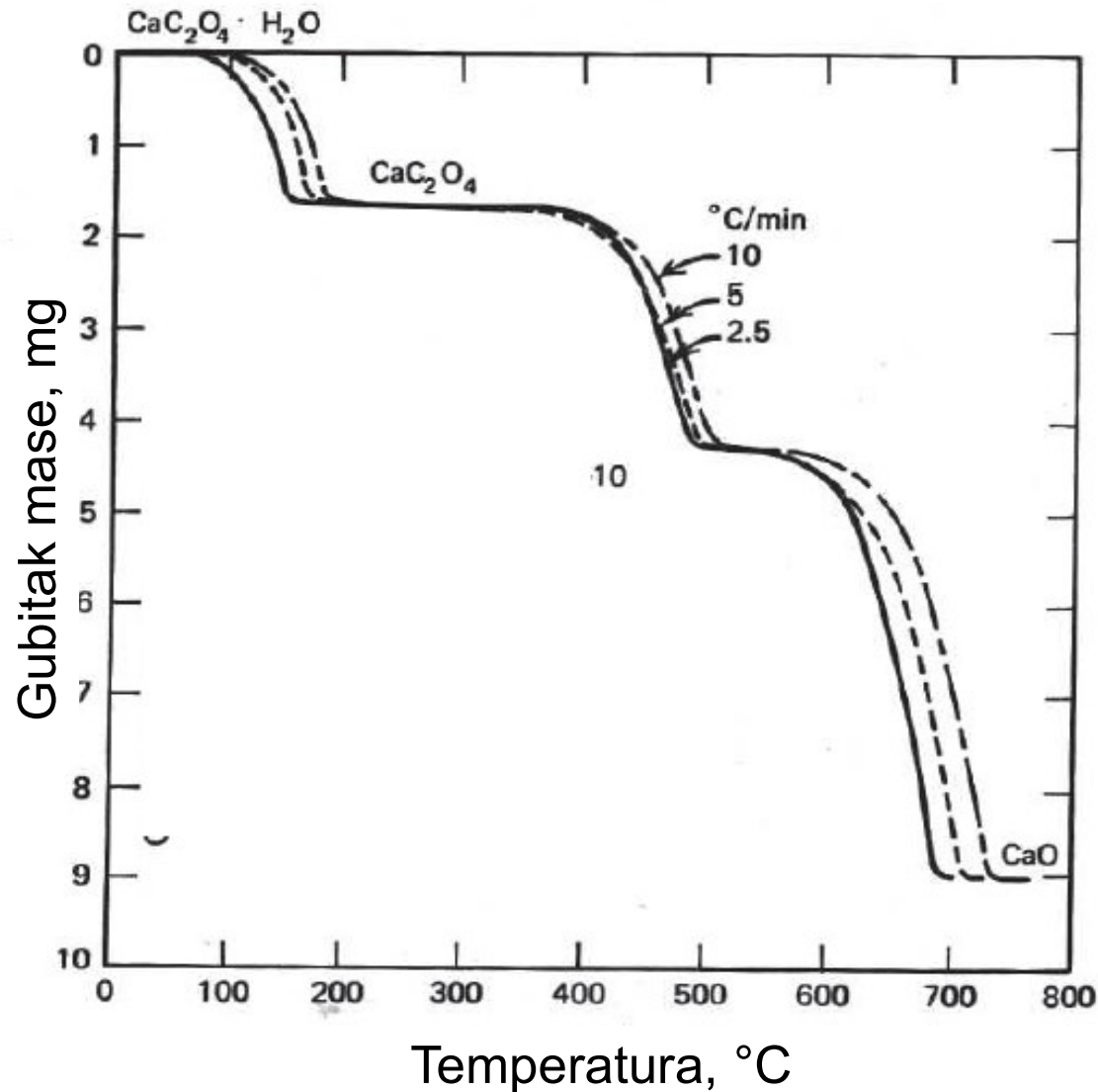


Rate

- Linearne, $\beta = 0,1 - 200$ K/min
- Pomak u temperaturama / Temp shift (osim početaka faznih prijelaza)



Rate



Raspad
kalcijevog
oksalata/
calcium oxalate
degradation

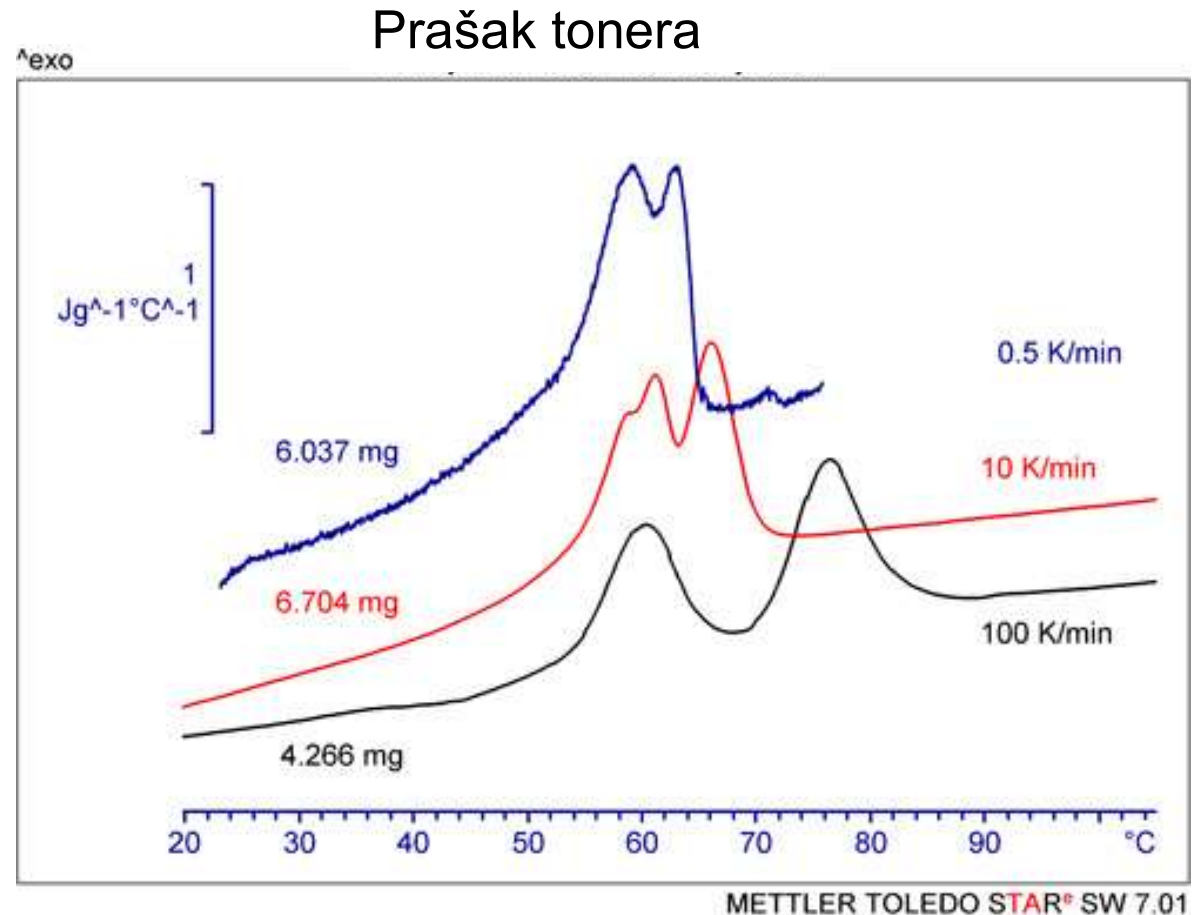
(modelna TGA
reakcija)

Rate

Veća brzina daje jači signal i veće preklapanje / higher rate stronger signal and more overlap

ALI

- Pomak na više temperature razdvaja taljenje i degradaciju



Cooling

- Jedinica za hlađenje / refrigerating unit
- Kapljeviti dušik / liquid nitrogen
- Termoelektrični Peltierov element / Peltier

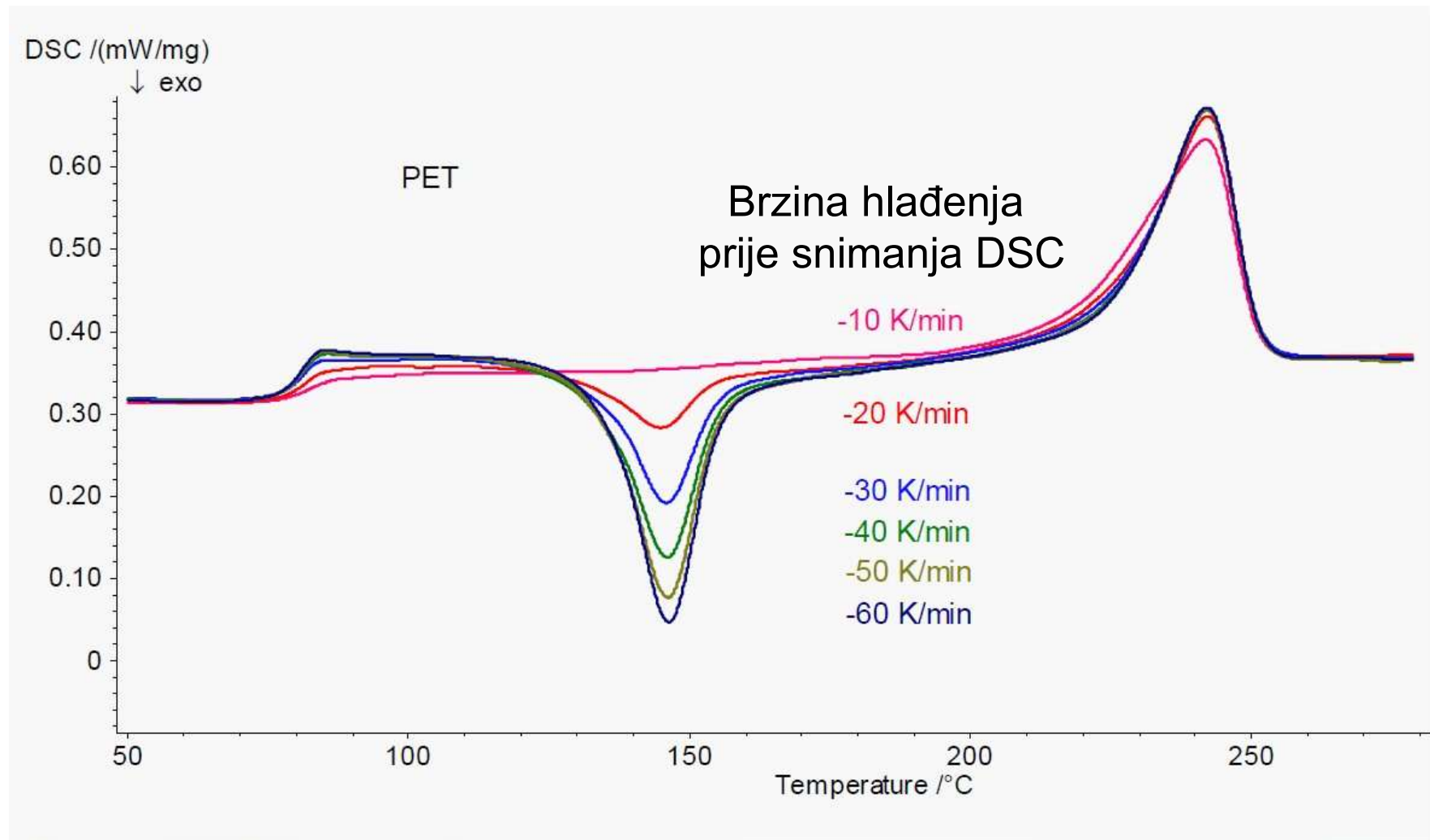


Cooling

Brzina hlađenja ovisi o ciljnoj temperaturi
(tekući dušik najbrži i najhladniji)

Brzina, K/min	donja granica		
	jednostupanj. hladnjak	dvostupanjski hladnjak	tekući dušik
100		300 °C	200 °C
50	175 °C	120 °C	0 °C
20	40 °C	-20 °C	-100 °C
10	0 °C	-50 °C	-150 °C
5	-15 °C	-75 °C	-165 °C
2	-40 °C	-90 °C	-180 °C

Cooling



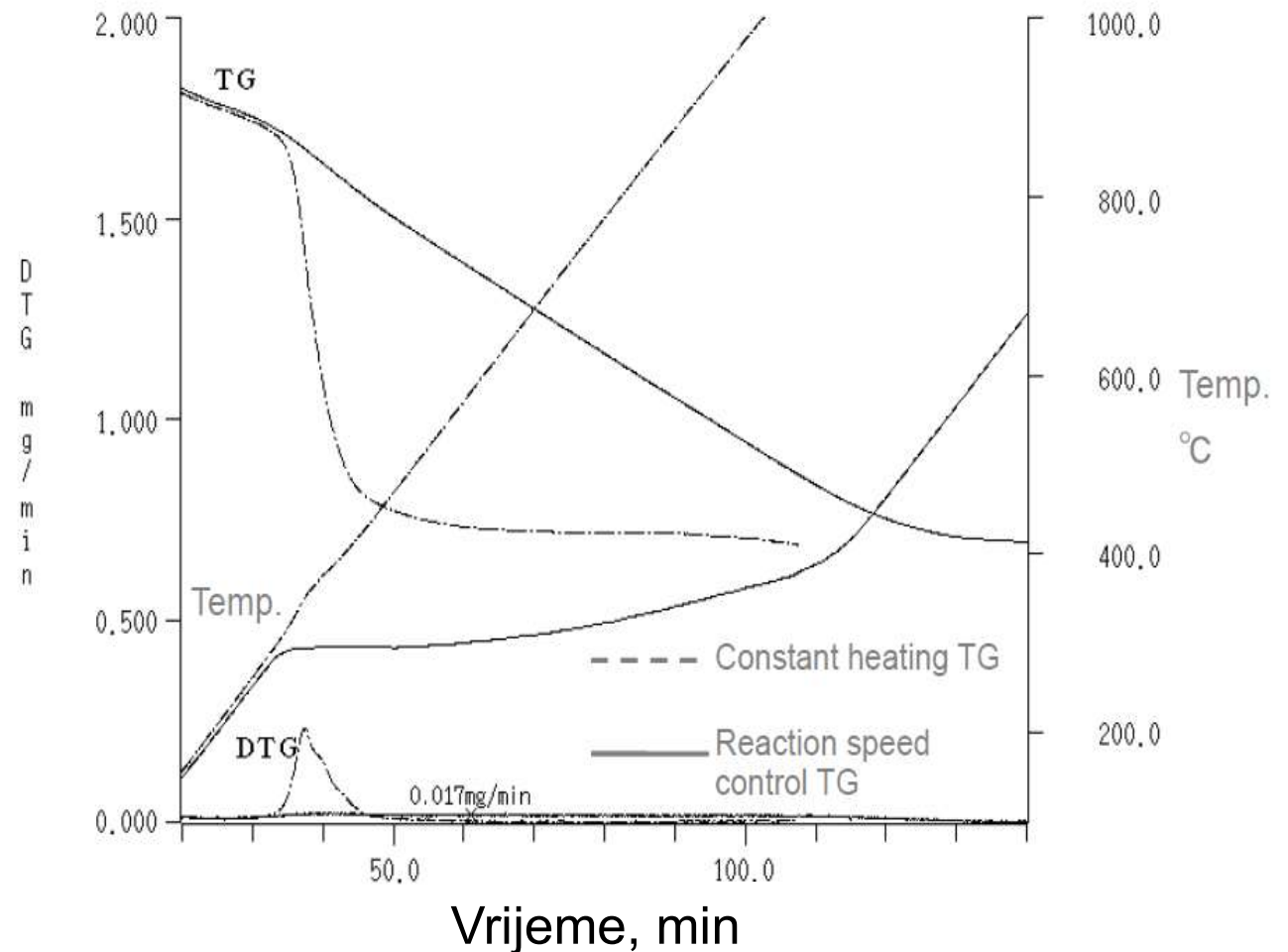
Non-linear rates

- Izotermno/isothermal

- Stepenasto/
Steps

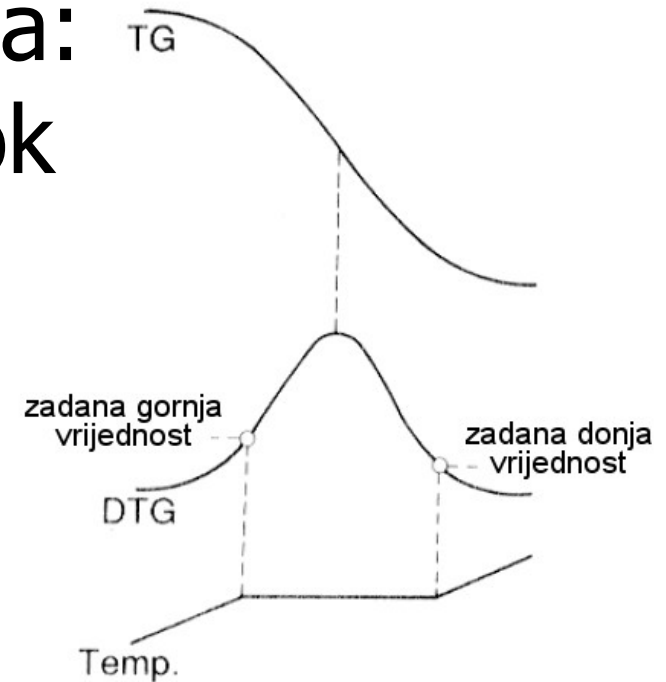
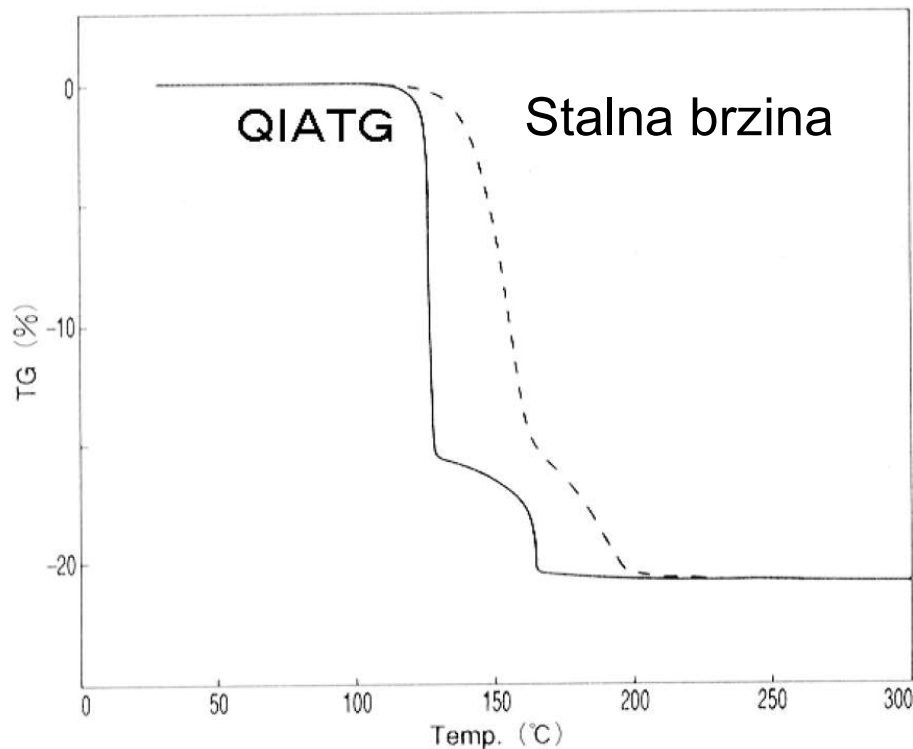
- Modulirano/
Modulated

- Uzorkom-
vođeno/Sampl
controlled



Sample-controlled methods

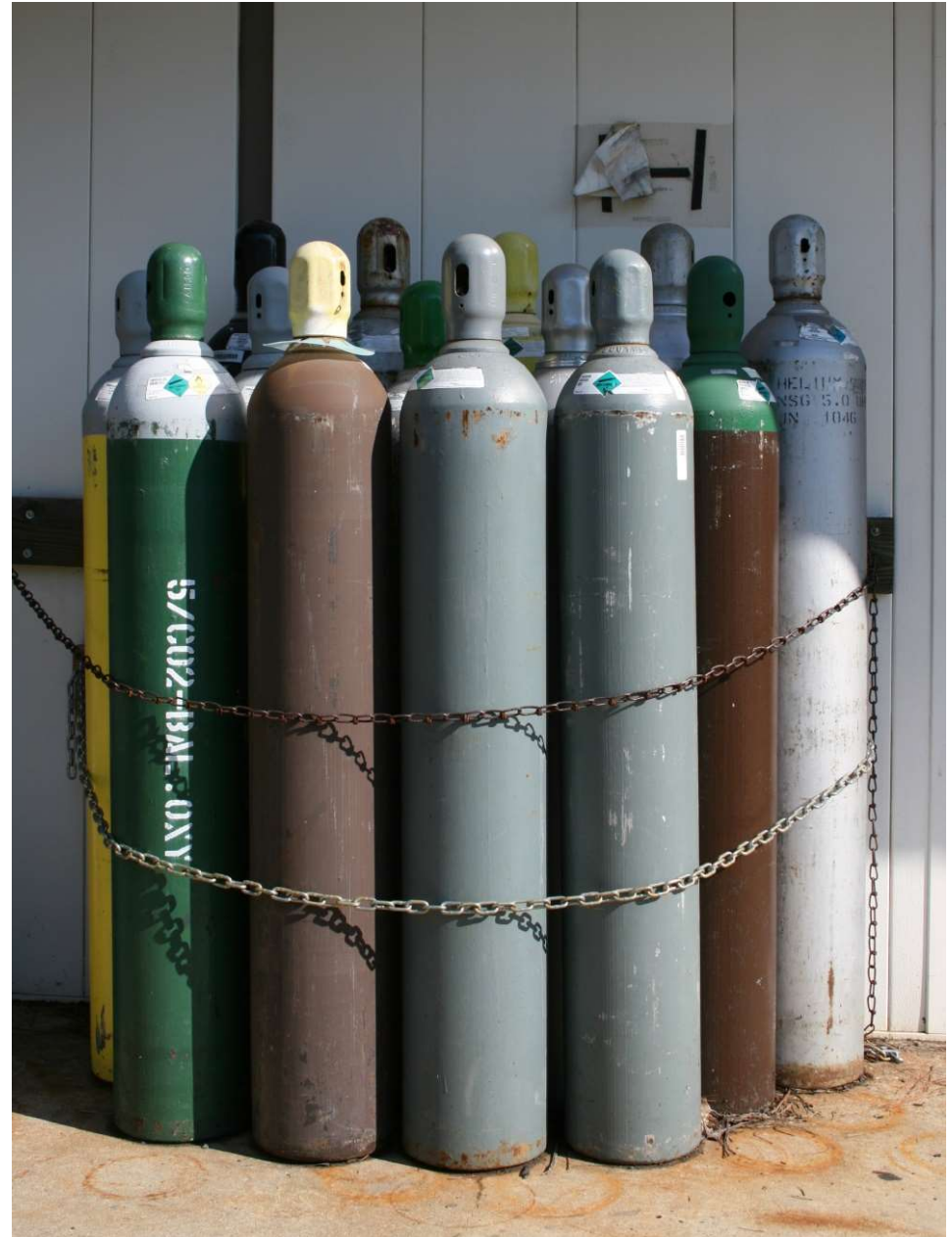
QIA – kvazi-izotermna analiza:
zaustavlja se zagrijavanje dok
traje promjena svojstva

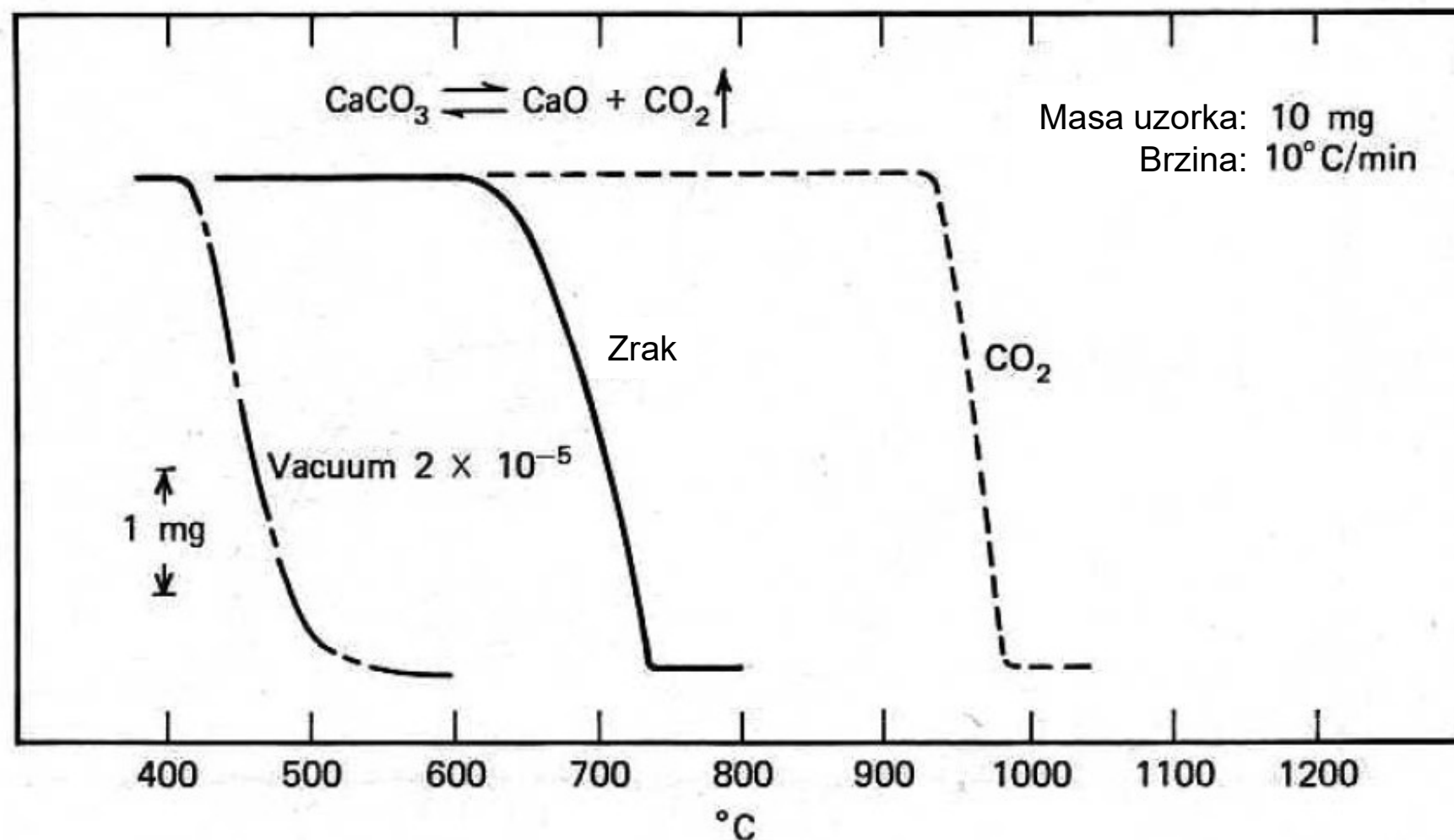


Bolje
razdvajanje
efekata

Atmosphere

- Reaktivna ili inertna
 - Oksidacijska
 - Redukcijska:
 H_2 u Ar
- Utjecaj vlage! / humidity!
- Visoki tlak, vakuum / high pressure, vacuum





Utjecaj atmosfere na termolizu CaCO_3

Influence of atmosphere on thermolysis

Atmosfera: protok

Protok plina (*purge*): održavanje stalnih reakcijskih uvjeta; 20 – 100 mL/min, bez fluktuacija!

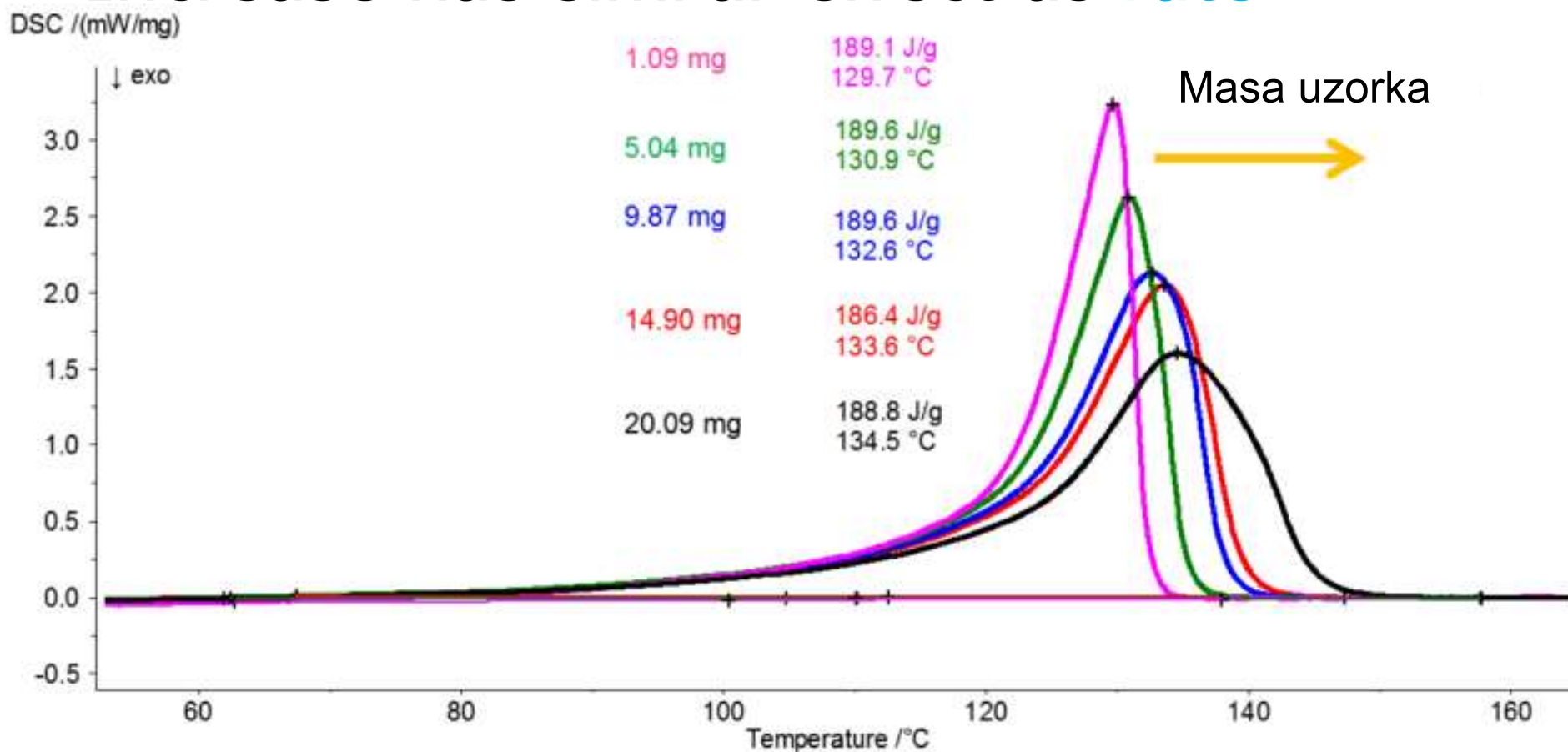
Zaštitni plin (*protective*): odnosi korozivne tvari i zagađivala

Vlastita atmosfera: najbolje zatvaranjem lončića s uzorkom



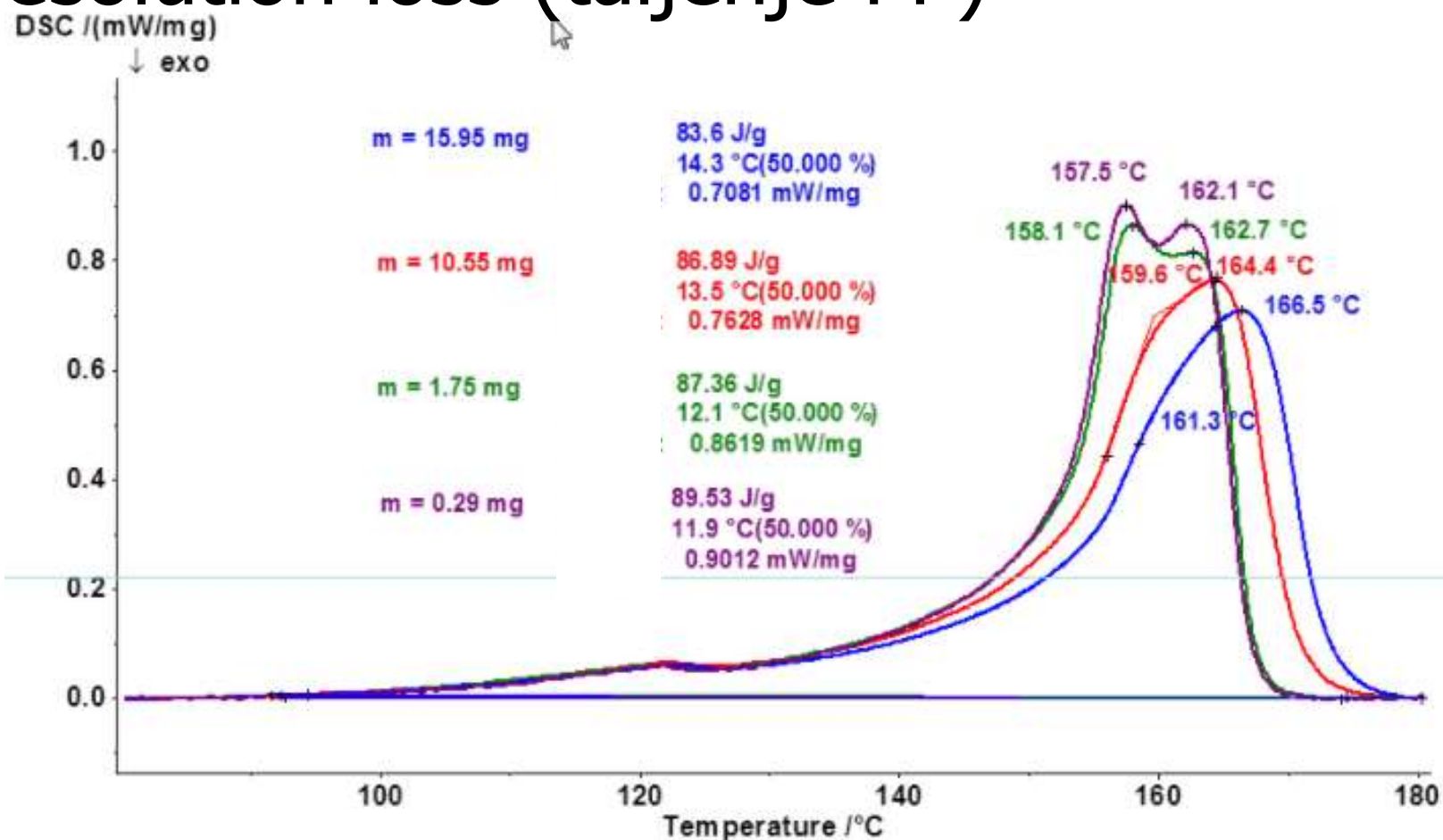
Mass

- Small mass: diffusion is negligible
- Increase has similar effect as **rate**



Mass

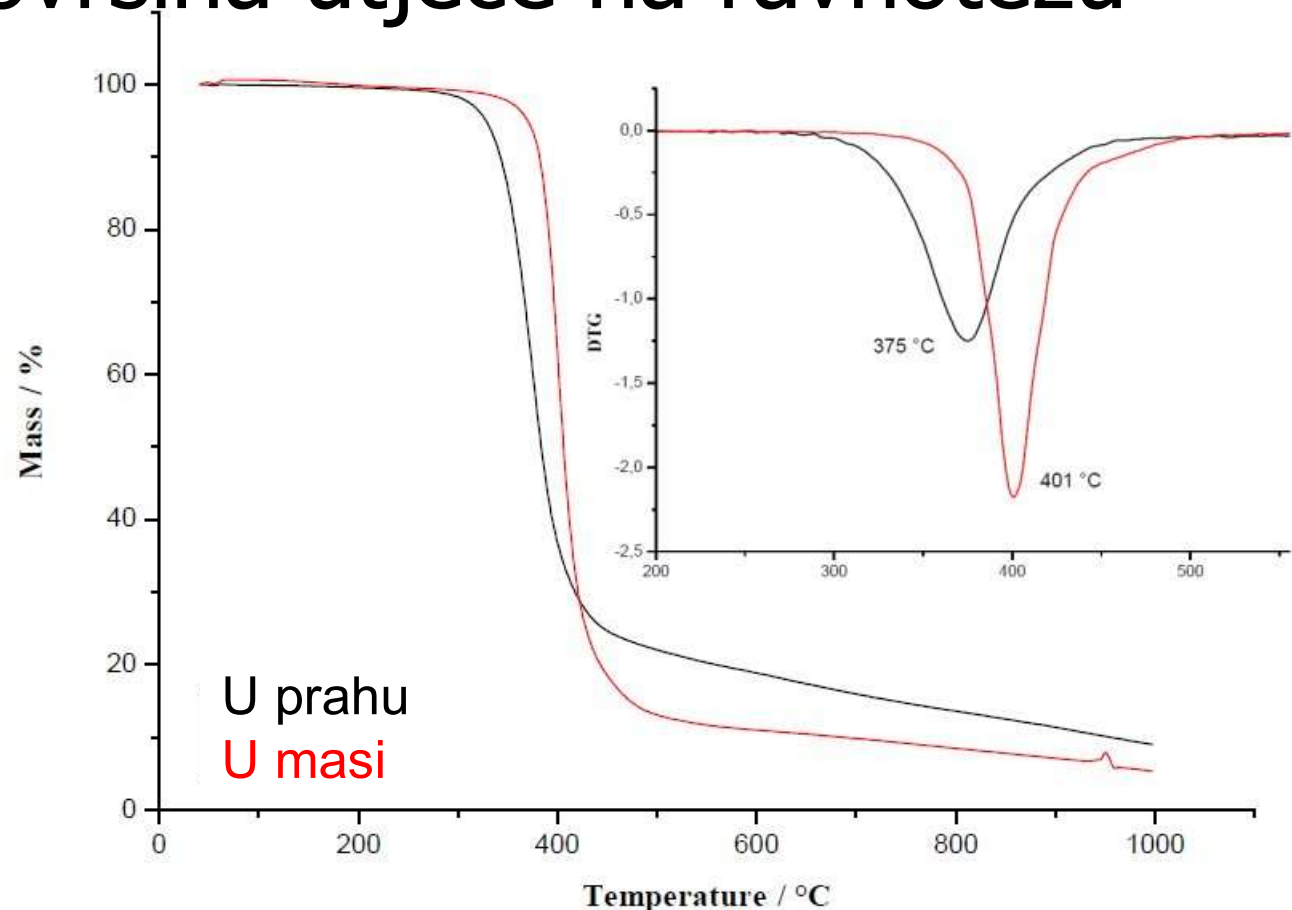
- Veća masa – gubitak razlučivanja / resolution loss (taljenje PP)



...and distribution

BULK vs. POWDER – specific surface

- Specifičná povrchina utječe na ravnotežu S-G
- Nasipna gustoća!

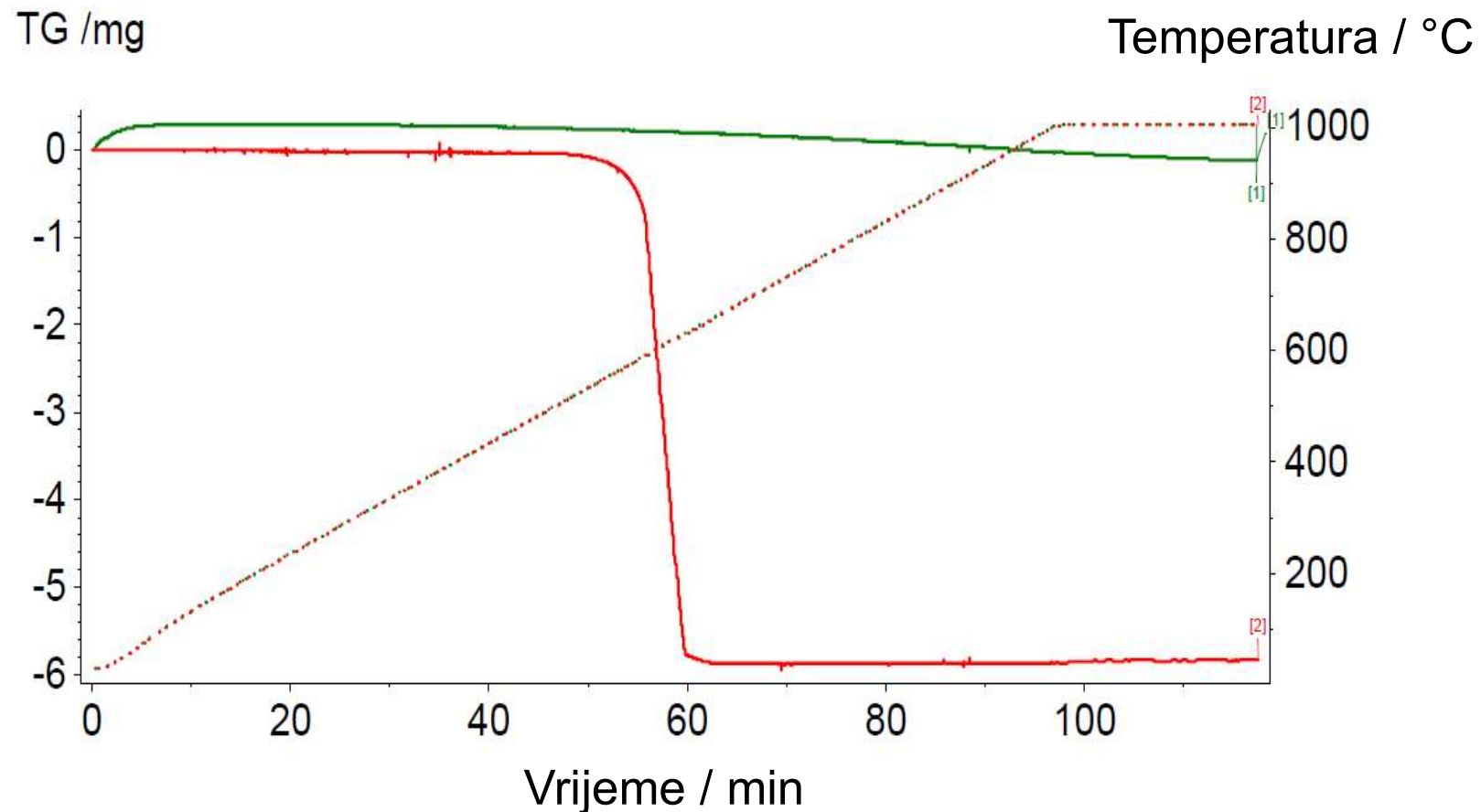


Instrument calibration

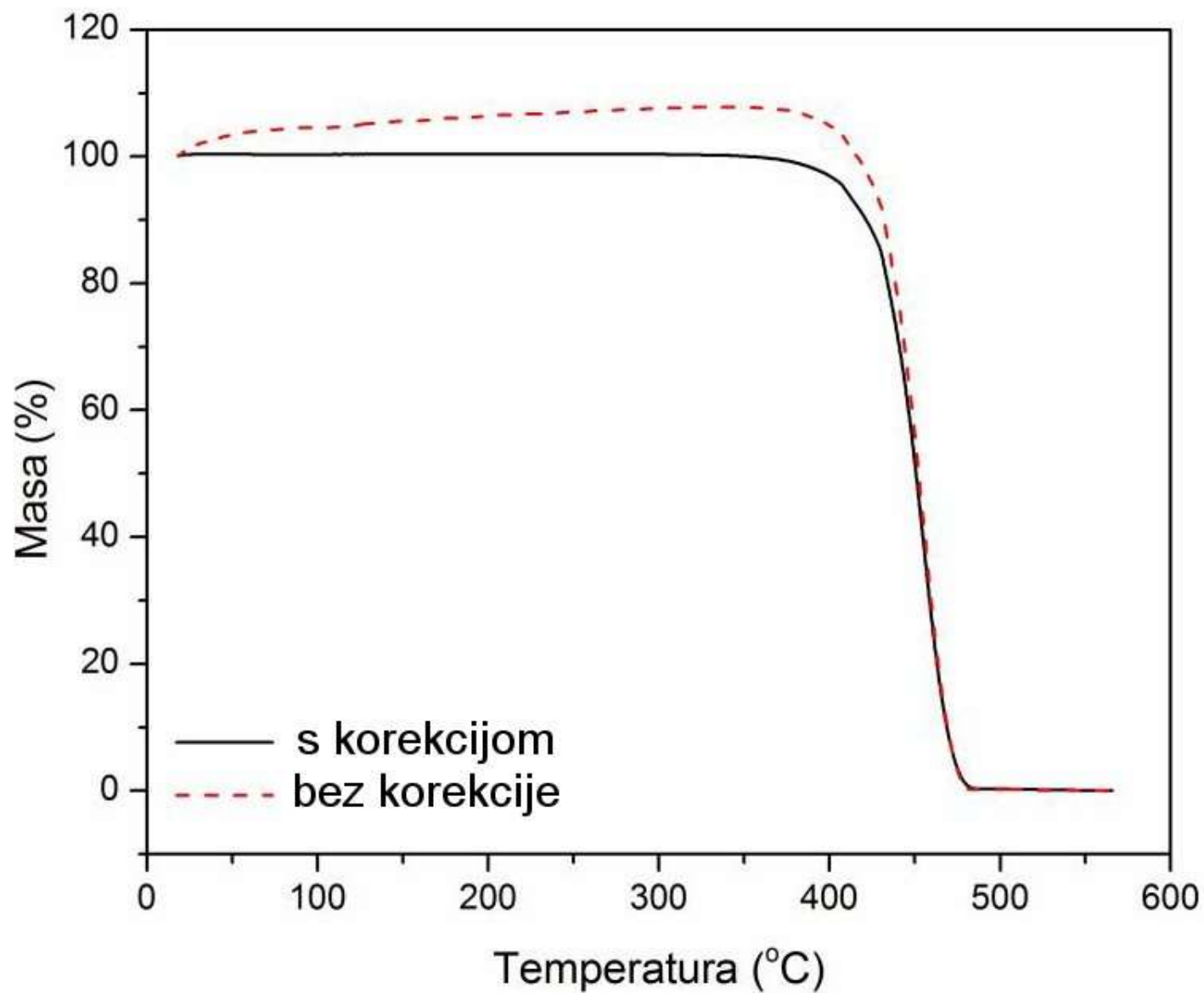
- Utjecaj konstrukcije instrumenta
- Utjecaj lončića, atmosfere itd.
- Zaostajanje temperature uzorka za onom u peći (*thermal lag*)
- Za TGA – feromagnetični materijali (T_C) u magnetskom polju
- Za DSC – niz čistih tvari poznatih tališta i entalpija (istovremeno T i ΔH)

Correction curves

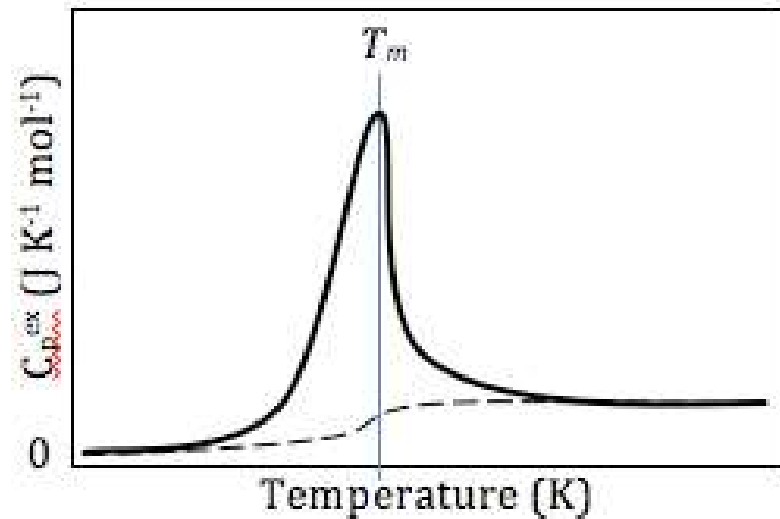
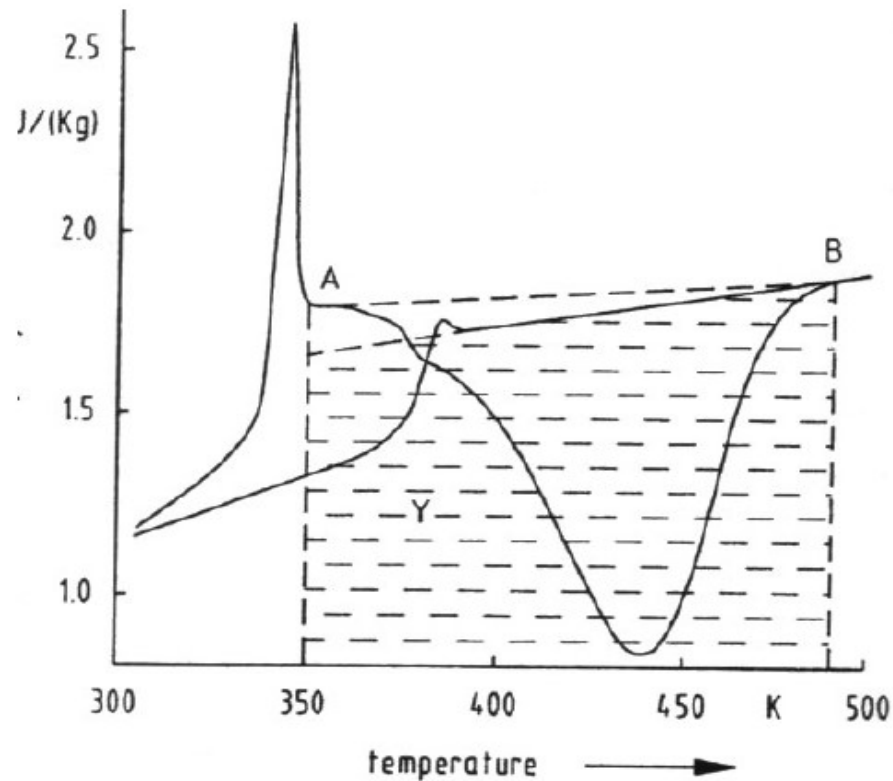
- Mostly TGA (buoyancy correction)



Correction curves

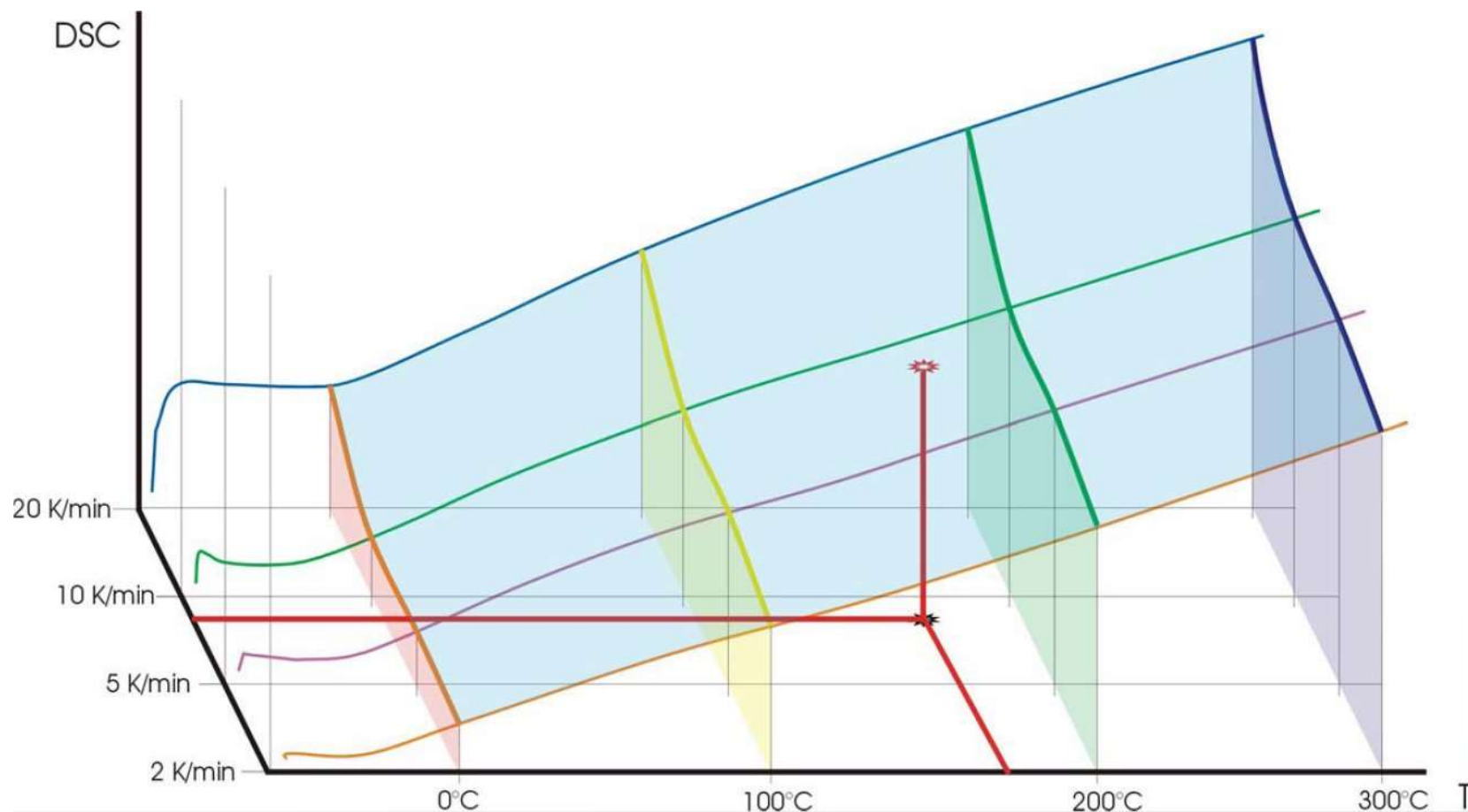


Baseline



Ponekad vrlo složeno provući odgovarajuću baznu liniju... / Can be difficult

Baseline



Softversko „peglanje” stvarne bazne linije
(Netzschov BeFlat) / Software corrections

~ intermission ~

Examples of applications and analyses



primjeri

Applications

- Znanost o materijalima / Materials sci
- Farmakologija / Pharmacology
- Kontrola kvalitete / Quality control
- Biologija / Biology

Lake za korišćenje, **ALI** treba biti pažljiv u interpretaciji! / difficult to interpret

Destruktivne metode / Destructive methods

Applications

- Kristalnost, talište, fazni prijelazi (**nije** termodinamički ravnotežno!)
- Reakcije, konverzija, kinetika
- Staklište, mekšanje
- Toplinsko širenje, bubrenje, sinteriranje
- Modul i viskoelastično ponašanje (polimera)
- Udio punila/pepela
- Toplinska/oksidacijska postojanost

Your application examples?

Personal experience or seen in
literature

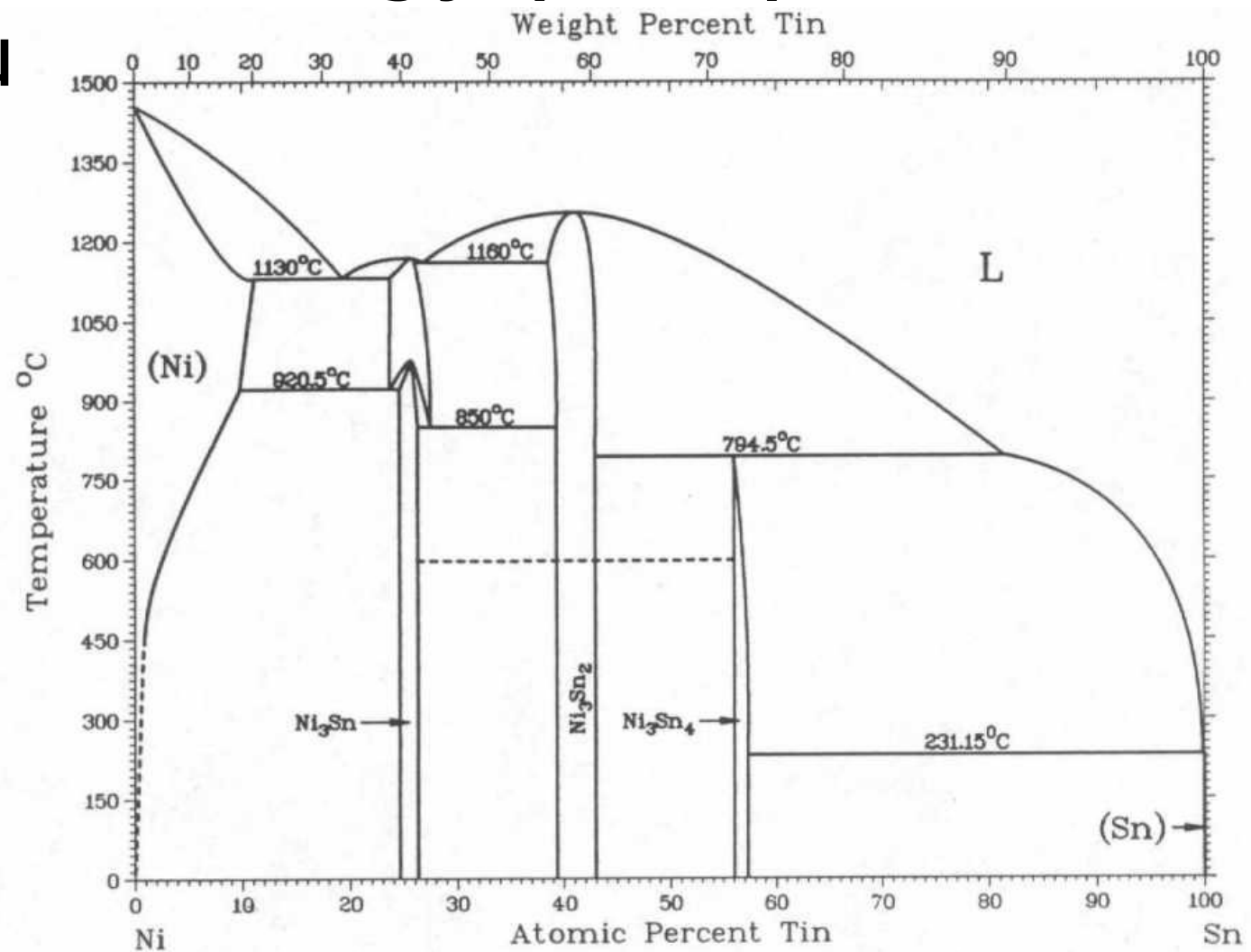
Odabir metode

	DSC	DTA	TGA	TMA	DMA	TOA	TCL	EGA
talište	+	○	-	○	○	+	-	-
kristalizacija i taljenje	+	○	-	○	-	+	-	-
fazni prijelazi čvrsto-čvrsto, polimorfizam	+	+	-	○	-	+	-	-
staklište	+	○	-	+	+	○	-	-
ispitivanje toplinske prošlosti	+	-	-	+	+	-	-	-
mekšište	-	-	-	+	○	-	-	-
toplinsko rastezanje/stezanje, bubrenje u otapalima	-	-	-	+	-	-	-	-
viskoelastično i prigušno ponašanje, Youngov modul	-	-	-	○	+	-	-	-
specifični toplinski kapacitet, entalpijske promjene	+	○	-	-	-	-	-	-

	DSC	DTA	TGA	TMA	DMA	TOA	TCL	EGA
sastav	+	-	+	-	-	-	-	+
sadržaj punila	o	-	+	-	-	-	-	-
sublimacija, hlapljenje, desorpcija	+	o	+	-	-	+	-	+
toplinska postojanost/degradacija piroliza	o	o	+	o	-	o	-	+
oksidacijska postojanost	+	+	+	o	-	-	+	-
reakcija (npr. polimerizacija)	+	o	o	+	+	-	o	-
čistoća kristalnih nepolimernih tvari	+	-	+	-	-	o	-	-
kinetika i modeliranje	+	o	+	-	-	-	-	o
osiguranje kvalitete, odabir proizvoda	+	o	+	o	o	+	o	+

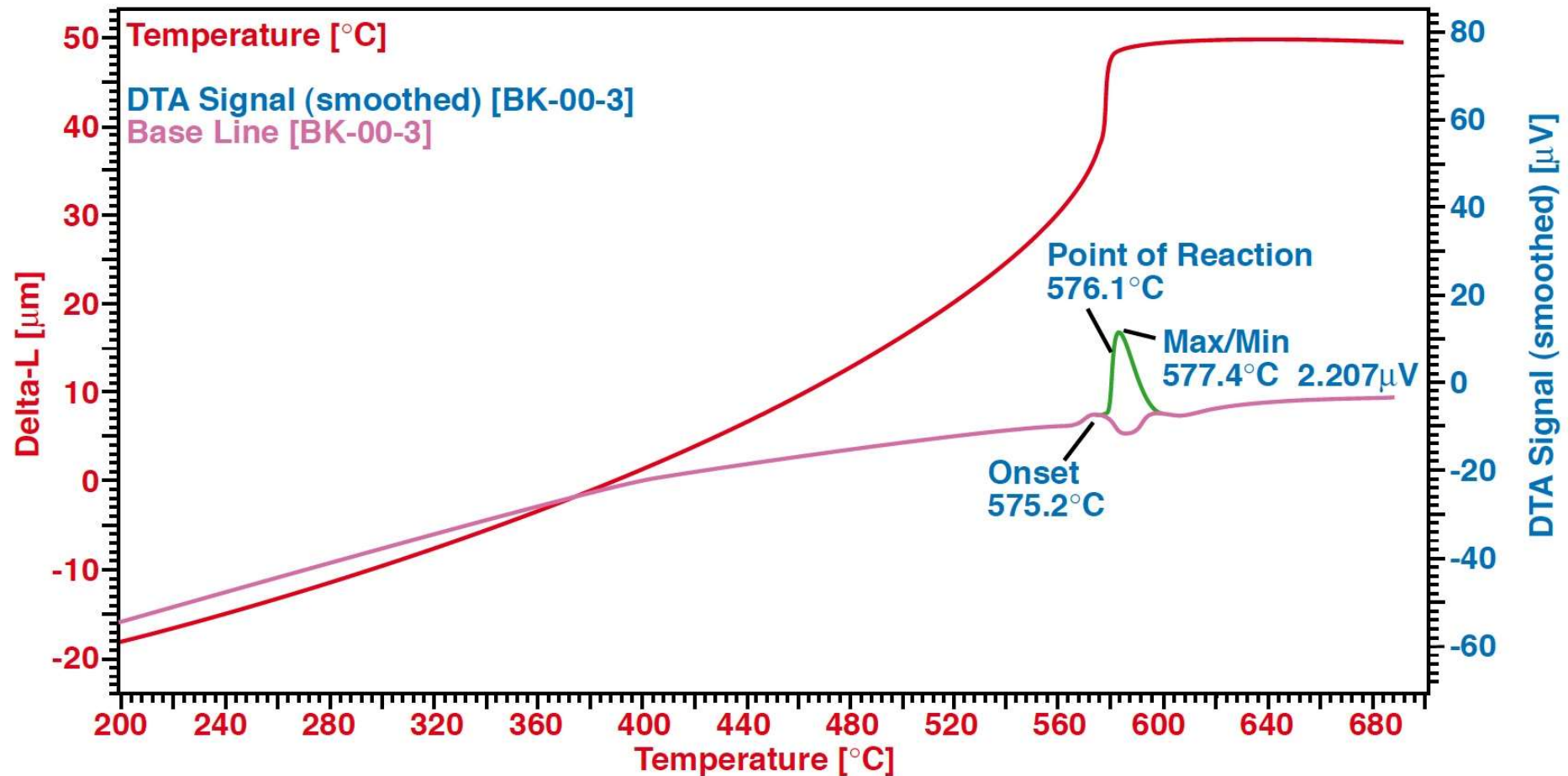
Phase diagrams

- Većinom u metalurgiji (slitine), ali i za keramiku



Ceramic sintering

- Kombinacija dilatometrije i DTA



Pharmaceutics

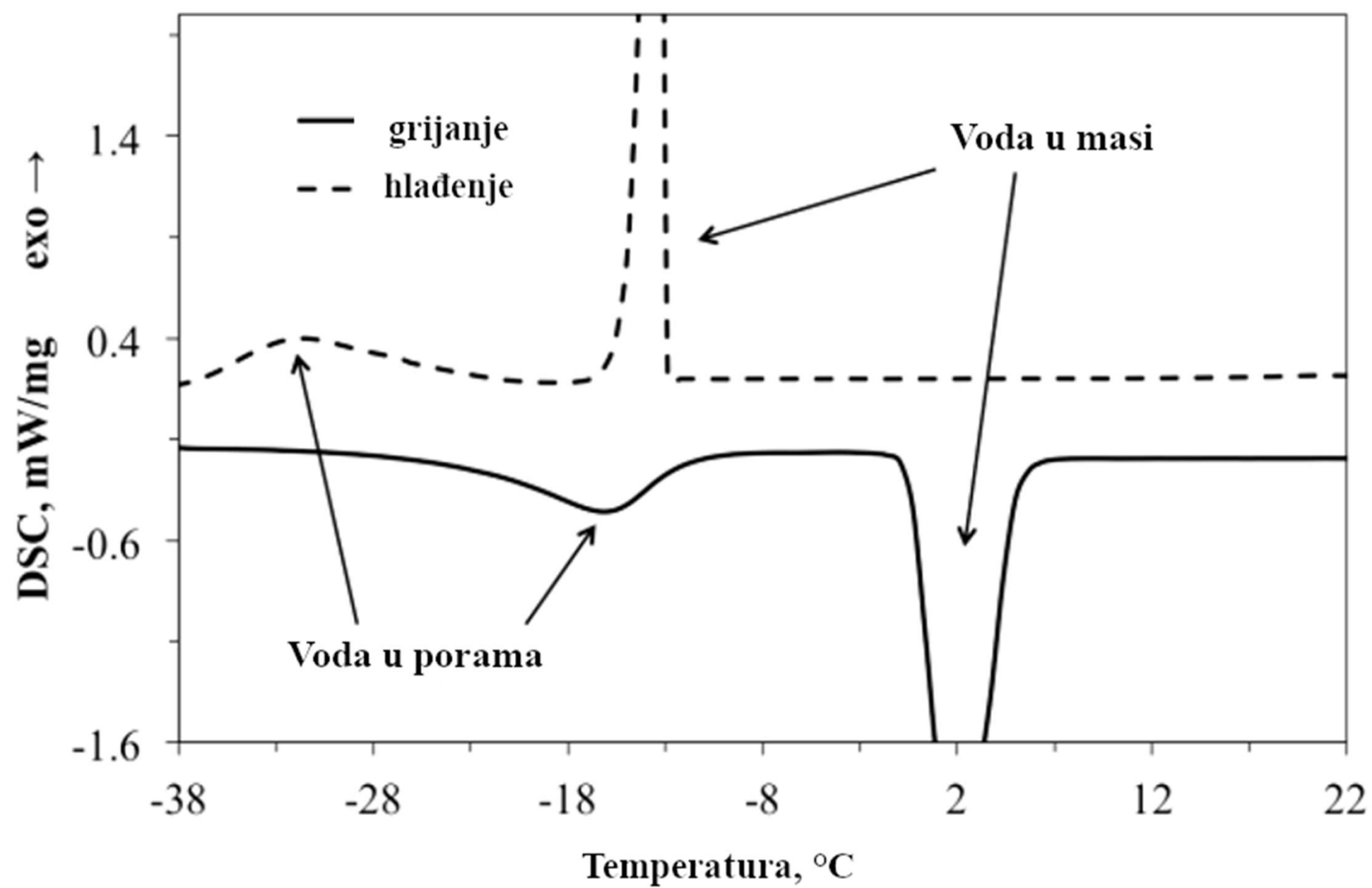
- Većinom kalorimterijska određivanja: mikrokalorimetrija, izotermna titracijska kalorimetrija
- Kemija složenih molekula i njihova međudjelovanja

Classical thermodynamics

- Klasična kalorimetrija – entalpija sagorijevanja, entalpija otapanja i solvatacije, entalpija miješanja
- Proračuni entalpijskih i entropijskih promjena

DSC for porosity determination

- Thermoporosimetry or thermoporometry
- Teže taljenje kapljevine (obično voda) adsorbirane u porama/uz stijenke pora / adsorbed water has shift in melting
- Zahtijeva baždarenje (npr. BET), ima prednost tamo gdje porozna struktura kolabira sušenjem/vakuumiranjem / must be calibrated but can be used „wet”



Kinetics from DSC and TGA

- Još uvijek dosta teorijskih rasprava i problema
- Slijepa primjena metoda na promjene (npr. staklište) koji ne odgovaraju teorijskim pretpostavkama
- Rezultati jako ovisni o načinu rada – daleko od “istinitih” podataka

Kinetic analysis

- Brzina reakcije i energija aktivacije:

$$r_A = \frac{d\alpha}{dt} = k(T)f(\alpha)$$

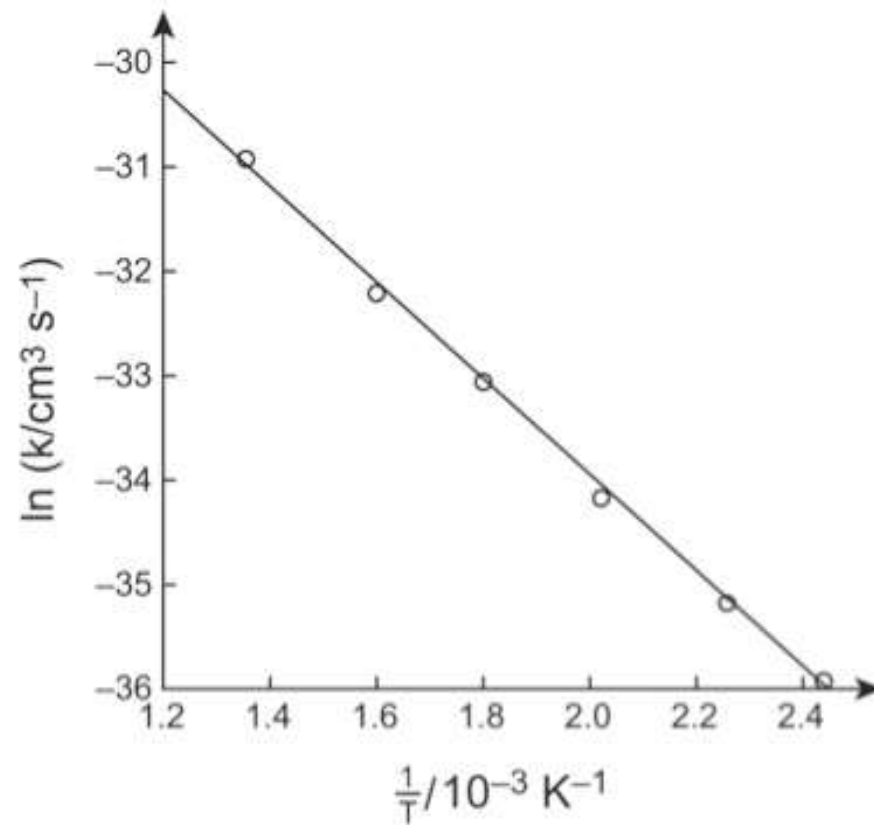
$f(\alpha)$ – kinetički model; mehanicistički ili (češće) empirijski

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \quad \text{Niz izotermnih mjerenja}$$

Arrhenius

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right)$$

Odsječak: k_0
Nagib: E_a

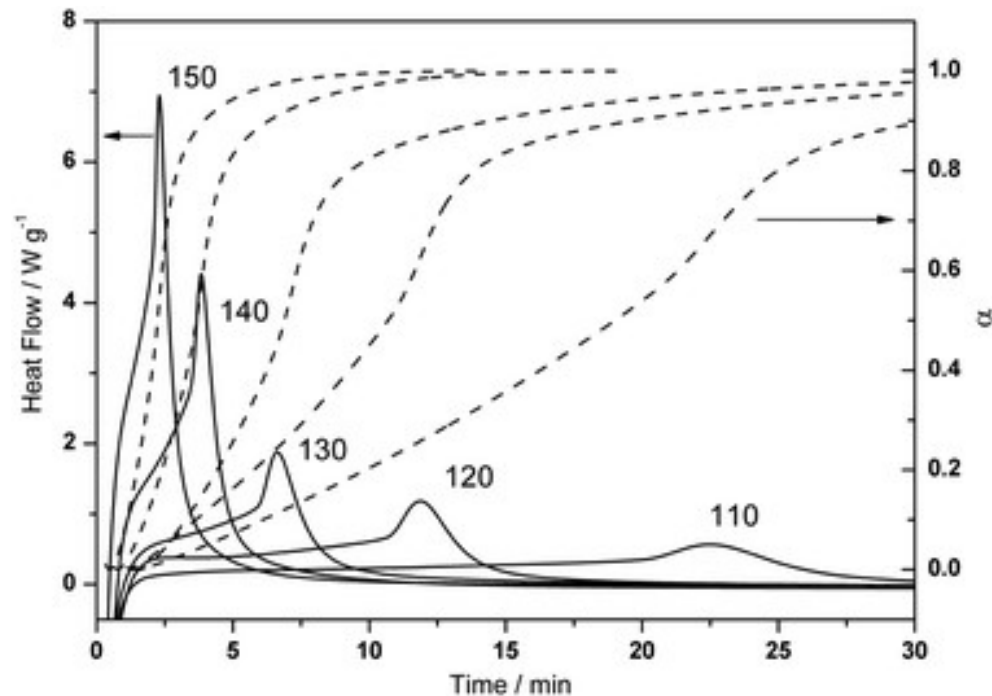


Kinetic analysis – DSC

- Povezivanje konverzije, α , s oslobođenom toplinom:

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H} \frac{dH}{dt}$$

$$\alpha(t) = \frac{1}{\Delta H} \int_0^t \frac{dH}{dt} dt$$



Pretpostavka **jedne/iste** reakcije! /
Assumption of one/same reaction!

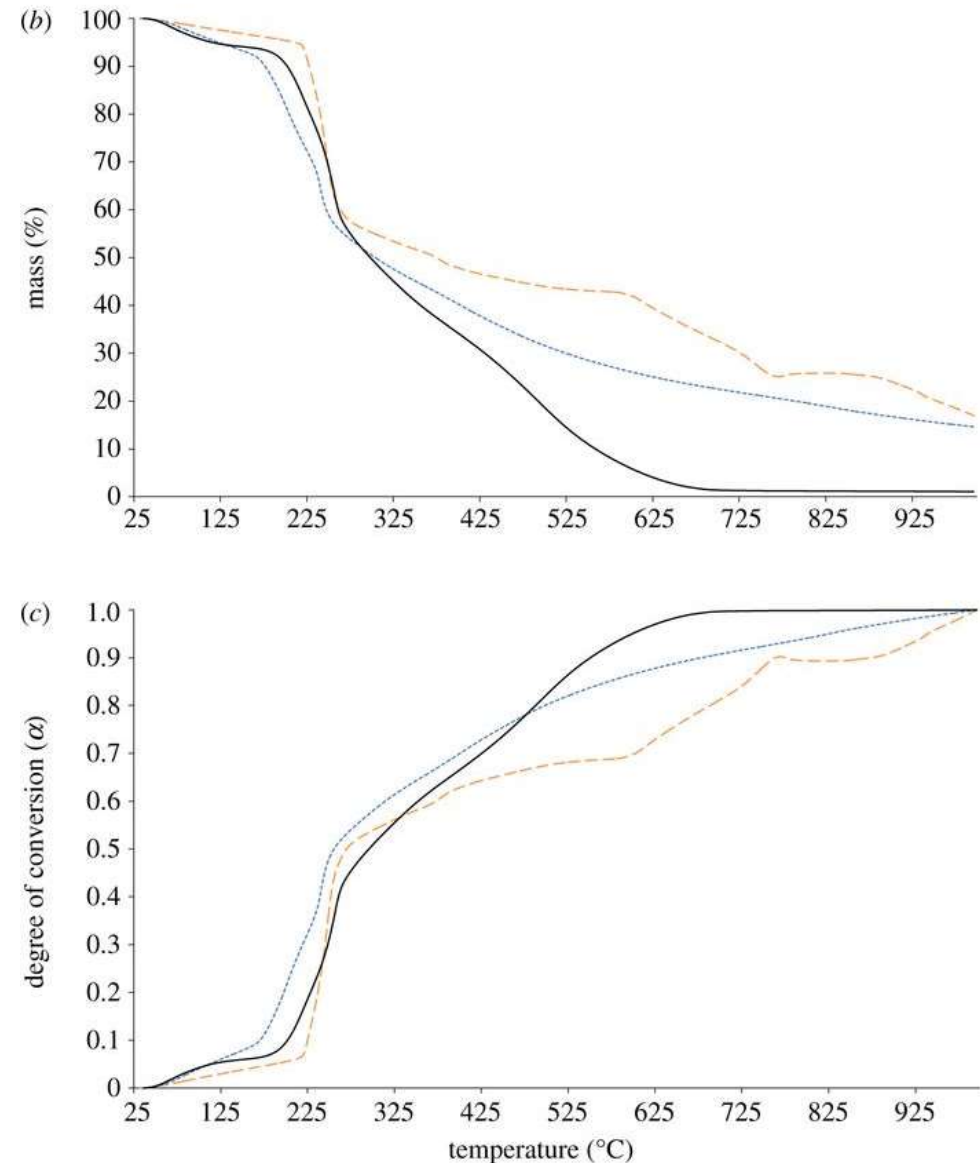
Kinetic analysis – TGA

- Analogno za TGA:

$$\alpha(T) = \frac{m_0 - m(T)}{m_0 - m_\infty}$$

Brzina reakcije
vremenskom
derivacijom
konverzije

Same assumptions!



Isoconversion methods

- Iz niza neizotermnih mjerenja različitih brzina zagrijavanja (pomak maksimuma!)
- Određivanje temperature pri kojoj se postigne ista konverzija za različite brzine
- Ovisnost prividne energije aktivacije o konverziji
- Više metoda (KAS, FWO, Friedman)

Isoconversion methods

- Diferencijalna – Friedman

$$\ln(d\alpha / dt) = -\frac{E_a}{R} \frac{1}{T} + \ln[k_0 f(\alpha)]$$

- Integralne:

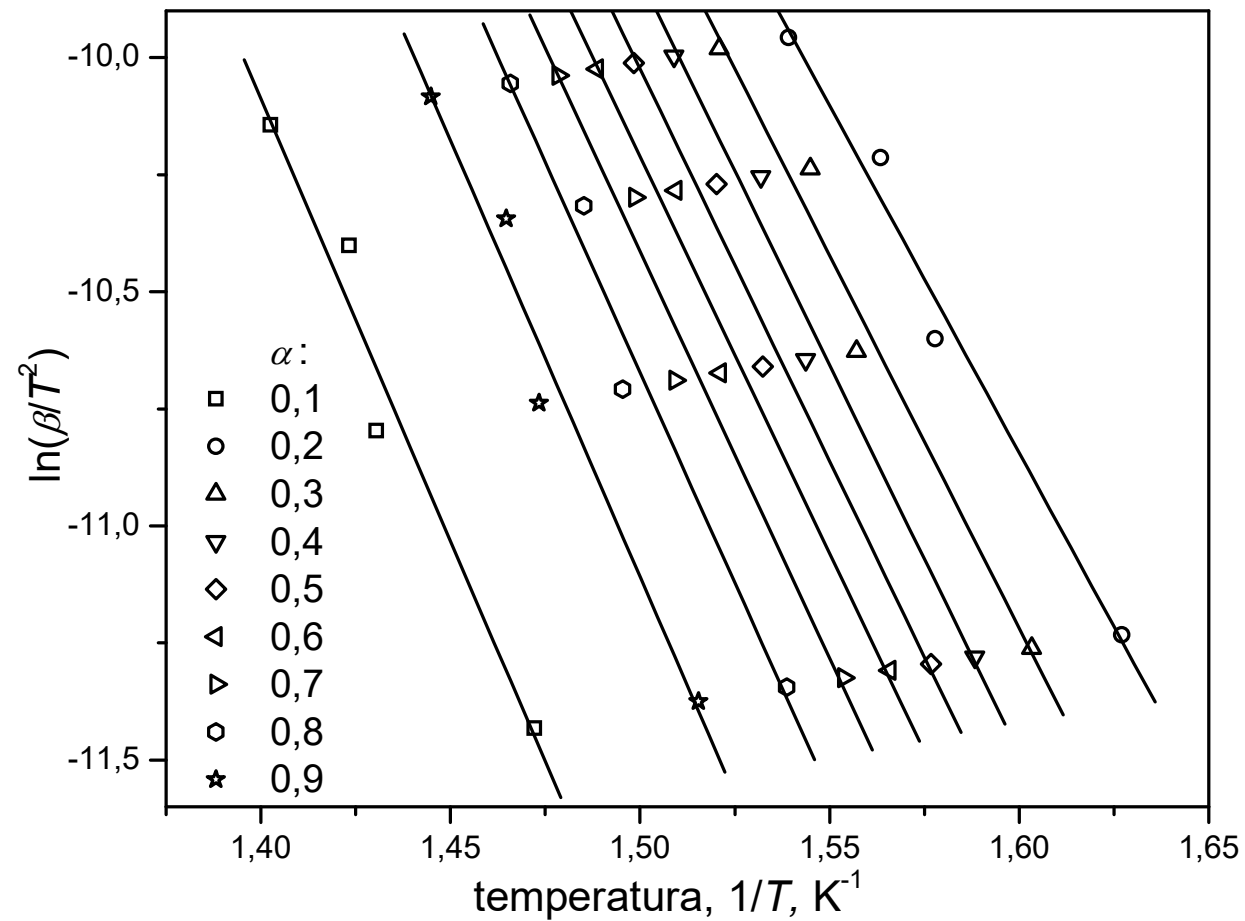
- Flynn-Wall-Ozawa

$$\ln \beta = \ln \left[\frac{0,0048 k_0 E_a}{R G(\alpha)} \right] - 1,0516 \frac{E_a}{R} \frac{1}{T}$$

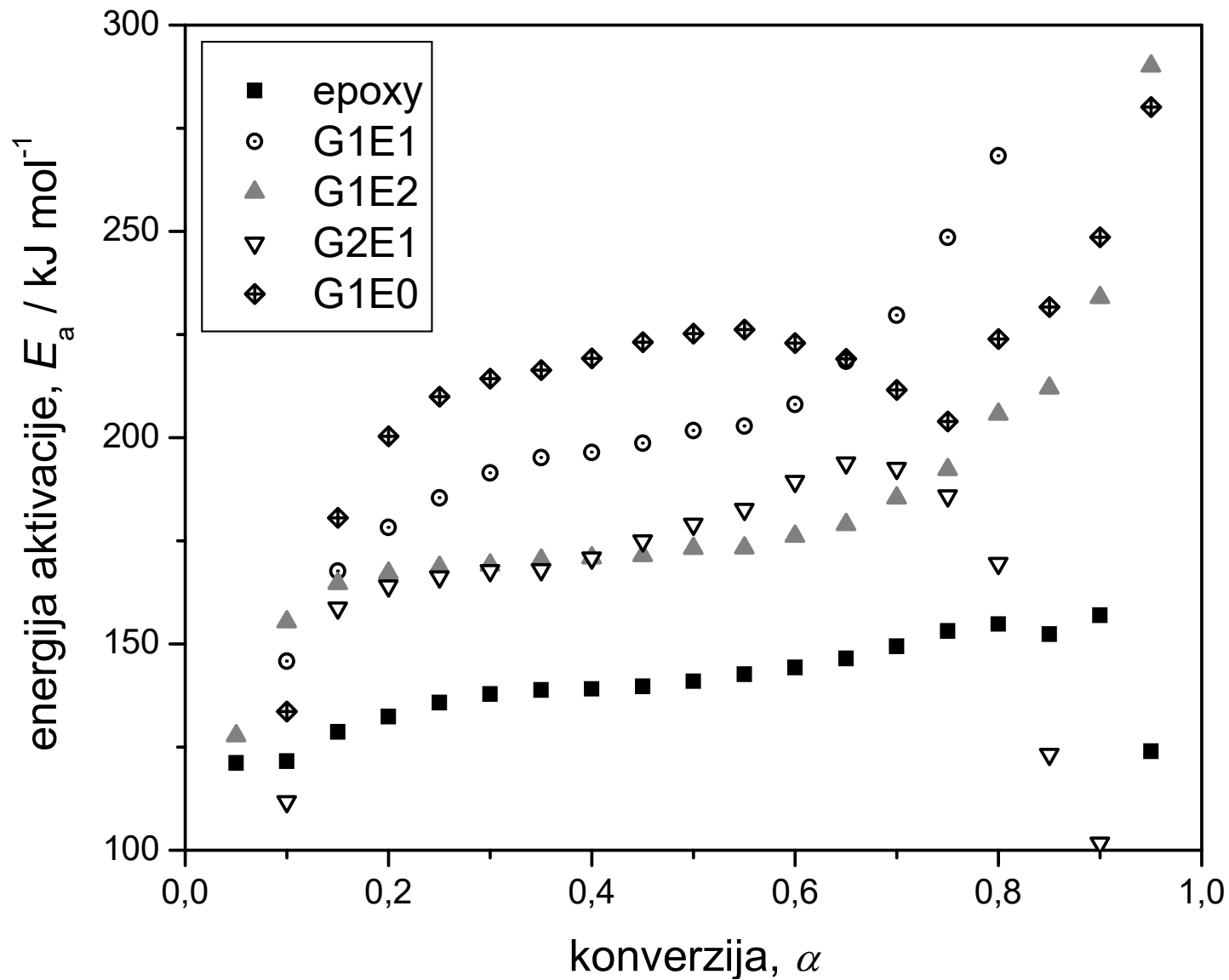
- Kissinger-Akahira-Sunose

$$\ln \left(\frac{\beta}{T^2} \right) = [\ln(k_0 R / E_a) - \ln G(\alpha)] - \frac{E_a}{R} \frac{1}{T}$$

Isoconversion methods



Isoconversion methods



Additional information

Mrežne stranice proizvođača:

NETZSCH

METTLER

TOLEDO

webinari, brošure, UserCom (MT)