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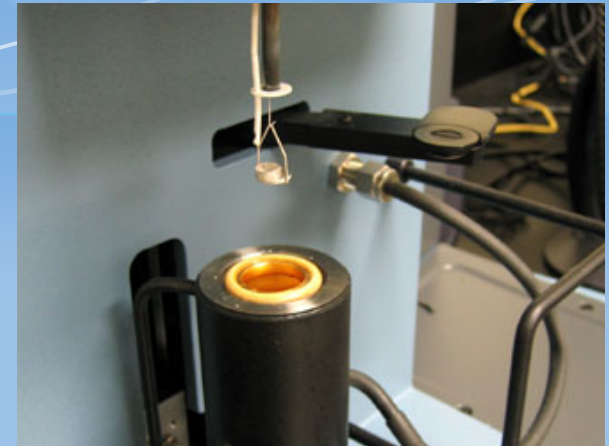


Termická analýza



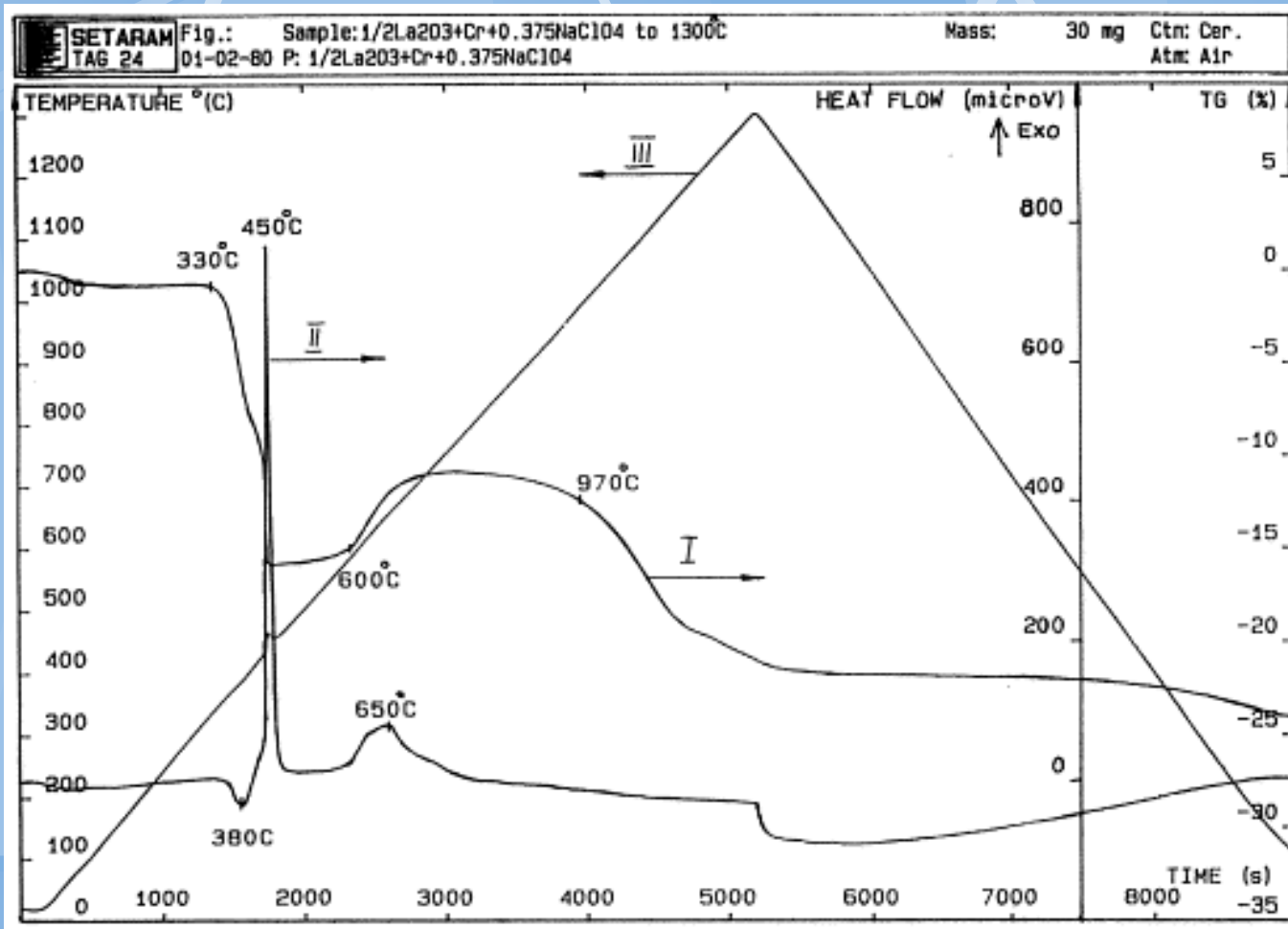
02 Termogravimetrická analýza – Thermogravimetric Analysis (TGA)

Přednášející: Doc. Jiří Sopoušek



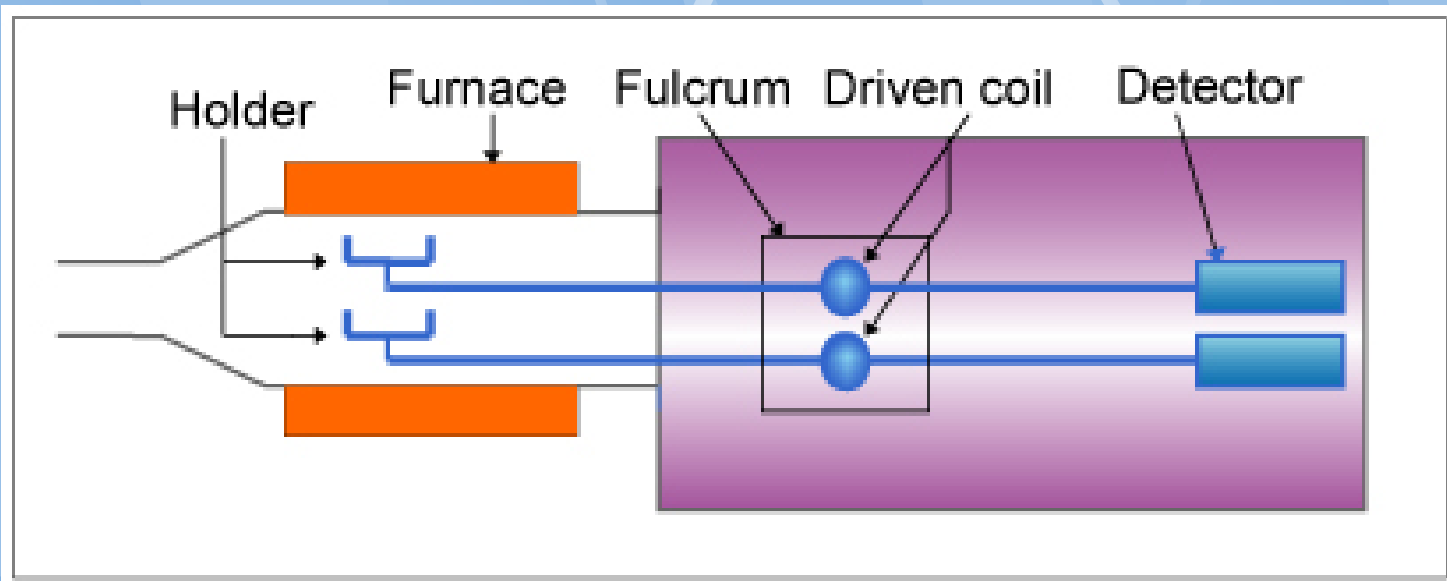
Princip

- Měření změn hmotnosti vzorku vystaveného změnám teploty (ohřev, chlazení, lineární, isothermická prodleva).



ICTAC definice TG

A technique in which the mass of the sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed.



Použití

(všude, kde jde o změnu hmotnosti)

Například

- **Sledování těkavých látek (schnutí, desorpce, adsorpce, ztráta krystalové vody,...), měření čistoty látek (vlhkost)**
- **Oxidace na vzduchu nebo ve směsích s kyslíkem (kovy, oxidační rozklad organiky, ..)**
- **Termické rozklady v inertu, pyrolýza, karbonizace, ...**
- **Heterogenní chemické reakce (produkt plynná složka)**
- **Reakce v redukční atmosféře**
- **Feromagnetické materiály (Magnetické vnější pole, Currie, Neel)**
- **Atd.**

Měřicí uspořádání

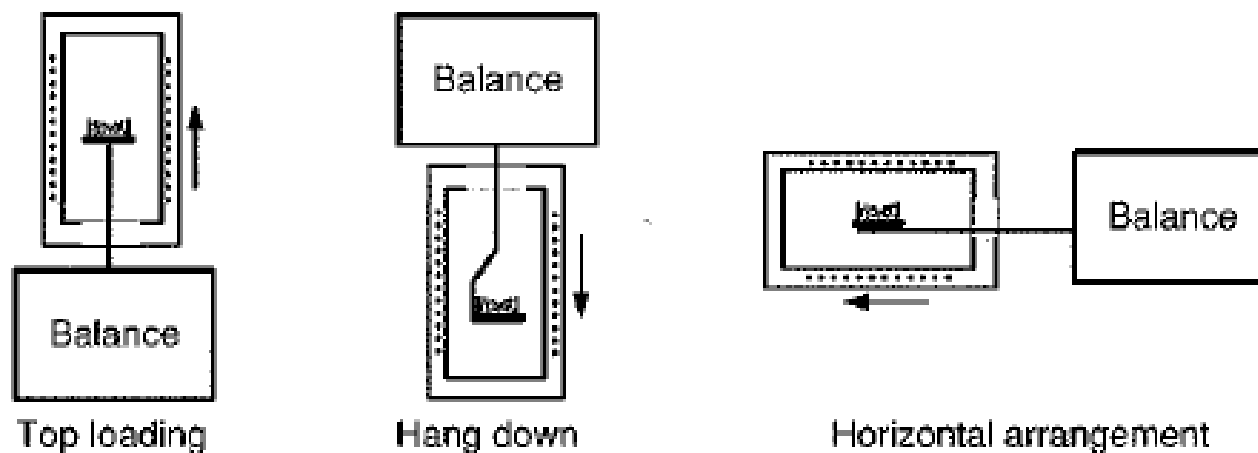


Figure 3.2 Thermobalance designs showing the top loading, hang down and horizontal arrangements.

Pozor na:

- Zahřívání vah, ovlivnění nosným plynem
- Princip měření (klasický vs. elektronický)
- Koroze a poškozování závěsu
- Rozdíly v složení atmosférz v peci a ve vahách (proplachy, **nelze vakuovat**)

Schéma měření TGA

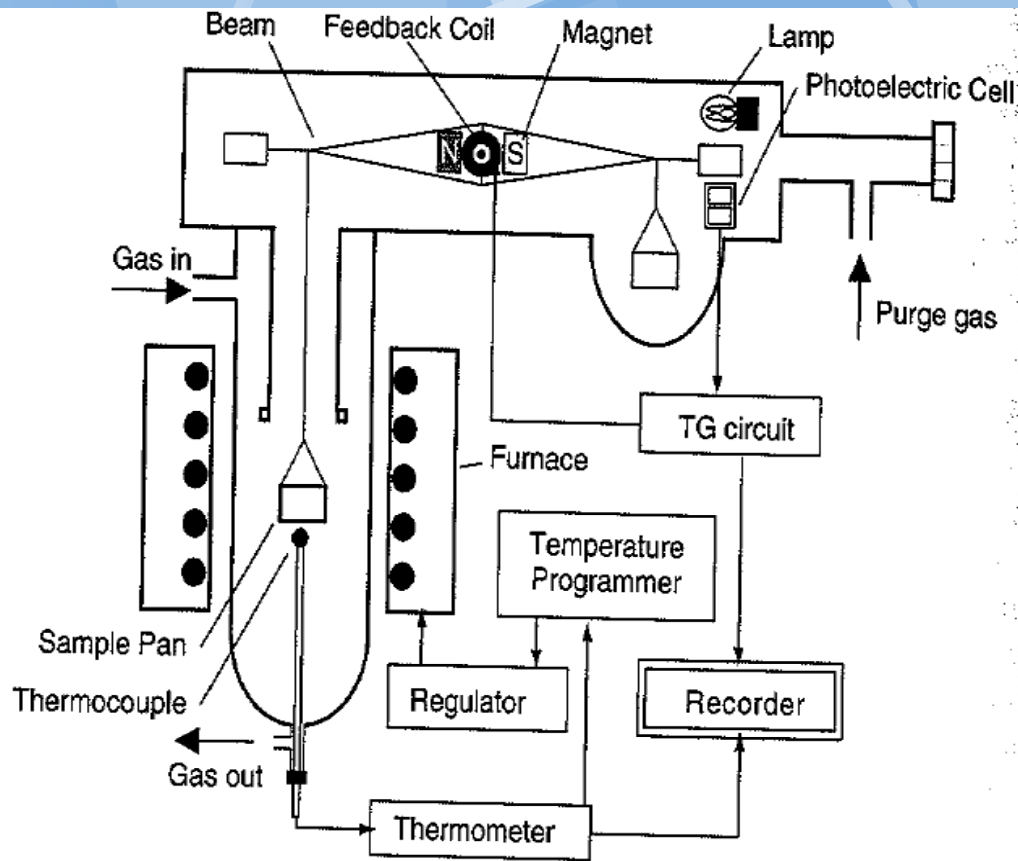
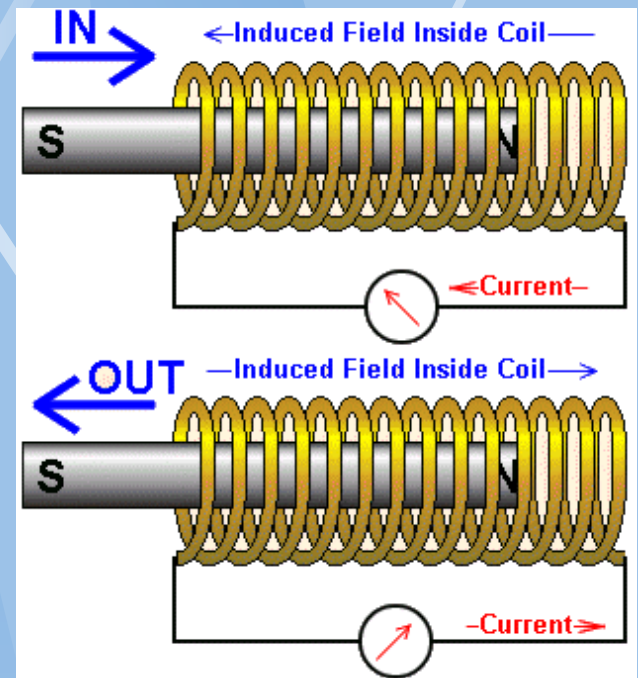


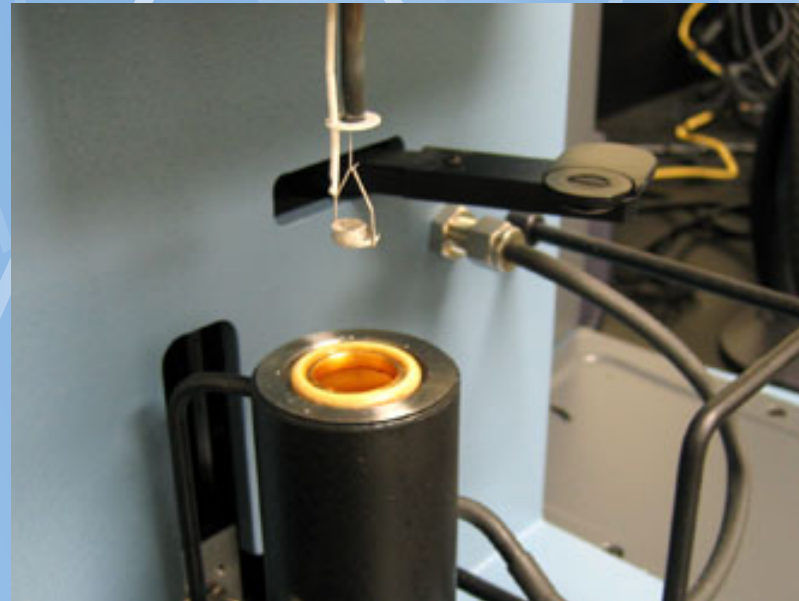
Figure 1 Schematic illustration of a TG apparatus of suspending type



Nutno provádět kalibraci vah standardem hmotnosti.

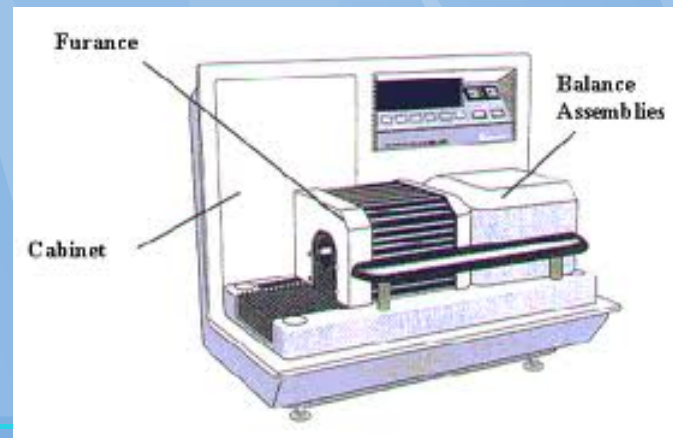
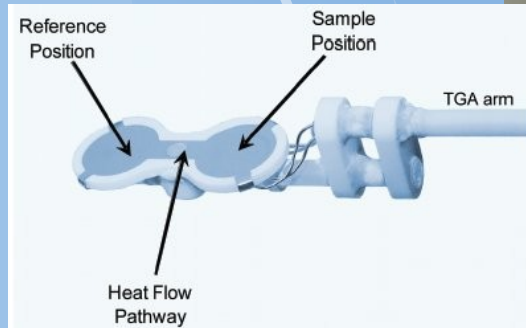
Vertikální - horní váhy

Setaram



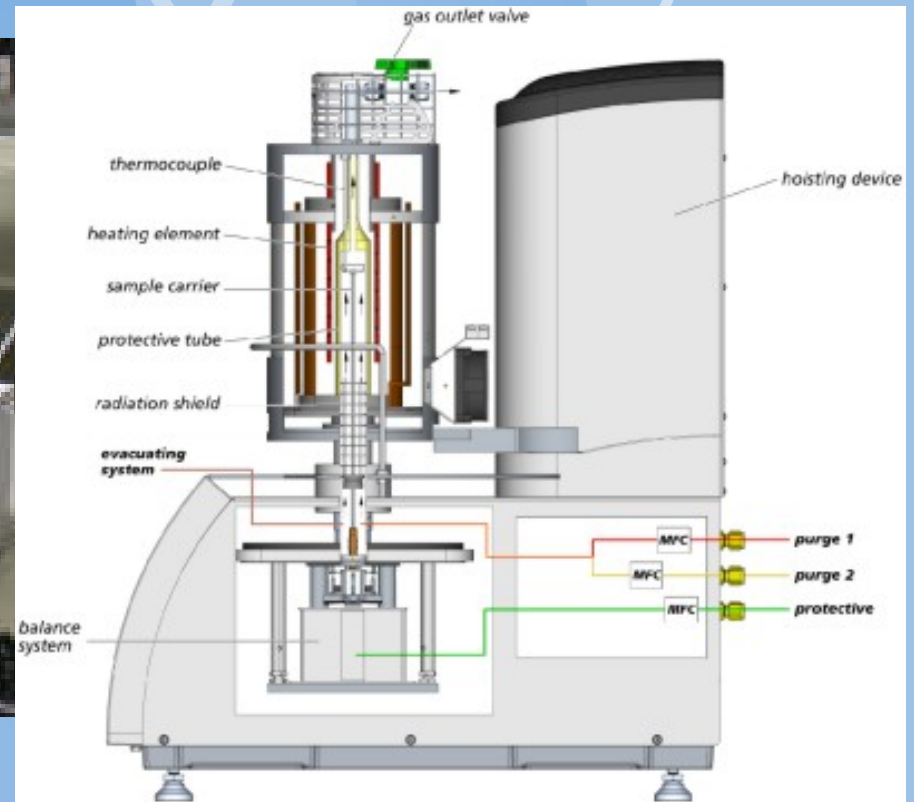
Horizontální TGA

TA instruments

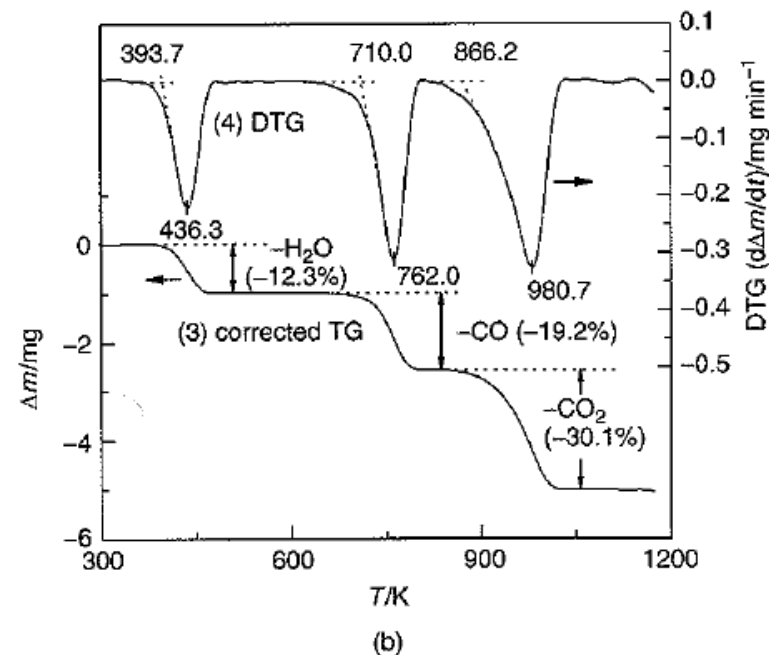
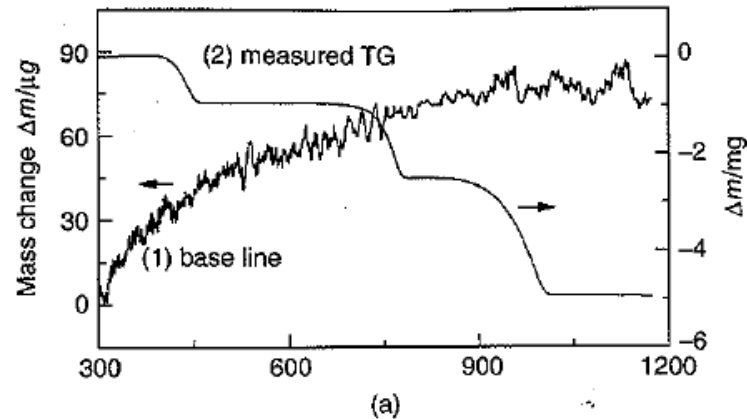


Verikální spodní váhy

Netzsch



Rozklad št'avenanu vápenatého



A: (100-226) °C, endo
 $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$

B1: (298-420) °C, v inertu, endo
 $\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO}$

B2: (289-420) °C, je-li O2, exo
 $\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO}$

C: (660-840) °C, endo
 $\text{CaCO}_3 + 1/2\text{O}_2 \rightarrow \text{CaO} + \text{CO}_2$

**Pozn.: je to standardní látka ,
 čistí aparaturu**

Figure 2 Analysis of TG curve as exemplified by the thermal decomposition of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$

Korekce na vztlak

Závisí na volbě nosného plynu

Table 3.1 Density of several gases at 25, 500 and 1000°C at a standard pressure of 101.3 kPa

Gas	Density (mg/mL) at 25°C	Density (mg/mL) at 500°C	Density (mg/mL) at 1000°C
Dry air	1.184	0.457	0.269
Nitrogen	1.146	0.441	0.268
Oxygen	1.308	0.504	0.306
Argon	1.634	0.630	0.383
Helium	0.164	0.063	0.038
Carbon dioxide	1.811	0.698	0.424

Vzorek při
zahřívání
„těžkne“

$$p = p_0 \frac{T_0}{T}$$

Ideal gass
approx.

Nutná baseline s
prázdným kelímkem
pokud není korekce
automatická díky SW

Vliv nosného plynu na TGA křivku (oxidace a reaktivita !)

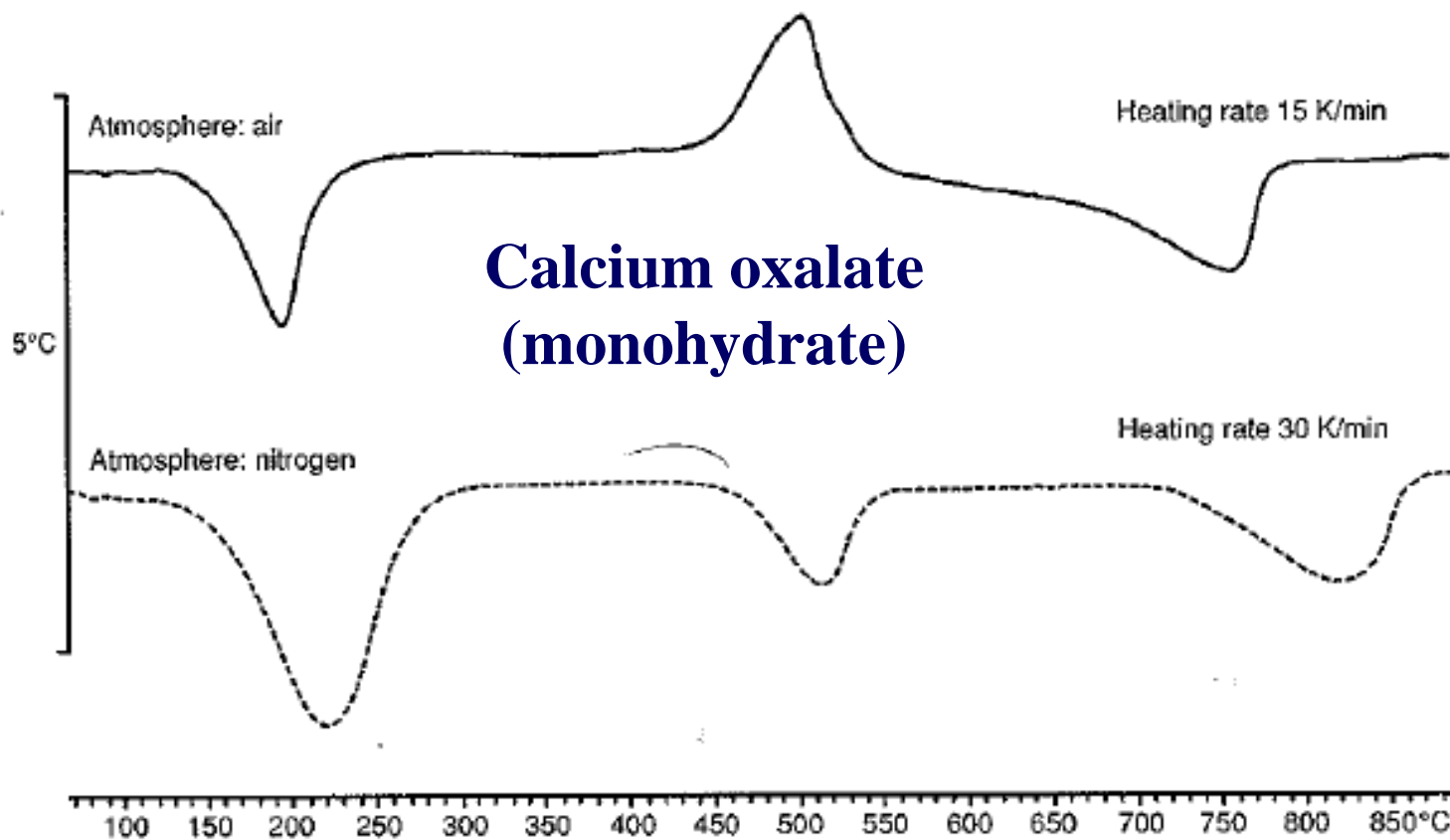


Figure 3.3 DTA curves of calcium oxalate monohydrate measured in air (upper curve) and in nitrogen (lower curve). The second effect at 500°C corresponds to the elimination of carbon monoxide, a process that is endothermic in an inert atmosphere. If oxygen is present, the CO immediately burns to CO₂, which produces an exothermic effect (above).

Příprava vzorku a podmínek experimentu

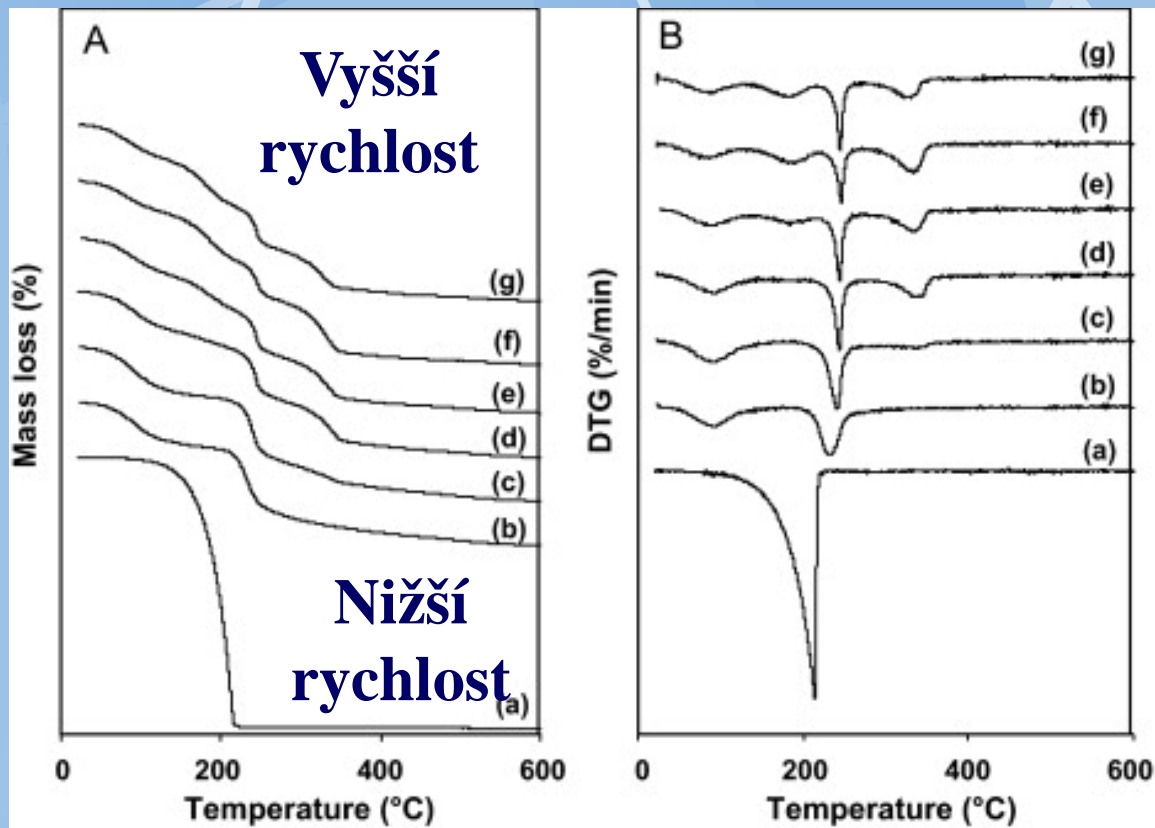
**Representativní vzorek: jemný, přiměřená hmotnost, co
nejméně poznamenat přípravou vč. kontaminace**

**Atmosféra: vhodná pro experiment, pozor na znečištění
(O₂, vlhkost, N₂,..., redukční a oxidační potenciál,...),
tlak (0.5Atm), vhodná rychlost vznosu (funkce teploty),
proplach vah (míšení s nosným plynem)**

Obvyklé podmínky experimentu

- **Rychlost ohřevu (10K/min, isoprodelevy,..), nastavení teplotního programu.**
- **Nosný plyn (inerty Ar, N₂, synt. vzduch, He, ...)**
- **STA-sample controlled thermal analysis (řízení rychlosti ohřevu změnou hmotnosti vzorku)**
- **Měření baseline (eliminuje řadu vlivů, ne např. emisivitu vzorku)**

Volba rychlosti ohřevu



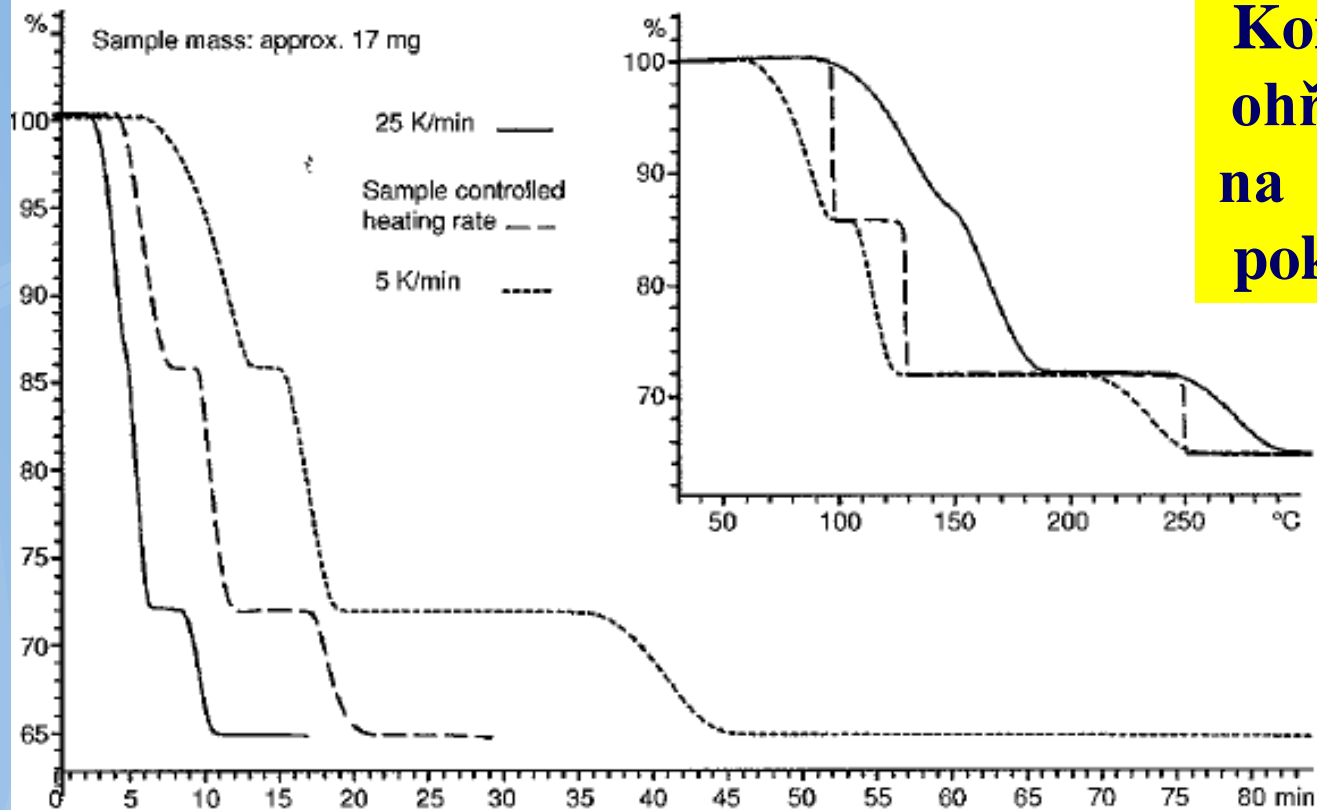
vyšší rychlosti
posouvají reakce k
vyšším teplotám

Isotermní
prodlevy:

-na startu

-Při měřených
dějích

Vliv rychlosti ohřevu a STA-sample controlled thermal analysis



Kontrola rychlosti ohřevu v závislosti na rychlosti změny poklesu hmotnosti

Figure 3.5 Influence of the heating rate on the resolution of partial reactions. In the inserted diagram on the right, the dotted and solid TGA curves of copper sulphate pentahydrate were measured conventionally at 5 and 25 K/min, whereas the dashed curve was recorded using the sample controlled heating rate. In this presentation of mass against temperature, the steps in the curve appear to be nearly vertical because, at low heating rates, the reaction takes place almost isothermally. In contrast, in the mass against time presentation (main diagram), the shapes of the three curves at first sight appear similar. On closer inspection, the better separation obtained using sample controlled heating rates – especially in the first two steps – becomes apparent.

Změna hmotnosti a tepelné efekty TG-DTA pro jemné a hrubé krystaly

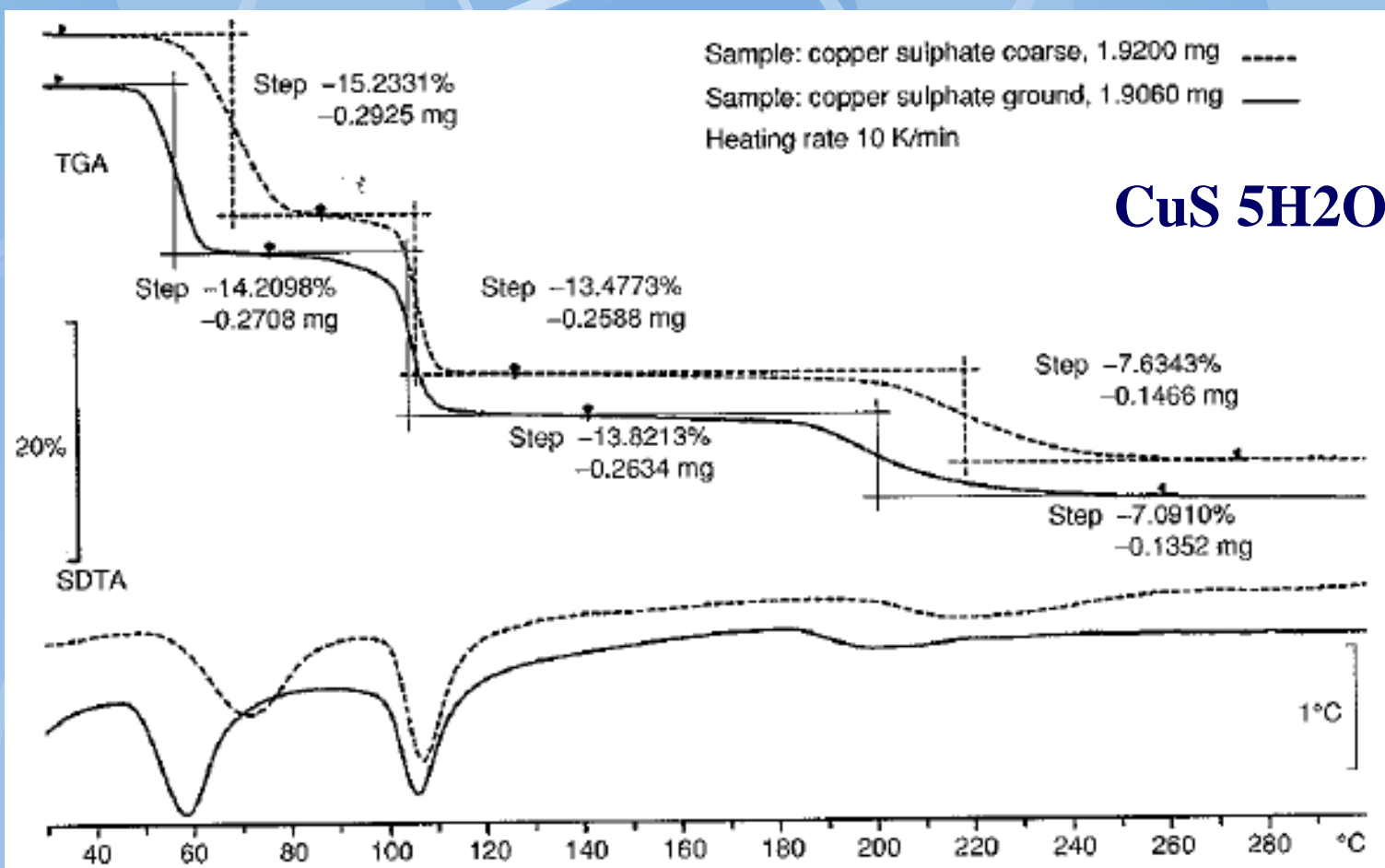


Figure 3.4 TGA and DTA curves showing the elimination of water of crystallisation from copper sulphate pentahydrate. The dotted curves were measured with rather coarse crystals, the solid curves with finely ground crystals. The first and third steps in the curve of the finely ground crystals are shifted more than 10 K to lower temperature. The heating rate was 10 K/min. Curves are offset for comparison.

Kelímky a atmosféra

Kelímky- nástřiky inertními oxidy (Al_2O_3 , Y_2O_3)

**Atmosféra (čisté plyny typicky 30ml/min
inertu nebo S-air, 4% H_2 +96%Ar,
200/CO, 200/ NO)**



Quartz



Pt



Safír



Alumina

Čistota atmosféry - Zdroje znečištění kyslíkem

Table 3.2 Sources of residual oxygen and precautions

Sources of residual oxygen	Precautions
Oxygen content of the purge gas Leaks in the gas supply tubing and other fittings and connections	Use an inert gas containing less than 10 ppm oxygen. Oxygen can diffuse through plastic tubing! Either use very short sections of plastic tubing (less than 50 cm) or metal tubing with a minimum number of connections and joints. Carefully check all joints for leaks.
Outgassing of constructional components (oxygen adsorbed on parts of the measuring cell) and dead volume	Switch on the flow of protective gas to the microbalance several hours before measurement. Purge the vacuum connection as well. Only open the furnace briefly to insert the sample. Active replacement of air through slight evacuation to about 1 kPa. Then flood with the desired purge gas (if necessary twice).
Ingress of atmospheric oxygen due to leaks	A possible cause of leakage is the furnace seal which could be damaged or dirty.
Ingress of atmospheric oxygen due to back diffusion at the purge gas outlet	Attach a long narrow tube to the outlet (this functions as a diffusion baffle).

Vliv změn tlaku (na elastomer)

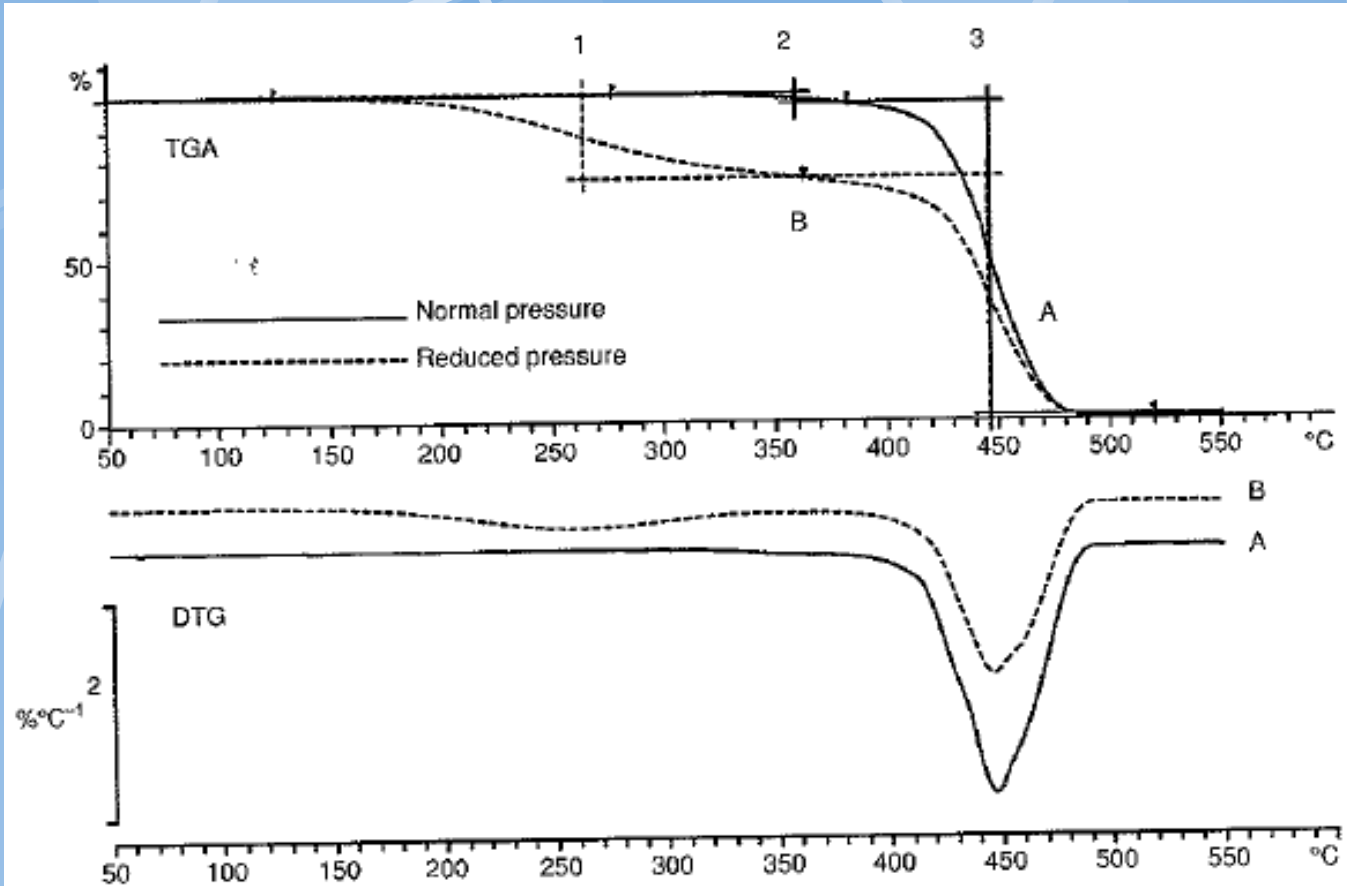


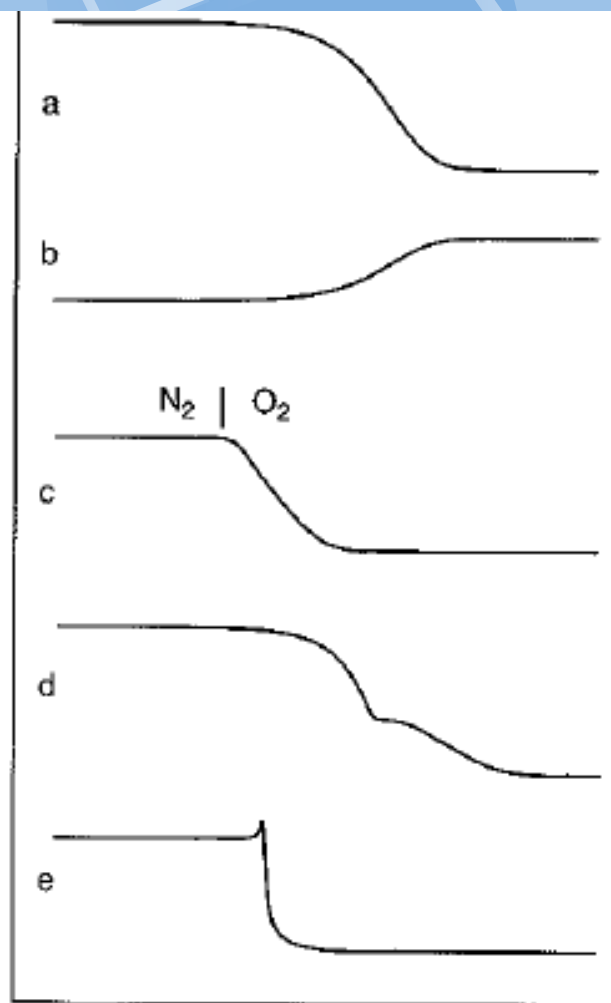
Figure 3.6 Effect of pressure on the decomposition of an elastomer: sample A is measured at normal (atmospheric) pressure, and B under reduced pressure, 1.5 kPa (1.5 mbar). Under reduced pressure, the vapourisation of the volatile components (additives, 1) is clearly separated from the decomposition of the elastomer (2,3). At normal pressure, the step height evaluated (on an expanded scale) from the stable region of the baseline at 270°C to next DTG maximum at 380°C does not correspond to the true additive content.

Další vlivy

- **vliv vlhkosti (dobře prožíhané kelímky!!!!!!!!!!!!!!!,)**
- **Zbytky vlhkosti v nosném plynu způsobují adsorpční parazitní efekty.**
- **Autosampler (AI kelímky nejlépe, kapsulovat s dírkou)**



Interpretace záznamů TGA



Termický rozklad

Oxidace

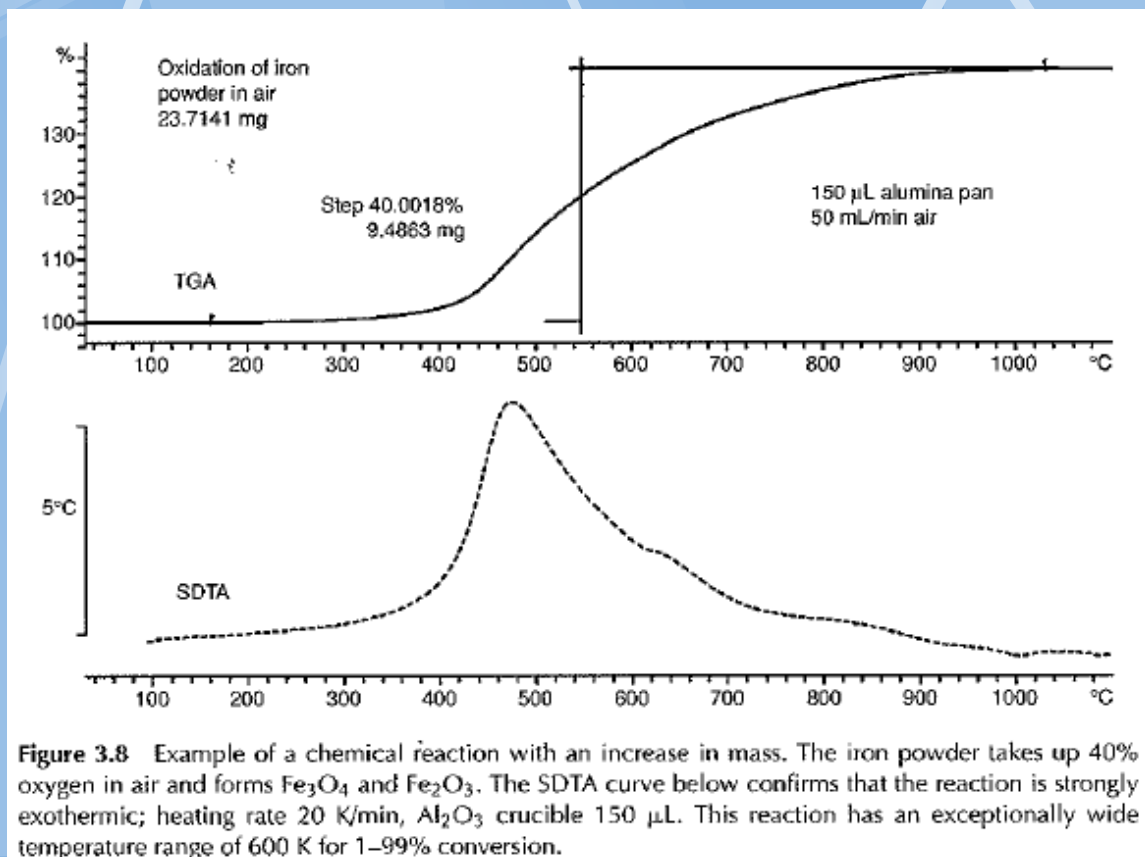
„Zhoření“

**Výcestupňový
rozklad**

„Výbuch“

Figure 3.7 TGA curves of different chemical reactions. (a) Thermal decomposition with the formation of volatile reaction products. (b) Corrosion, oxidation of metals (formation of non-volatile oxides). (c) Combustion of carbon black on switching from N₂ to O₂. (d) Multi-step decomposition. (e) Explosive decomposition with recoil effect.

Přítomnost chemické reakce



Rozklad aspartanu

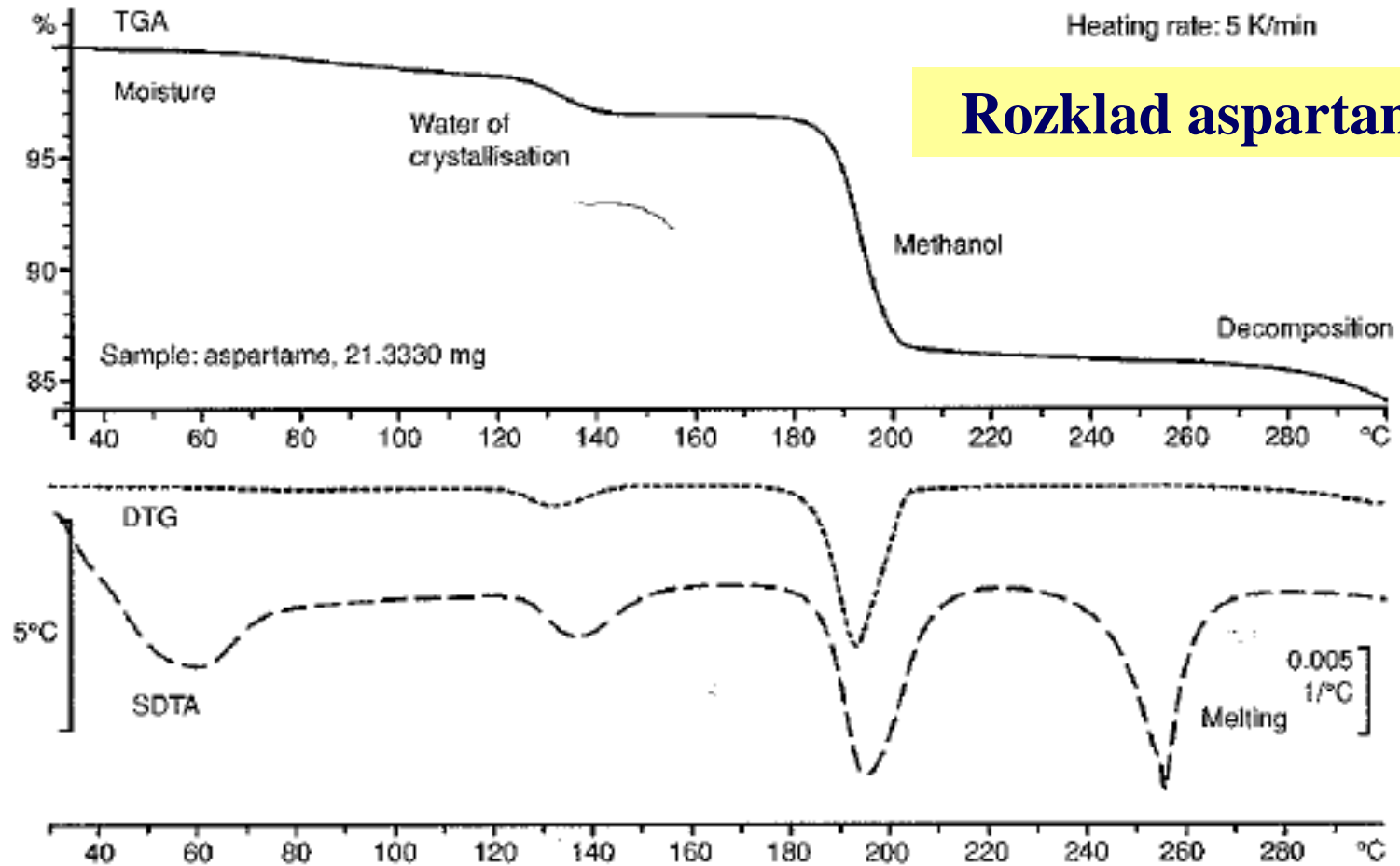
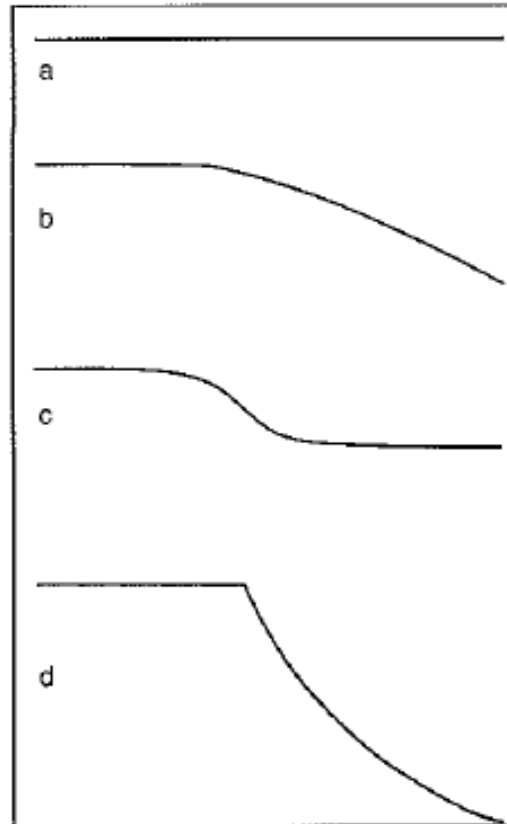


Figure 3.9 The decomposition of the artificial sweetener aspartame appears to be relatively complex. First, the water of crystallisation is lost at about 130°C. This is followed by the elimination of methanol at 180°C and the formation of a piperazine ring. This reaction takes place in an extremely narrow temperature range of just 20 K for 1–99% conversion. The SDTA curve shows that the piperazine derivative melts at 250°C.

Tanění na TG křivce



OK

Malý odpar (Zn, Se, ..)

**Ztráta něčeho při tání
(vlhkost)**

**Tanění spojené s
rozkladem**

Figure 3.10 Thermogravimetric effects on melting. (a) Sample with low vapour pressure (no TGA effect). (b) Volatile melt (the liquid sample evaporates). (c) Moisture escapes on melting. (d) Sample melts and decomposes.

Další efekty

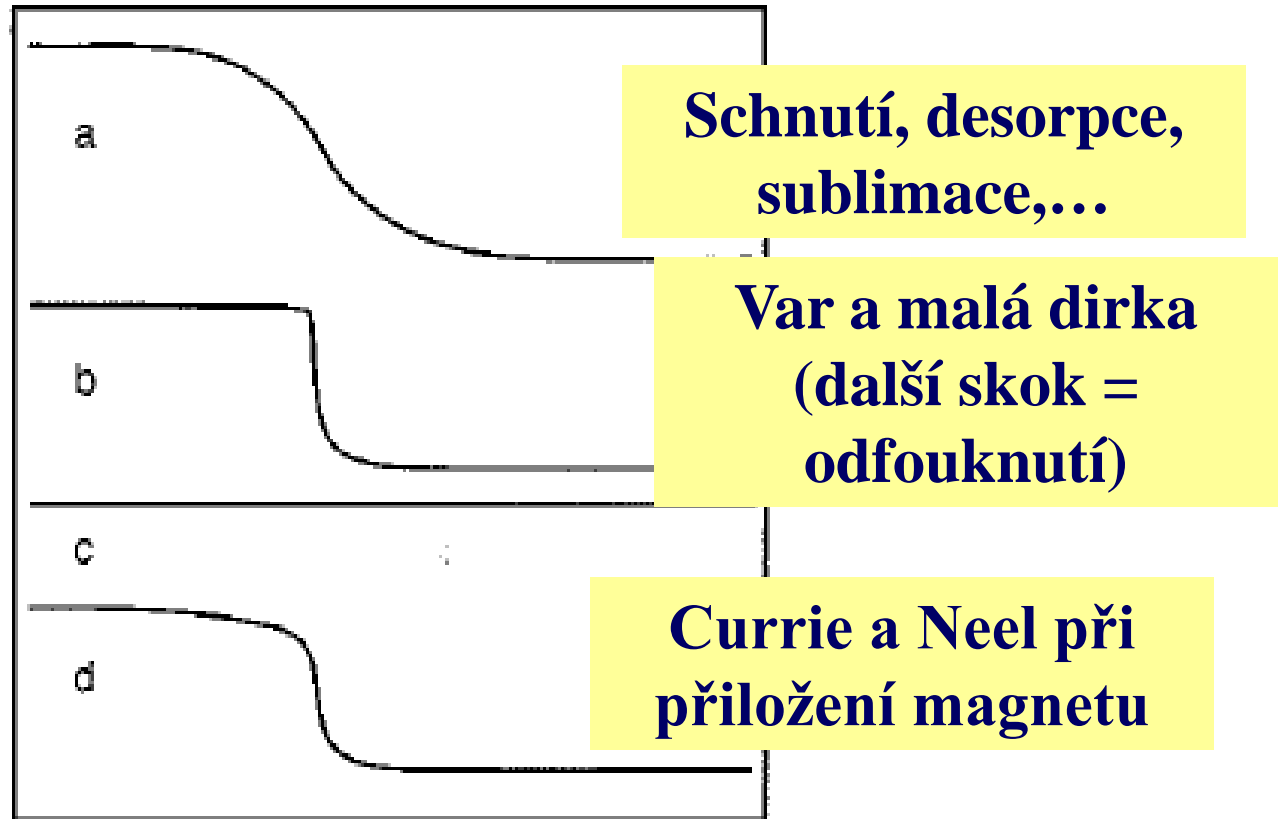
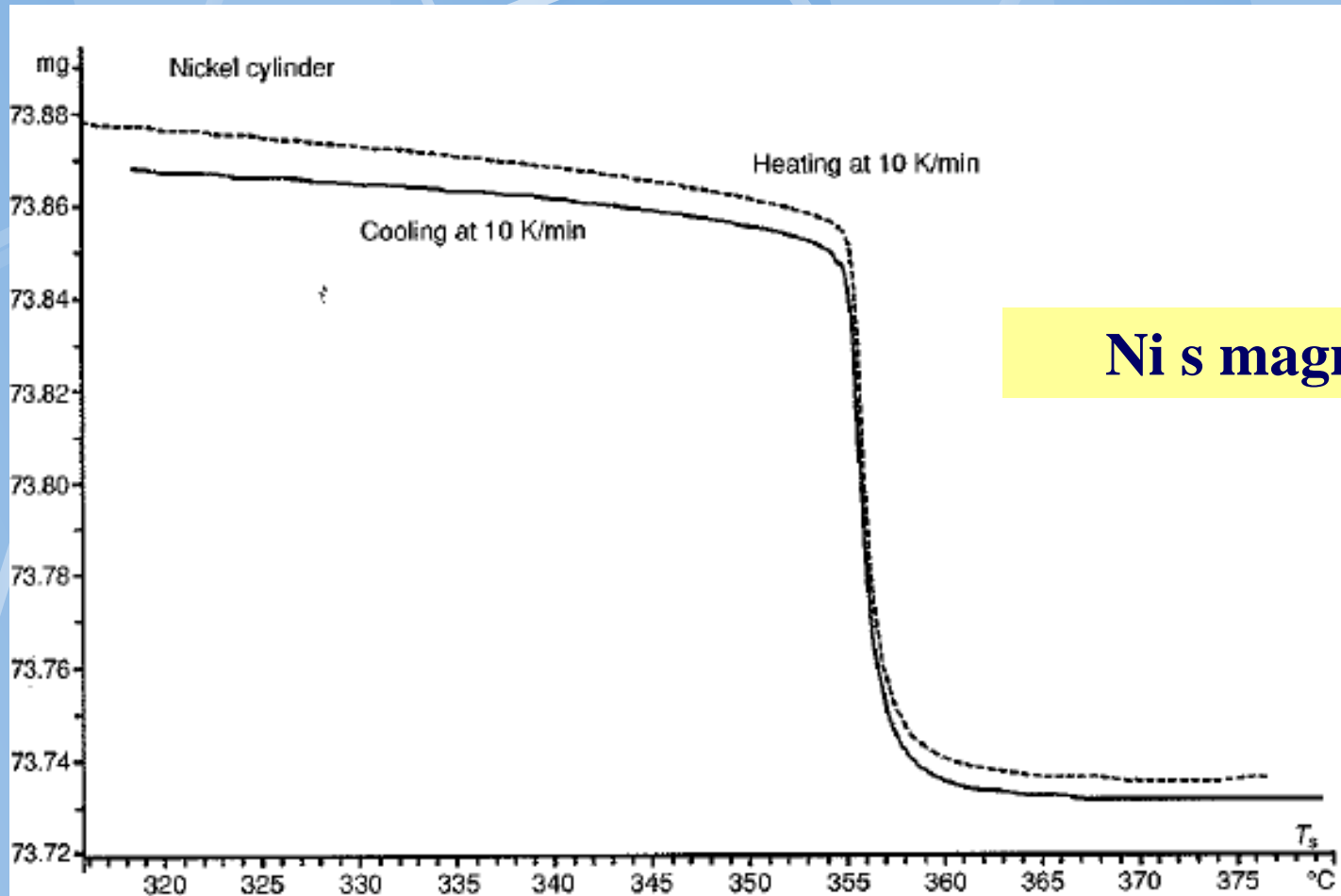


Figure 3.12 Other thermogravimetric effects. (a) Drying, desorption, sublimation. (b) Boiling in a crucible with a small hole in the lid. (c) Ferromagnetic Curie transition without a magnet: no TGA effect. (d) The same sample with a permanent magnet below the furnace.

Vliv rychlosti t na magnetické efekty



Ni s magnetem

Figure 3.13 A permanent magnet placed below the furnace of the thermobalance attracts a ferromagnetic material and causes an apparent increase in mass. When the Curie temperature of the sample is exceeded, the force is no longer exerted and there is a sudden loss in apparent mass. This effect is reversible and occurs again on cooling. The abscissa shows the sample temperature, T_s .

Vyhodnocení křivek TG

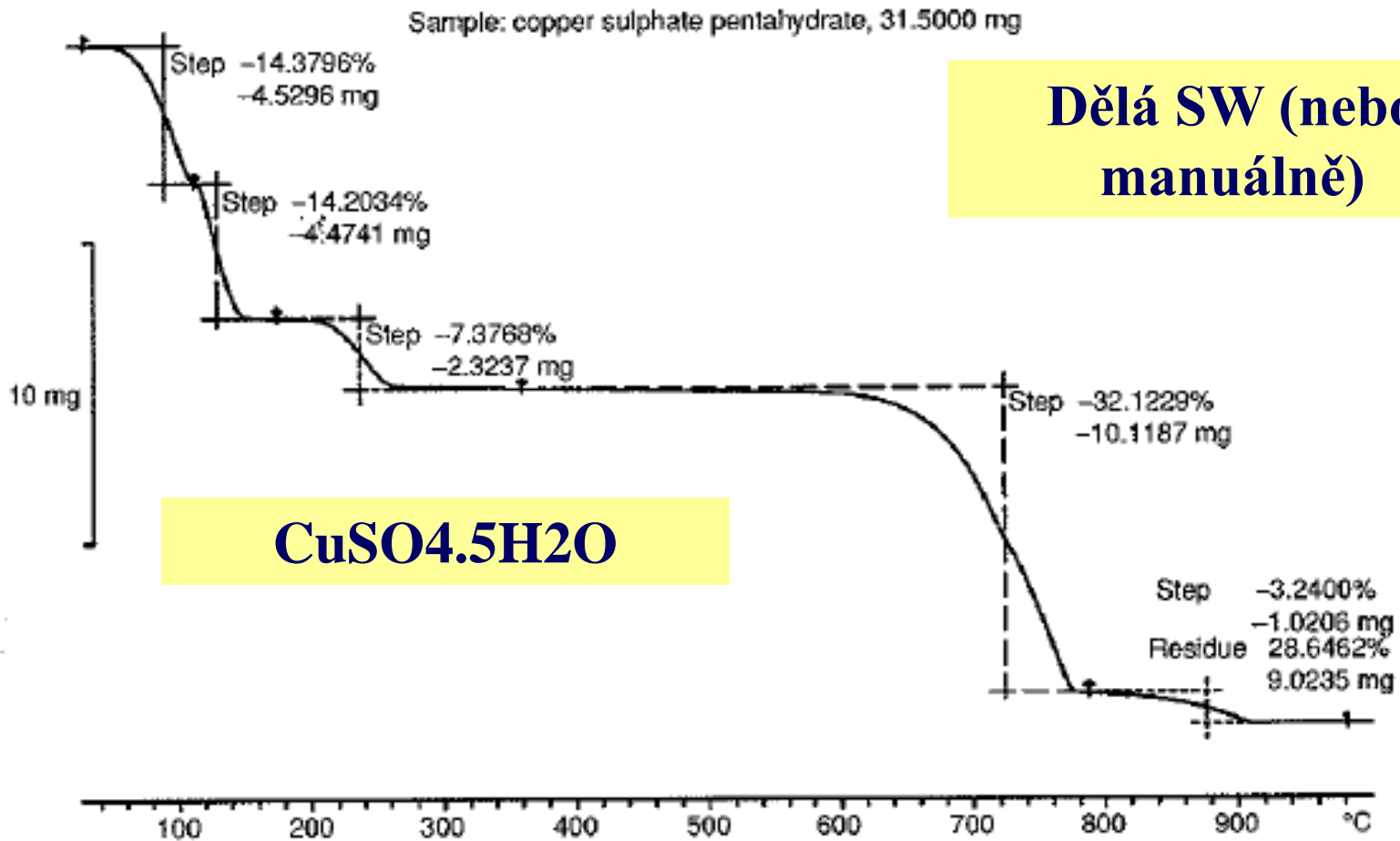
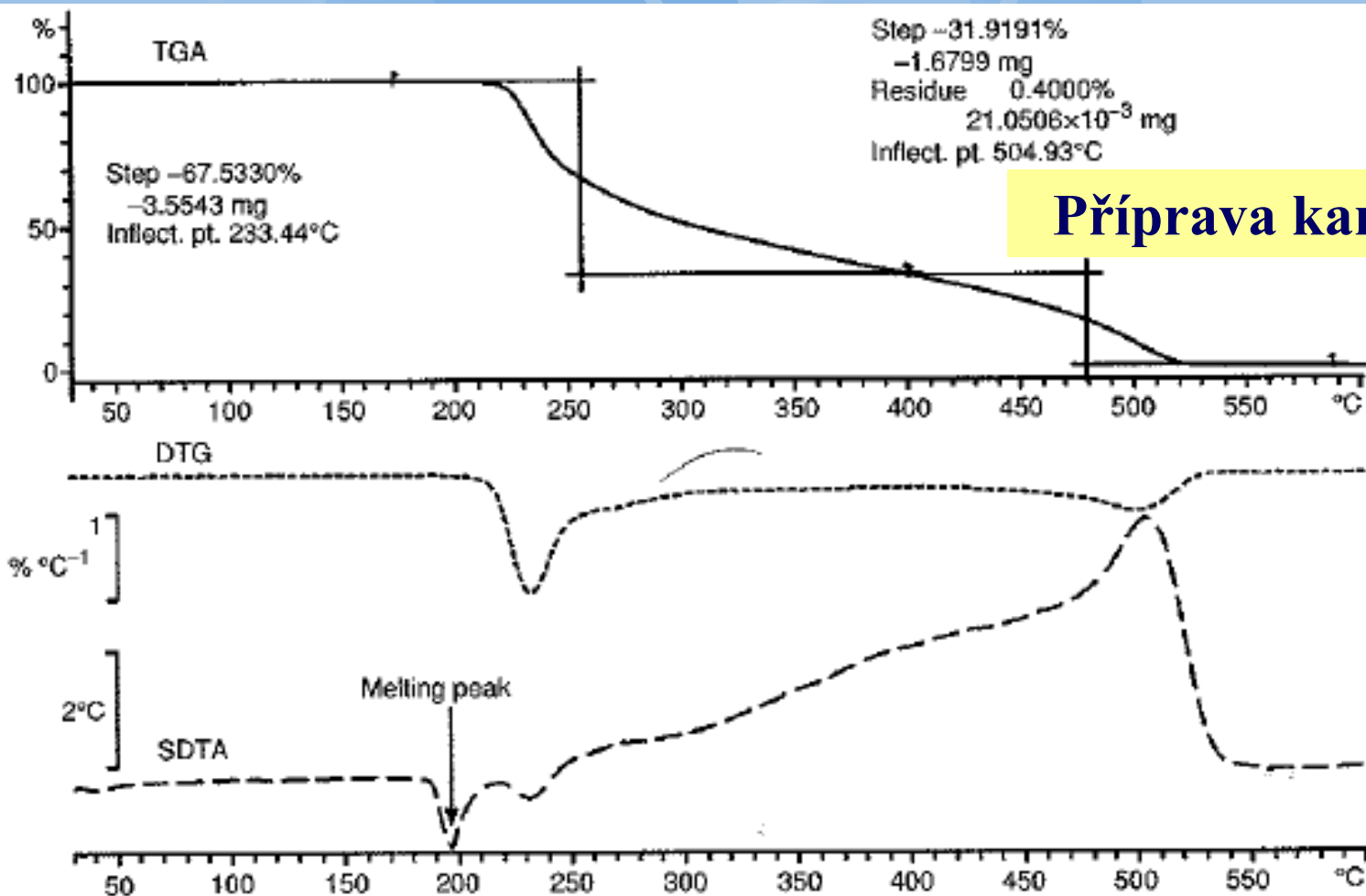


Figure 3.14 Separation in a TGA curve of copper sulphate pentahydrate at 10 K/min. The individual steps correspond to the consecutive elimination of the following molecules: 2 H₂O, 2 H₂O, 1 H₂O, SO₃, 0.5 O₂. The residue is Cu₂O.



Příprava karamelu

Figure 3.15 The decomposition of sucrose at 10 K/min in air occurs in two consecutive steps, the second directly following the first. In the evaluation, a value of 405°C was used for the end of the first step and the beginning of the second step. The simultaneously measured SDTA curve shows the endothermic melting peak followed by the endothermic caramelisation, at which stage the exothermic decomposition/combustion occurs. An almost white residue of 0.4% remains at the end of the measurement. This corresponds to the ash content.

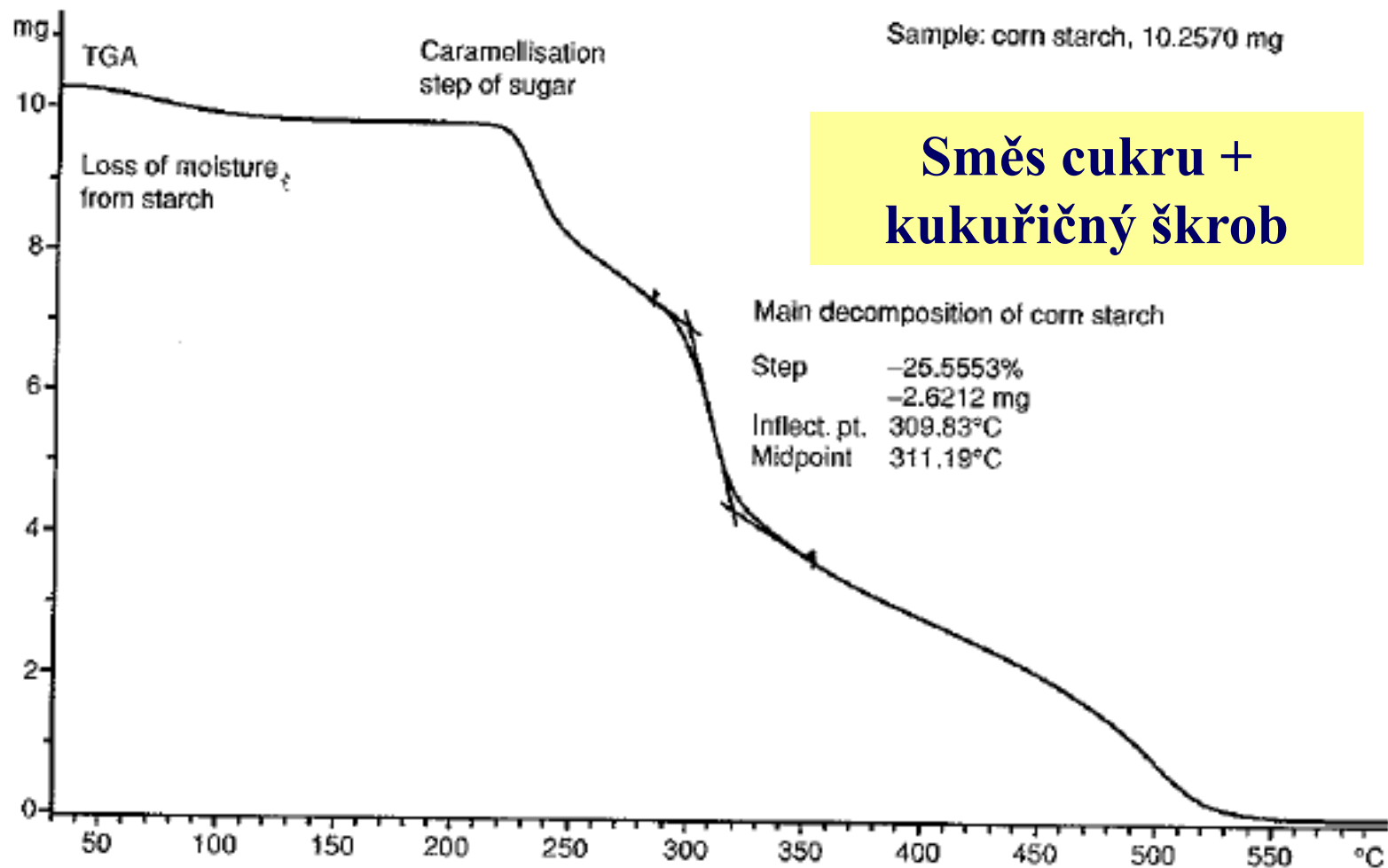


Figure 3.16 TGA curve of a 1:1 mixture of maize-corn starch and crystalline sugar: heating rate 10 K/min, purge gas air at 50 mL/min. The main decomposition step of corn starch occurs at roughly 310°C (midpoint). In a mixture with crystalline sugar, the 'starch' step occurs in a region in which the mass of the sugar continuously decreases. The step obtained using a 'horizontal' evaluation would be too large. This error can be avoided using a 'tangential' baseline evaluation. The measured step of 25.5% refers to the initial total mass of the mixture at the beginning of the measurement (see Section 3.6.3).

Metodika vyhodnocení TGA

Změna hmotnosti v %:

$$G\% = 100 \cdot \Delta m / m_0$$

Stupeň přeměny reakce (solid state reakce např oxidace, rozklad,...)

$$\alpha = \frac{m_0 - m}{m_0 - m_f}$$

m_0 , m_f and m

Počáteční, konečná a aktuální hmotnost

Rychlostní rovnice přeměny

$$\frac{d\alpha}{dt} = kf(\alpha)$$

Integrovaná rychlostní rovnice přeměny

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = kt$$

Obecně pro isothermní i neisothermní ohřevy platí:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) a(\alpha, T, P, \dots)$$

a ...akomodační funkce (často=1)

Nukleace a růst

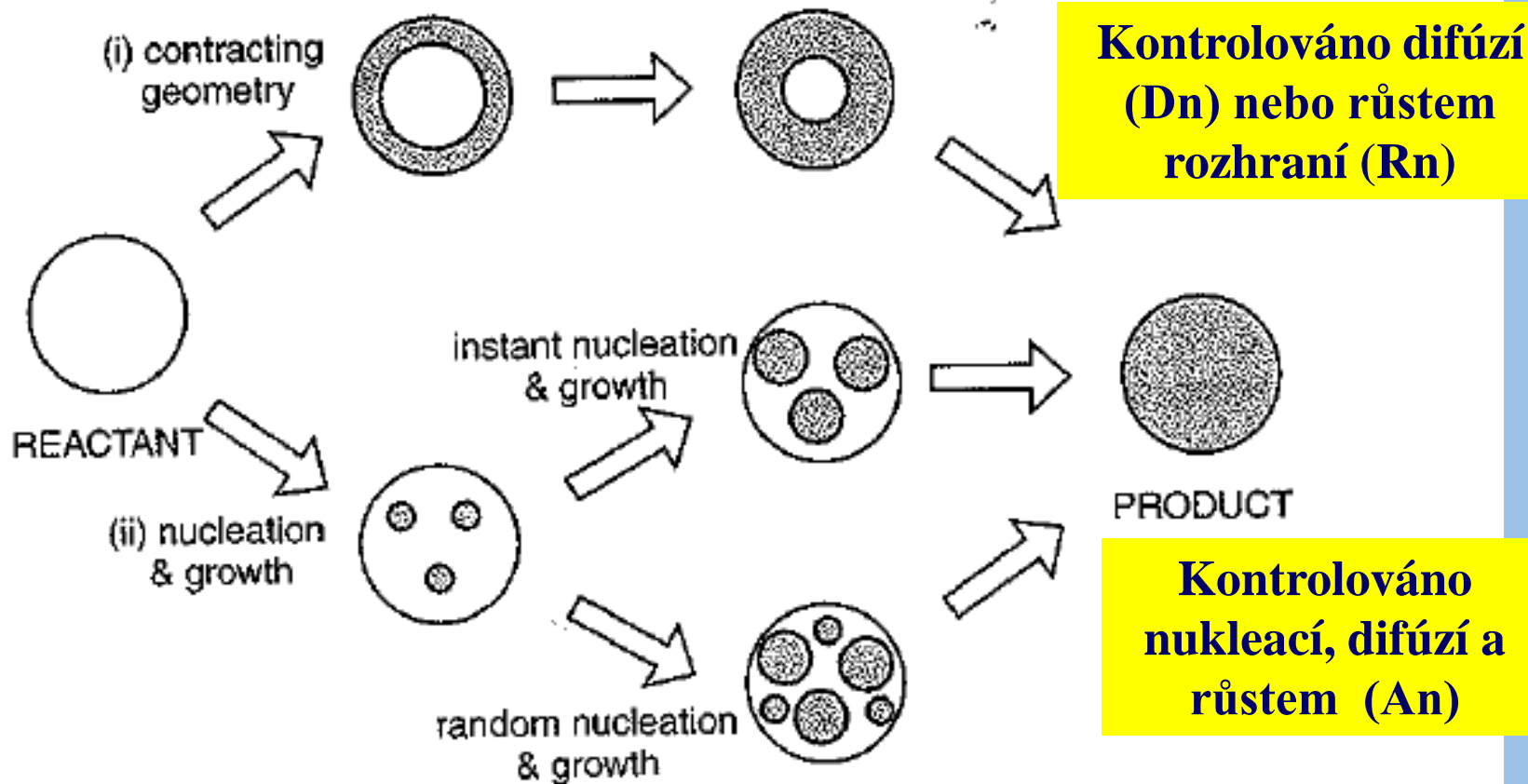
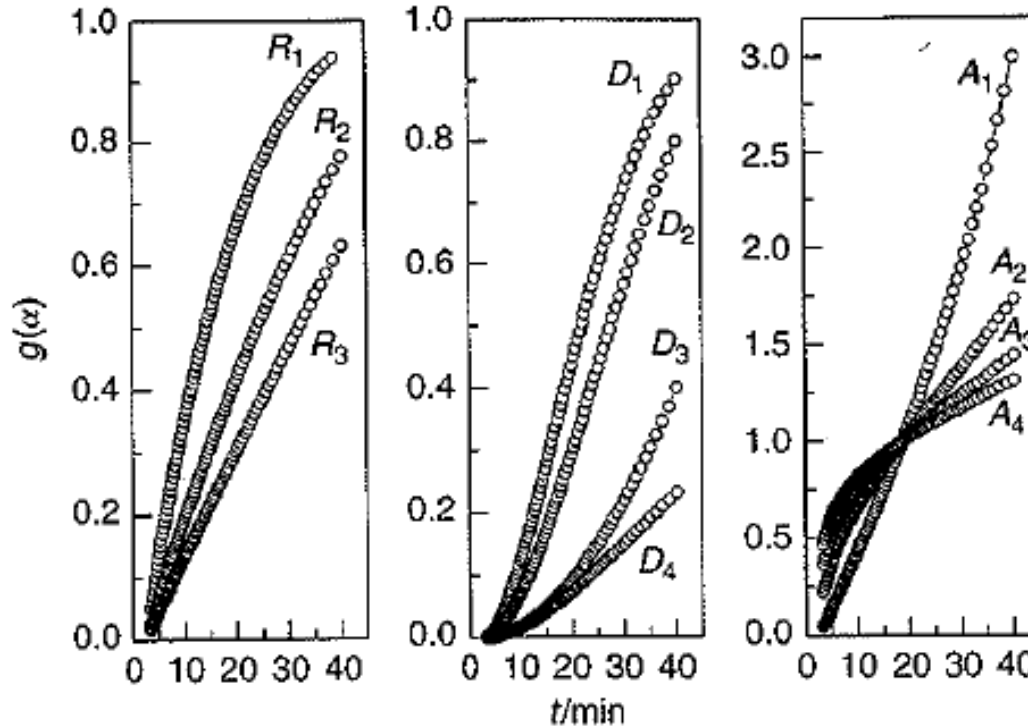


Figure 1 Schematic representation of the contracting geometry and nucleation–growth models

Cesta A: např. oxidace,
cesta B např. vznik hydridů

Isotermní ohřev



Dehydratace Zn Ac.2H₂O

Figure 1 Typical plots of $g(\alpha)$ against t for the isothermal dehydration of zinc acetate dihydrate

Z křivek určíme k za
dané teploty pro
různé teploty platí:

$$\ln k = \ln A - \frac{E_a}{RT}$$

Určení typu kinetiky pro isothermní ohřev

Table 1 Typical kinetic model functions derived for the solid-state reactions

Model	Symbol	$f(\alpha)$	$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$
Phase boundary controlled reaction	R_n ($n = 1, 2$ or 3)	$n(1 - \alpha)^{1-1/n}$	$1 - (1 - \alpha)^{1/n}$
1D diffusion	D_1	$\frac{1}{2\alpha}$	α^2
2D diffusion	D_2	$-\frac{1}{\ln(1 - \alpha)}$	$\alpha + (1 - \alpha) \ln(1 - \alpha)$
3D diffusion (Jander)	D_3	$\frac{3(1 - \alpha)^{2/3}}{2[1 - (1 - \alpha)^{1/3}]}$	$[1 - (1 - \alpha)^{1/3}]^2$
3D diffusion (Ginstring-Brounshtein)	D_4	$\frac{3}{2[(1 - \alpha)^{-1/3} - 1]}$	$1 - \frac{2\alpha}{3} - (1 - \alpha)^{2/3}$
Nucleation and growth (Avrami-Erofeev)	A_m ($m = 0.5, 1, 1.5, 2, 2.5, 3$ or 4)	$m(1 - \alpha)[- \ln(1 - \alpha)]^{1-1/m}$	$[- \ln(1 - \alpha)]^{1/m}$

Zjistíme, který model vyhovuje z linearizovaných tvarů f a g a určíme typ kinetiky.

Určení typu kinetiky pro neisotermní ohřev (např. lineární)

Table 1 Typical methods of kinetic analysis for nonisothermal data

Methods	Form	Reference	Approximation	Kinetic equation
Single run	Differential	Achar <i>et al.</i> ⁴	non	$\ln \left[\frac{d\alpha}{dt} \frac{1}{f(\alpha)} \right] = \ln A - \frac{E_a}{RT}$
	Integral	Coats and Redfern ⁵	$p(x)$	$\ln \frac{g(\alpha)}{T^2} = \ln \left[\frac{AE_a}{\beta R} \left(1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{RT}$
Isoconversional	Differential	Friedman ⁶	non	$\ln \frac{d\alpha}{dt} = \ln[Af(\alpha)] - \frac{E_a}{RT}$
	Integral	Ozawa ⁷	$p(x)$	$\log \beta = \log \frac{AE_a}{g(\alpha) \cdot z} - 2.315 - 0.4567 \frac{E_a}{RT}$
Peak	2nd differential	Kissinger ⁸	$f(\alpha) = -\ln(1 - \alpha)$	$\ln \frac{\beta}{T_p^2} = \ln \left[\frac{df(\alpha_p)}{d\alpha} \frac{AR}{E_a} \right] - \frac{E_a}{RT_p}$

Detaily viz lit. Sorai

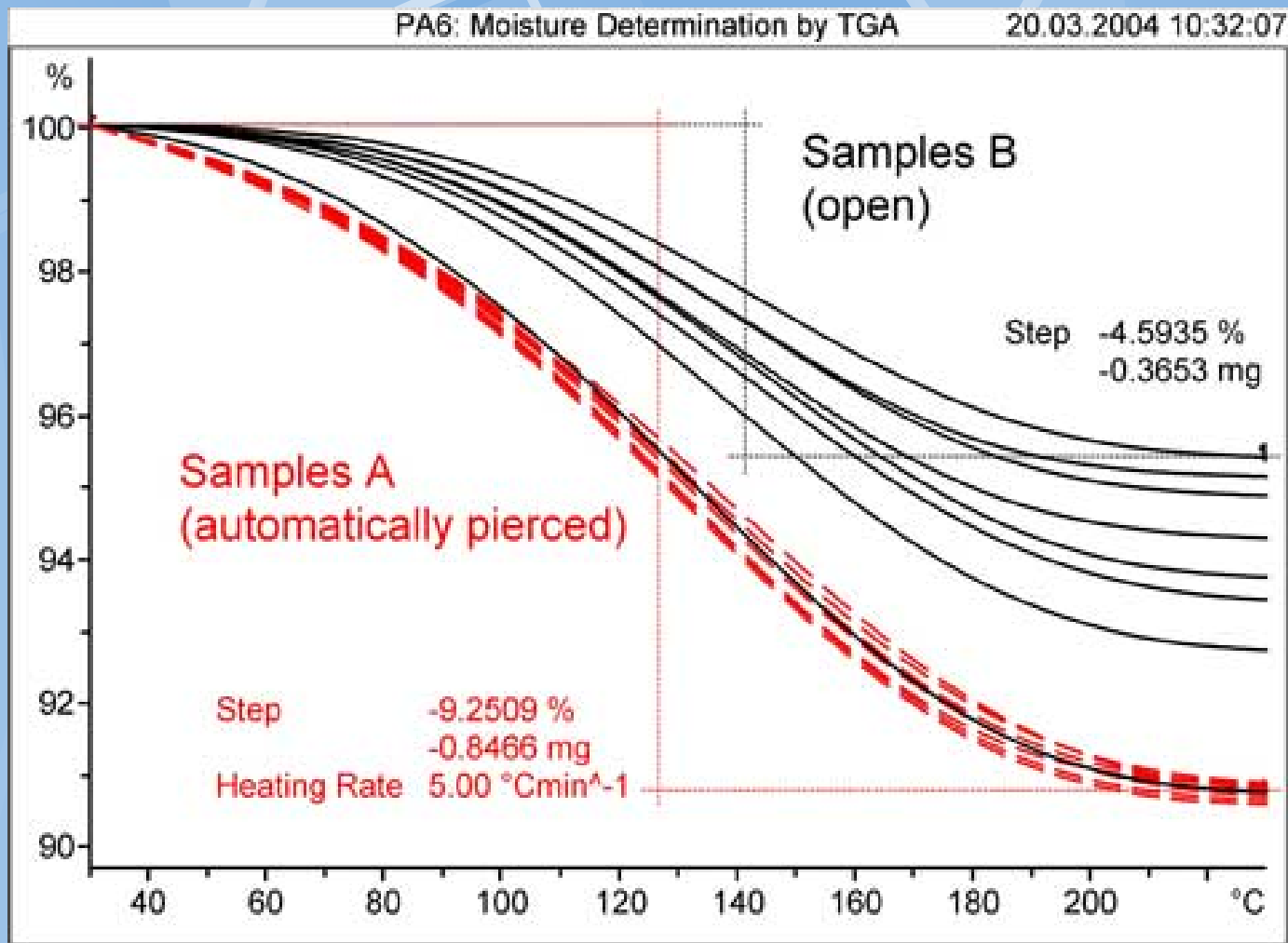
Časté aplikace TGA

Zajímá nás

Z TGA křivky vyhodnocujeme

Effect, property of interest	Evaluation used
Composition	Step evaluation, residue
Thermal stability, decomposition	Step evaluation
Stoichiometry of reactions	Content
Kinetics of reactions	Conversion, kinetics
Adsorption/desorption processes	Step evaluation
Vaporisation behaviour	Step evaluation, DTA, integration
Influence of reactive gases	Step evaluation
Moisture	Step evaluation
Oxidation stability	Onset

Stanovení vlhkosti vzorku



**Vlhkost
4,59%**

**Vlhký
cca
9,25%**

Diskuze

