Investigation of the change in thermal and shock sensitivity by ageing of RDX charges bonded by HTPB-IPDI and GAP-N100

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Motivations and Objectives

- Insensitivity of ammunition against impacts by
  bullets, fragments, EFP, SCJ (all address mainly shock sensitivity)
  and thermal threads (all types of cook-off)
  is an ongoing demand.
- To achieve this demand two ways are possible:
  Mitigation of the threads by construction measures;
  Sensitivity reduction of the energetic materials against the impacts;
  Probably the best is to combine both lines.
- After finding an insensitive energetic material for ammunition use the question arises, if its insensitivity is maintained during in-service time period.
  This is the question about the ageing behaviour of insensitive energetic materials.

- Investigation of the ageing behaviour of the insensitivity of energetic materials.

  Methods should be sensitive to changes in thermal and shock sensitivity.

  Further on:
  methods should be found, which could be used for understanding of changes.

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Context of the presented work

The work presented here is a part of the German contribution to a six nations colaboration on the subject of Insensitive Munitions and Ageing, performed under contract with EDA (European Defence Agency).

Contributing nations

France
Czech republique
Germany
The Netherlands
Sweden
Finland

It is planned to present the work done by each nation on the ICT conference in June 2014.

Selected compositions and components

Used components I-RDX: insensitive RDX from Eurenco, SME S-RDX: standard RDX from Dyno	GAP diol, I-RDX / S-RDX, class 1 and 5 HTPB R45M, I-RDX / S-RDX, class 1 and 5
Composition (high explosive charge, HEC) Two formulations with I-RDX (class 1 and 5) Two formulations with S-RDX (class 1 and 5) for comparison	**GAP-N100 bonded I-RDX / S-RDX** 75% RDX (I or S), 15% binder GAP-N100, 10% plasticizer BDNPF/A **HTPB-IPDI bonded I-RDX / S-RDX** 80% RDX (I or S), 12% binder HTPB (R45M) - IPDI (+AO) 8% plasticizer DOA

Used RDX types to manufacture bimodal charges

RDX type		mean particle diameter (mpd) [µm]	R [N]	S [Nm]	HMX content [mass-%]
SME - Eurenco (Woolwich process)					
I-RDX, Class 1	coarse	225	96	7.5	0.01
I-RDX M3C	fine	10.5	112	7.5	0.01
Dyno (Bachmann process)					
S-RDX, Type I, Class 1	coarse	195	160	7.5	0.84
S-RDX, Type I, Class 5	fine	17.6	168	10	0.52

Basic stability data of the formulations

	GX 147 I-RDX-GN-PL	GX 148 S-RDX-GN-PL	HX 458 S-RDX-HI-PL	HX 459 I-RDX-HI-PL
AIT at 5°C/min [°C]	215	214	210	211
AIT at 20°C/min [°C]	228	227	224	223
S [Nm] impact sensitivity	20	15	15	15
R [N] friction sensitivity	324	324	358	358
VST at 100°C 40 h [ml/g]	0.063	0.074	0.025	0.08

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Investigations on RDX samples

Ageing at 90°C, 15 and 30 days at ICT

years at 25°C:	15	25	(with GvH, F=2.5)
years at 25°C:	52	104	(with GvH, F=3.0)

ARC (Accelerating Rate Calorimetry) at ICT

Heat flow microcalorimetry at ICT

DSC measurements at ISL

Density measurements at ISL

X-ray scattering at ICT

GvH: generalized van‘t Hoff rule

$$t_T[d] = t_E[a] \cdot F^{-(T_T - T_E)/\Delta T_F} * 365.25$$

$$t_E[a] = t_T[d] \cdot F^{+(T_T - T_E)/\Delta T_F} / 365.25$$

1 year = 365.25 days (averaged with leap years)
1 month = 365.25 / 12 = 30.44 days

t_E	in-use time in years at temperature T_E
t_T	test time in days at test or ageing temperature T_T
T_T	test or ageing temperature
T_E	in-use temperature
F	acceleration or deceleration factor per 10°C temperature change
ΔT_F	temperature interval assigned to actual value of factor F, mostly 10°C

Investigations on the formulations

Ageing at 80°C over 16d, 35d, 60d for projectile impact at ISL, 30 mm in diameter, 50 mm long
years at 25°C: 6.8 15 25

Ageing at 80°C over 16d, 35d, 60d for gap test at ICT, 21 mm in diameter, 42 mm long

Ageing at 90°C over 6d, 15d, 25d for gap test at ICT, 21 mm in diameter, 42 mm long
years at 25°C: 6 15 25

ARC (Accelerating Rate Calorimetry) at ICT

DMA measurements at ICT (not included here)

Shore hardness at ICT

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Accelerated ageing plan based on TEL (thermal equivalent load)

Applied accelerated ageing conditions (temperatures and times) to simulate an in-service time of up to 25 years at 25°C.

The given ageing times are rounded up.

Natural or in-service ageing						
In service temperature T_E [°C]	In-service time t_E [year]					
25	5	10	15	20	25	30
Accelerated ageing conditions based on TEL principle using van't Hoff with F = 2.5						
Ageing temperature T_T [°C]	Ageing time t_T [day]					
90	5	10	15	20	25	30
85	7.5	15	22.5	30	37.5	45
80	12	24	35	48	60	72
70	30	60	90	120	150	180
60	75	150	225	300	375	450

Ageing in glass vials, samples ready for tests, means maximum effect on sample (= surface ageing) no humidity control, RF values always < 10%

Heat flow microcalorimetric (HFMC) measurements

Used heat flow microcalorimeter (HFMC):

Type TAM III from TA Instruments, equipped with two 6-pack minicalorimeters (built-in reference)

Measurement conditions with RDX samples

Measurement temperatures: 130°C to 150°C

Sample amount: 175 mg to 700 mg

Stainless steel ampoules with inserted glass vials, closed

Atmospheres: enclosed air or argon (argon by use of a glove box)

Free volume of empty ampoule arrangement: 3.23 ml

Volume degree of filling: 175mg $\propto$ 0.03; 700 mg $\propto$ 0.12

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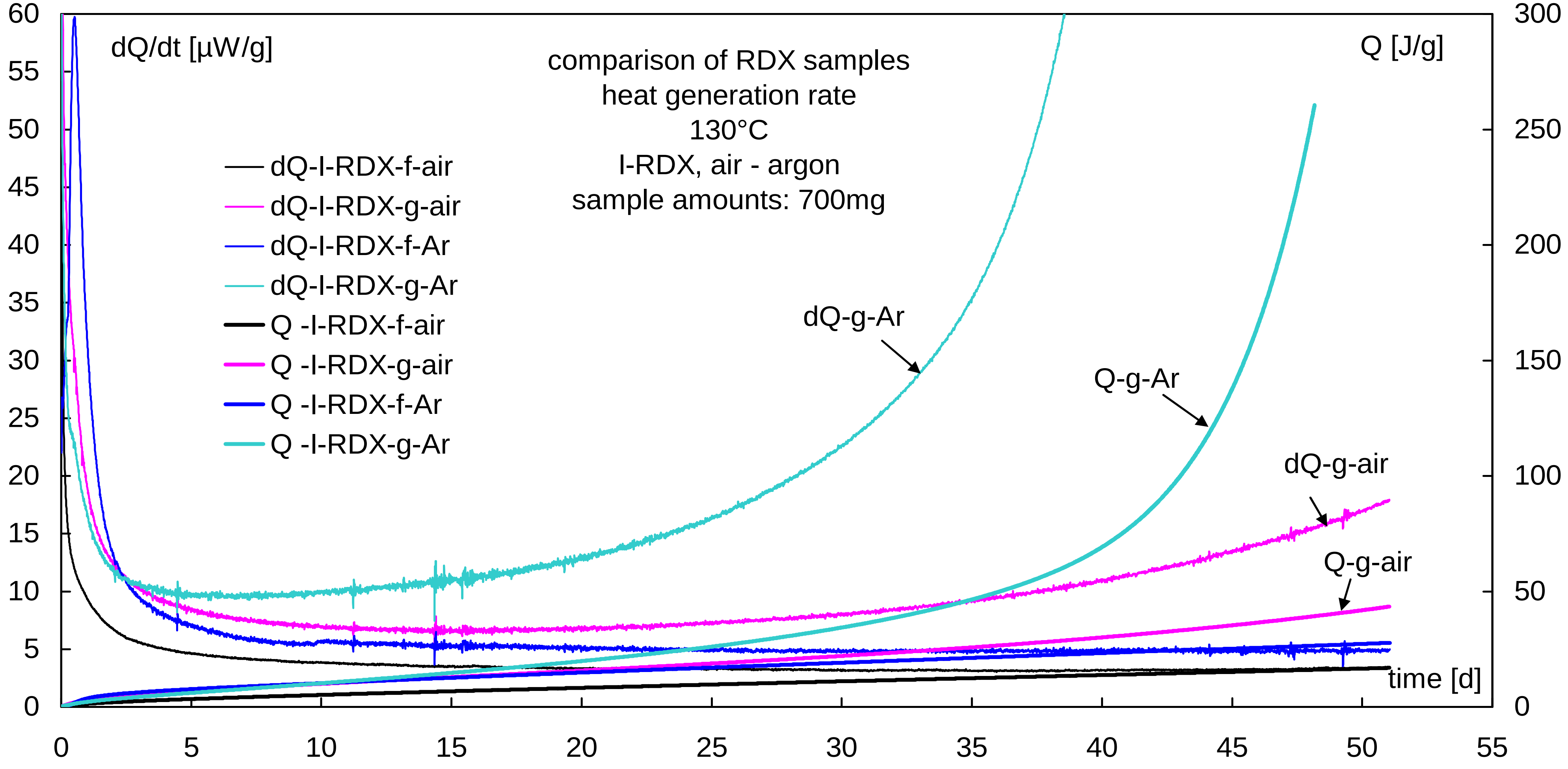
HFMC at 130°C on I-RDX samples, coarse (g) and fine (f)

Sample amount: about 0.7 g
under argon and air



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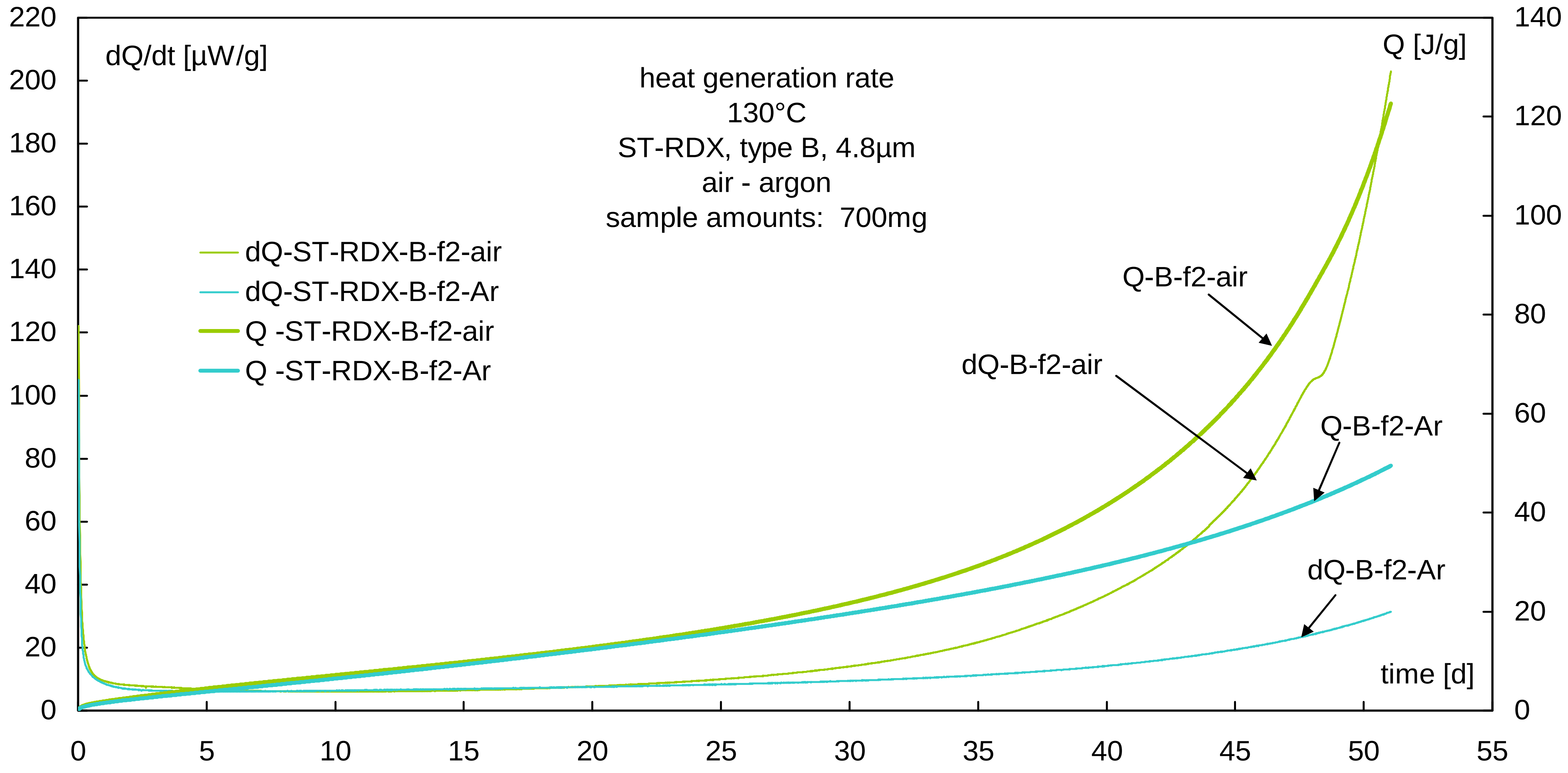
HFMC at 130°C on S-RDX sample, type B

Sample amount: about 0.7 g
under argon and air



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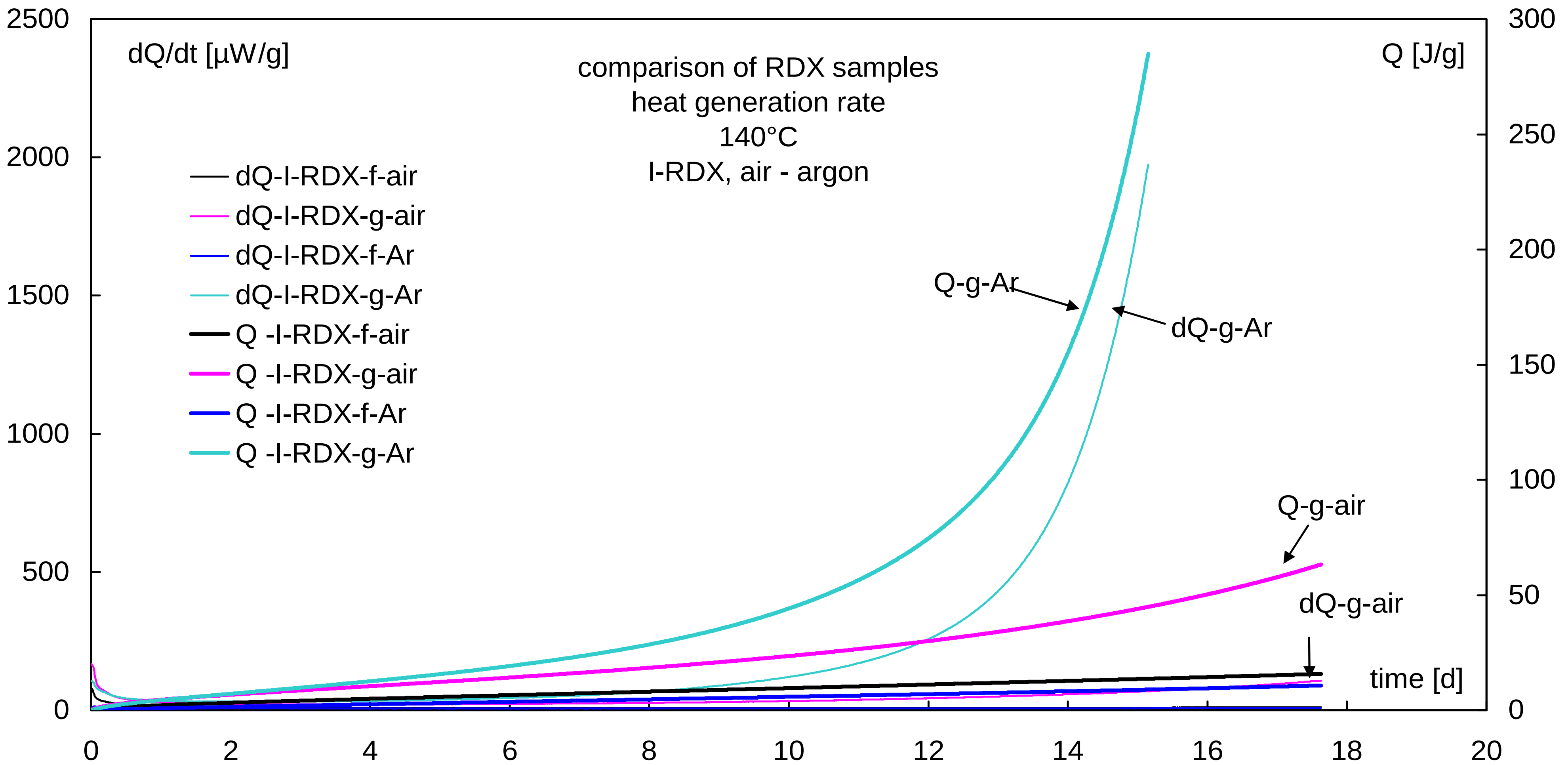
HFMC at 140°C on I-RDX samples, coarse (g) and fine (f)

Sample amount: about 0.7 g
under argon and air



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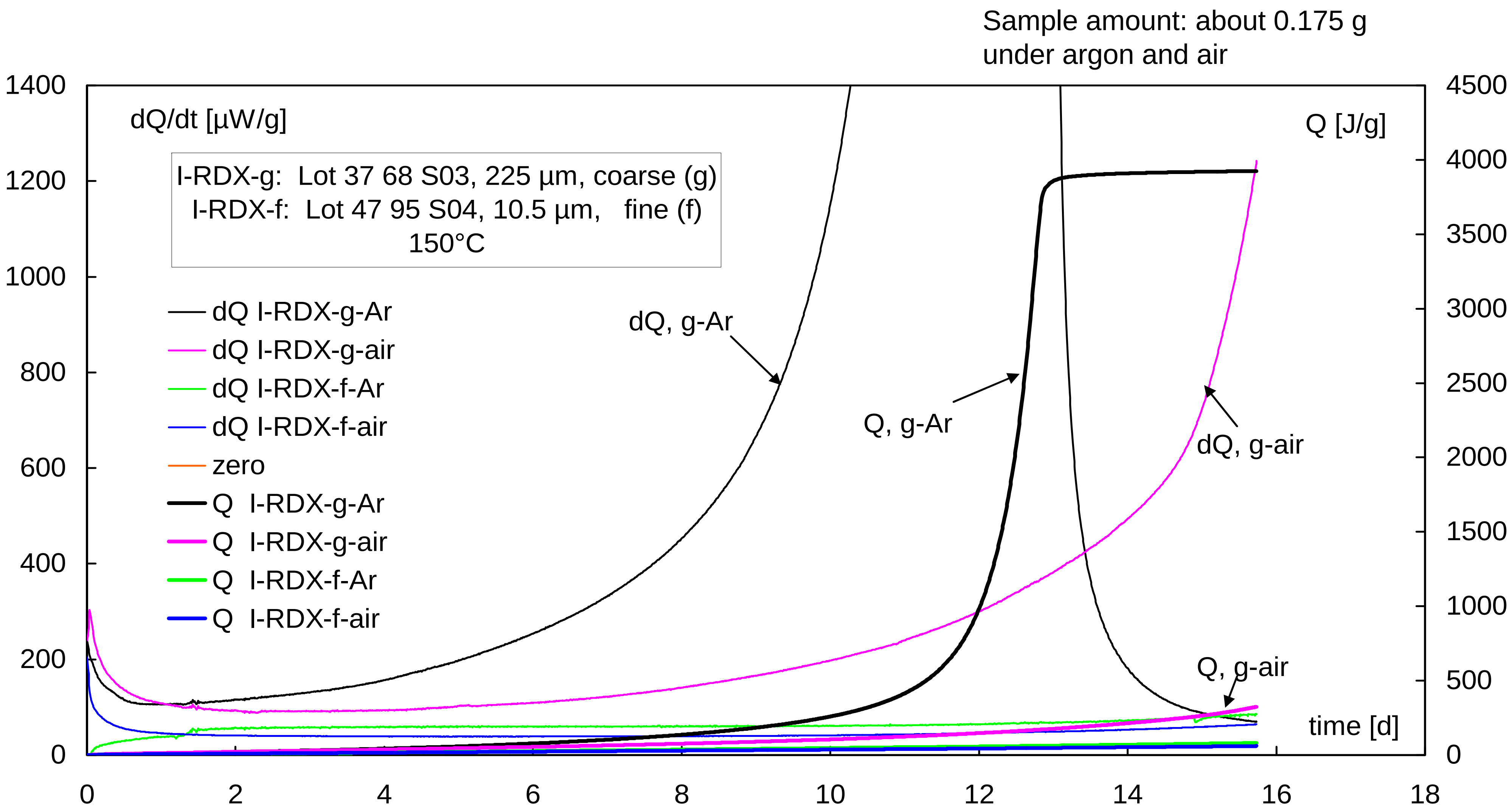
HFMC at 150°C on I-RDX samples, coarse (g) and fine (f)



Principle of Friedman analysis of thermoanalytical data

Friedman analysis is a so-named differential iso-conversional method of data description

General kinetic expression of a chemical reaction rate $d\alpha/dt$: reaction rate constant $k(T)$ times kinetic model $f(\alpha)$

$$\frac{d\alpha(t)}{dt} = k(T)\cdot f(\alpha(t)) = Z\cdot \exp\left(-\frac{Ea}{RT(t)}\right)\cdot f(\alpha(t))$$

- α reaction conversion or conversion, dimensionless
- $f(\alpha)$ kinetic model function, dimensionless
- Z pre-expon. factor of Arrhenius Eq., in 1/time
- Ea activation energy in kJ/mol of Arrhenius Eq.
- T absolute temperature in K
- t time

Mostly some assumption are made about $f(\alpha)$, then it is tried to describe the measured data.
Friedman had the idea to perform data analysis without any a-priori knowledge or assumption about $f(\alpha)$

$$\frac{d\alpha(t)}{dt} = Z(\alpha(t))\cdot \exp\left(-\frac{Ea(\alpha(t))}{RT(t)}\right)\cdot f(\alpha(t))$$

$$\ln\left(\frac{d\alpha(t)}{dt}\right) = \ln(Z(\alpha)) - \frac{Ea(\alpha(t))}{RT(t)} + \ln(f(\alpha(t)))$$

$$\ln\left(\frac{d\alpha(t)}{dt}\right) = \ln(Z'(\alpha(t))) - \frac{Ea(\alpha(t))}{RT(t)}$$

$$Z'(\alpha) = Z(\alpha)f(\alpha)$$

Friedman analysis is the determination of Z' und Ea as function of conversion α. Therewith one obtains a great number of reaction rate constants and the experimental data can be described very accurately.

By this the reaction rate $d\alpha(t)/dt$ is obtained, which can be used in FE calculations to determine heat generation rates as function of temperature and conversion.

$$\frac{d\alpha(t)}{dt} = Z'(\alpha(t))\cdot \exp\left(-\frac{Ea(\alpha(t))}{RT(t)}\right)$$

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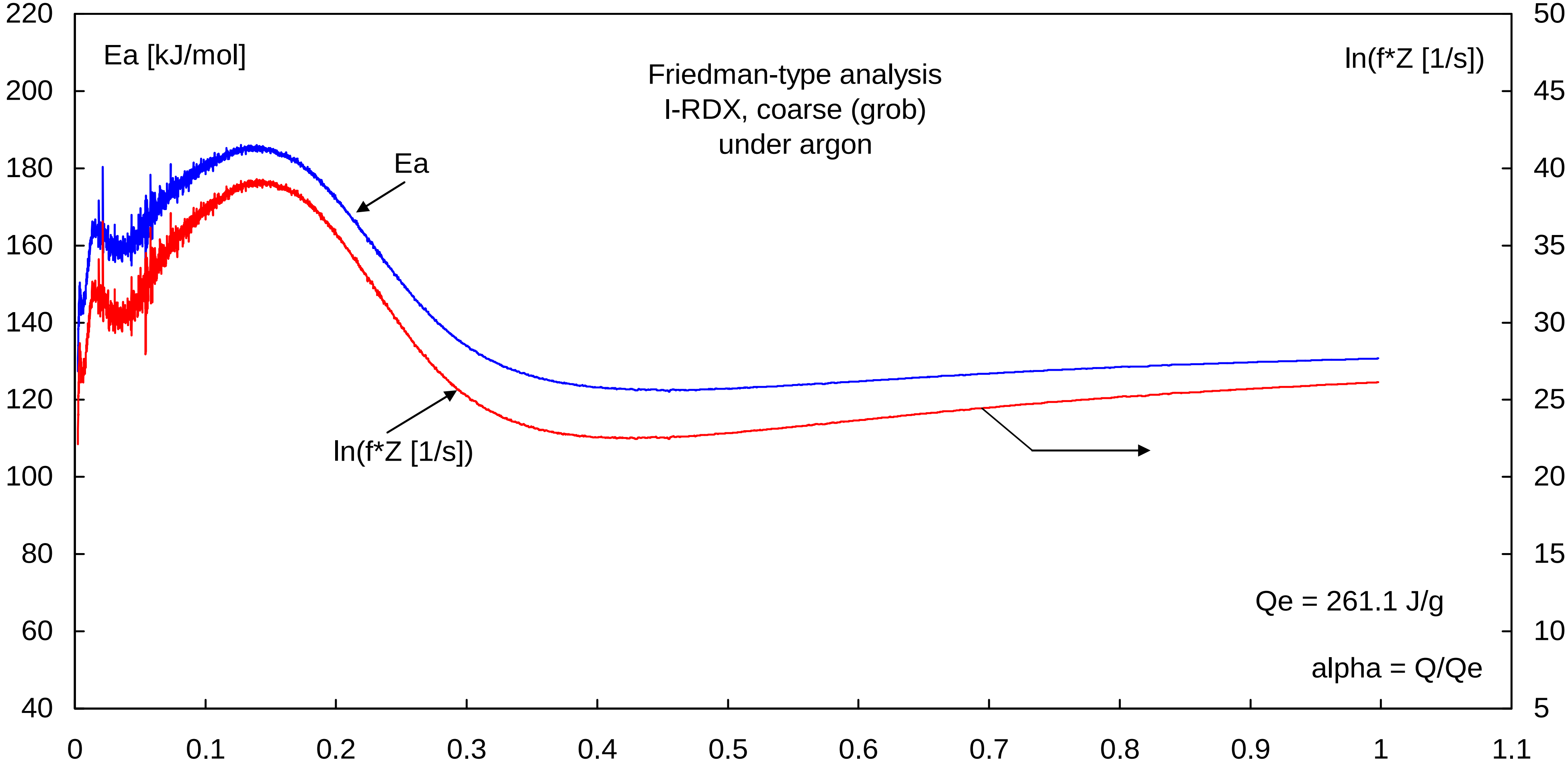
Friedman-type analysis, I-RDX coarse under argon



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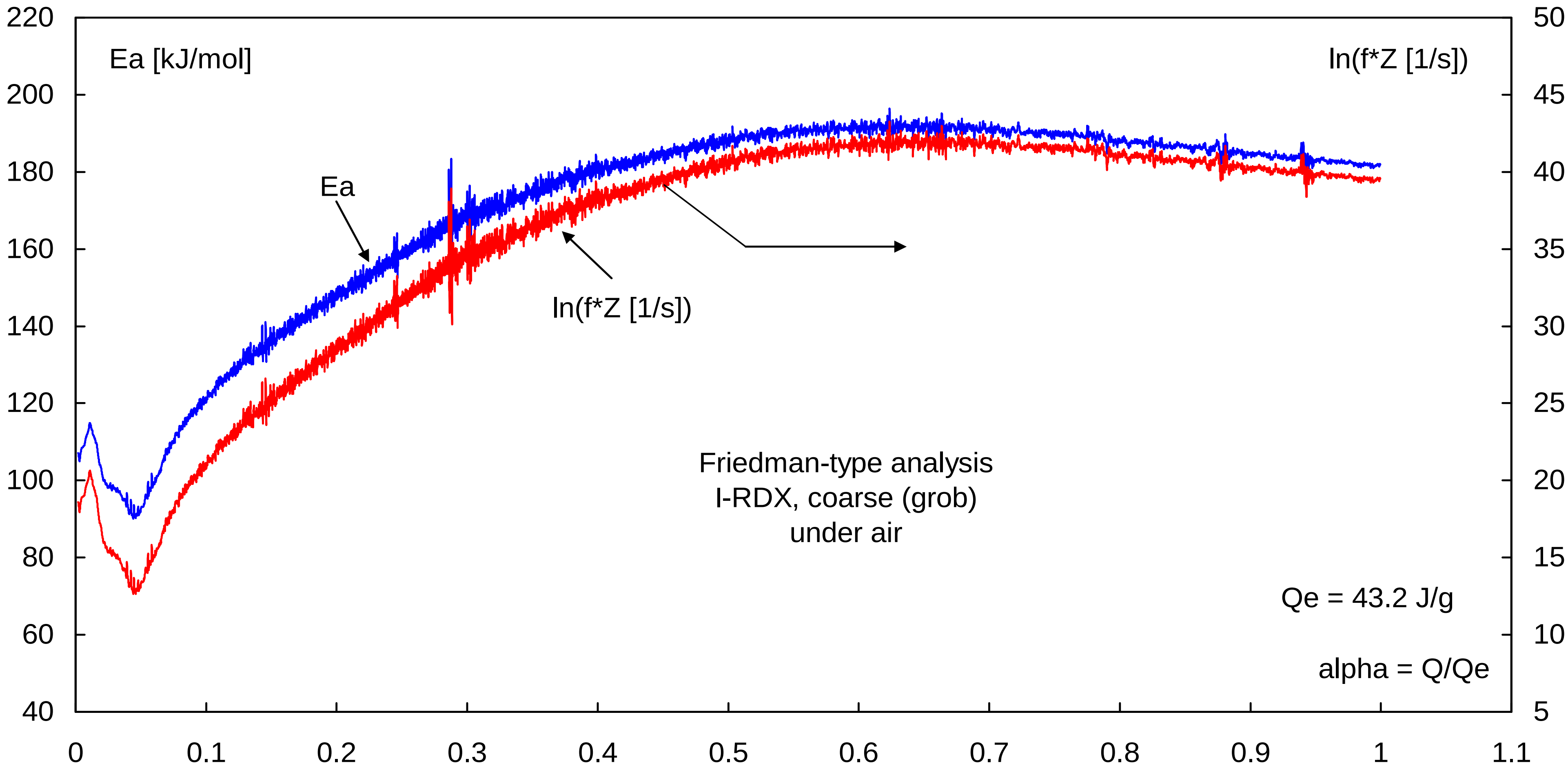
Friedman-type analysis, I-RDX coarse under air



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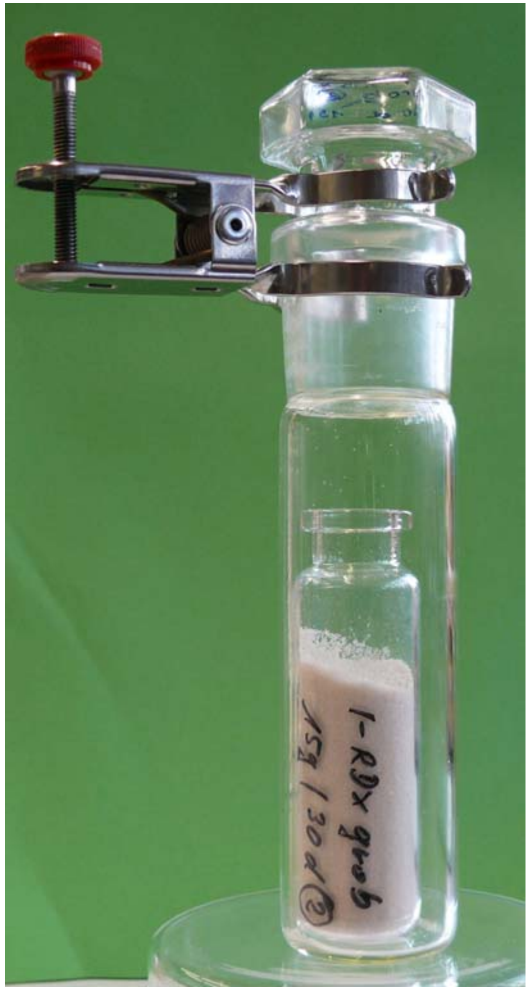
Ageing of RDX samples

Ageing was performed in vials with ground stoppers

For ageing in air:
No grease used, every week the stoppers have been lifted to allow fresh air going in.

For ageing in argon:
in vials with grease in the ground closure
argon filled in using a glove box

in air



in argon

Ageing at 90°C, over 15d and 30d

I-RDX coarse
I-RDX fine

S-RDX coarse
S-RDX fine

Appearance of the aged samples (photograph from ISL)

S-RDX			I-RDX		
pristine	aged 15 days at 90°C under argon	aged 30 days at 90°C under argon	pristine	aged 15 days at 90°C under argon	aged 30 days at 90°C under argon

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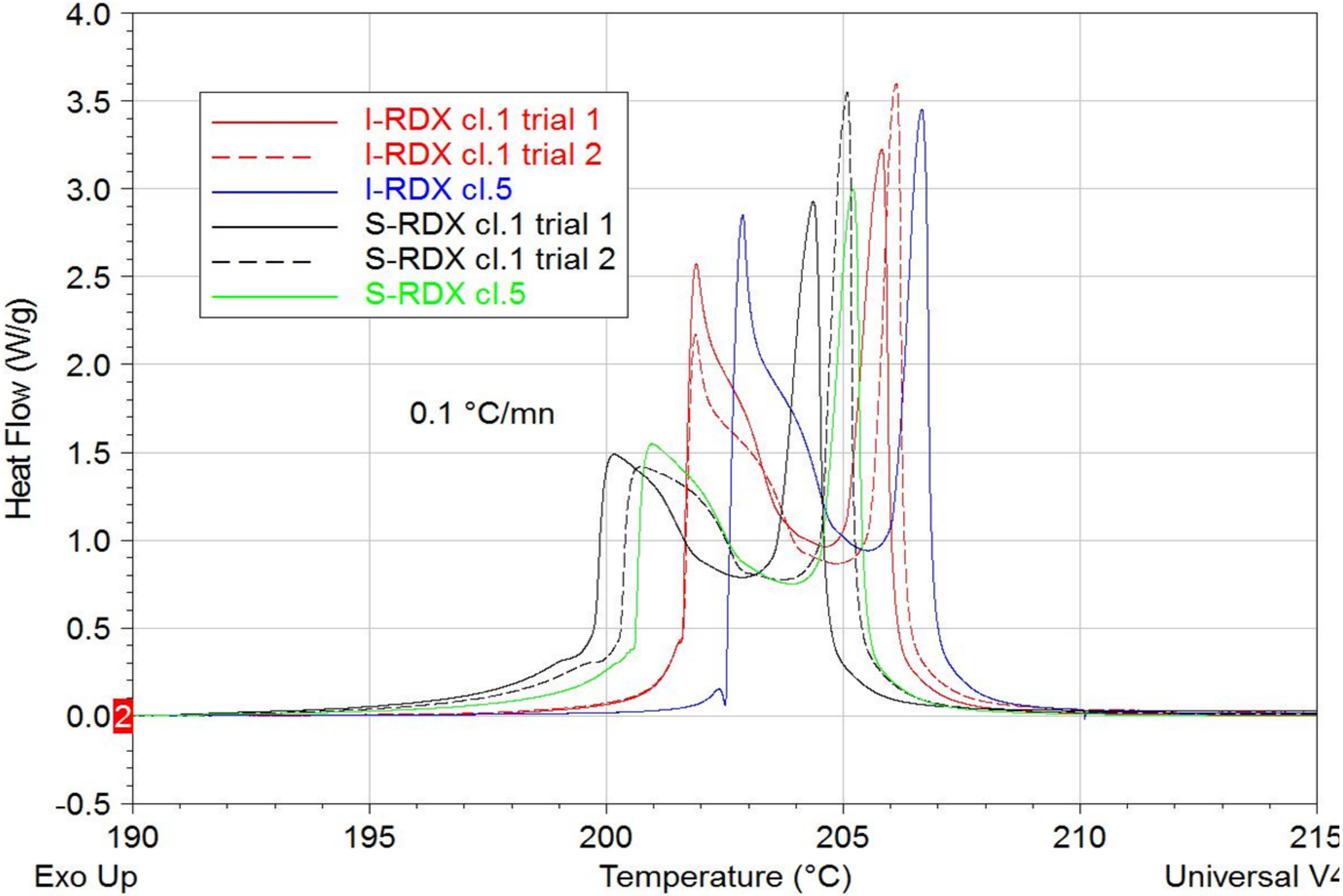
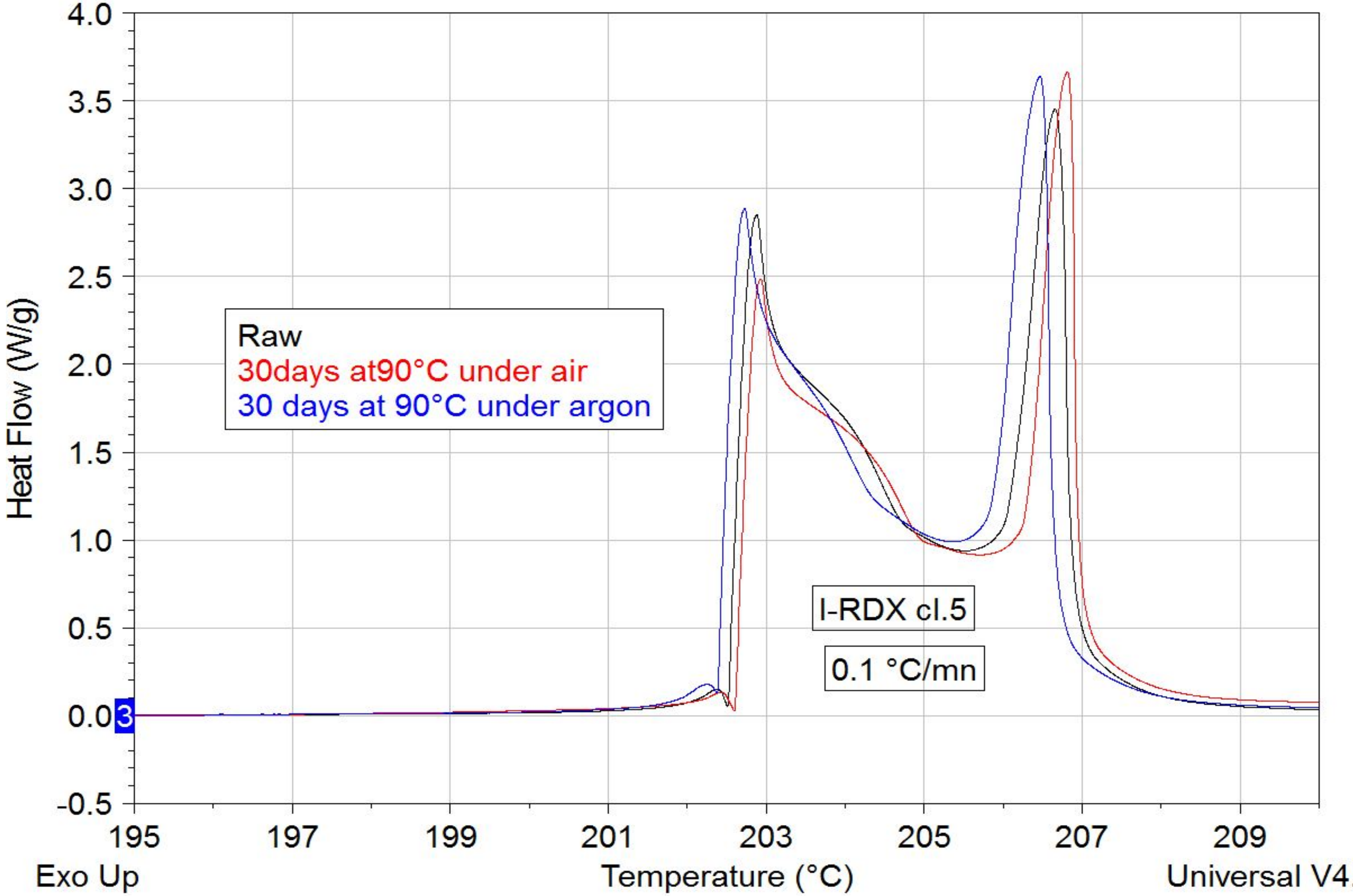
DSC results on unaged lots with heating rate of 0.1 °C/min, coarse and fine

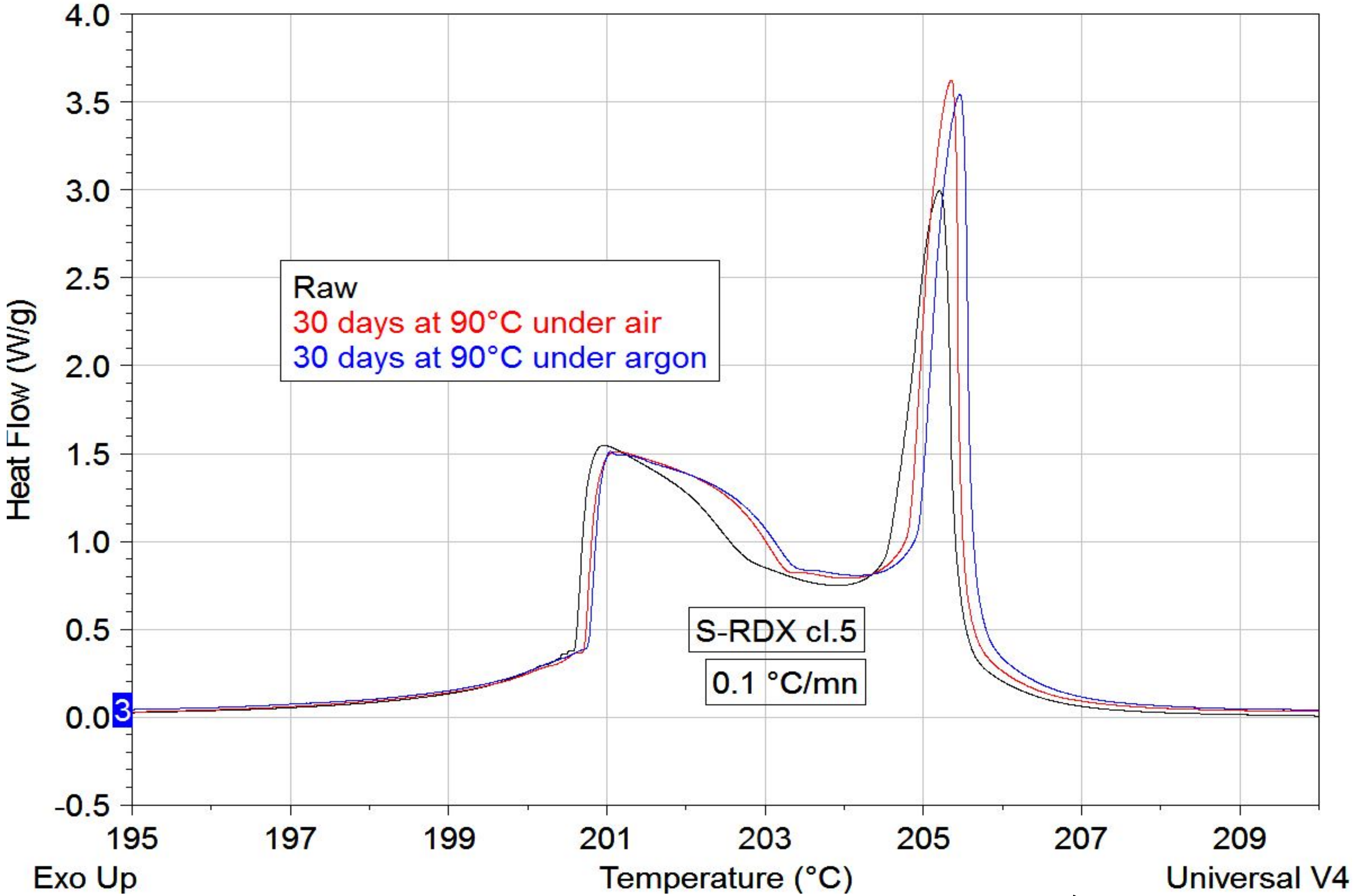


DSC results: Ageing effects on I-RDX class 5 (fine particles)



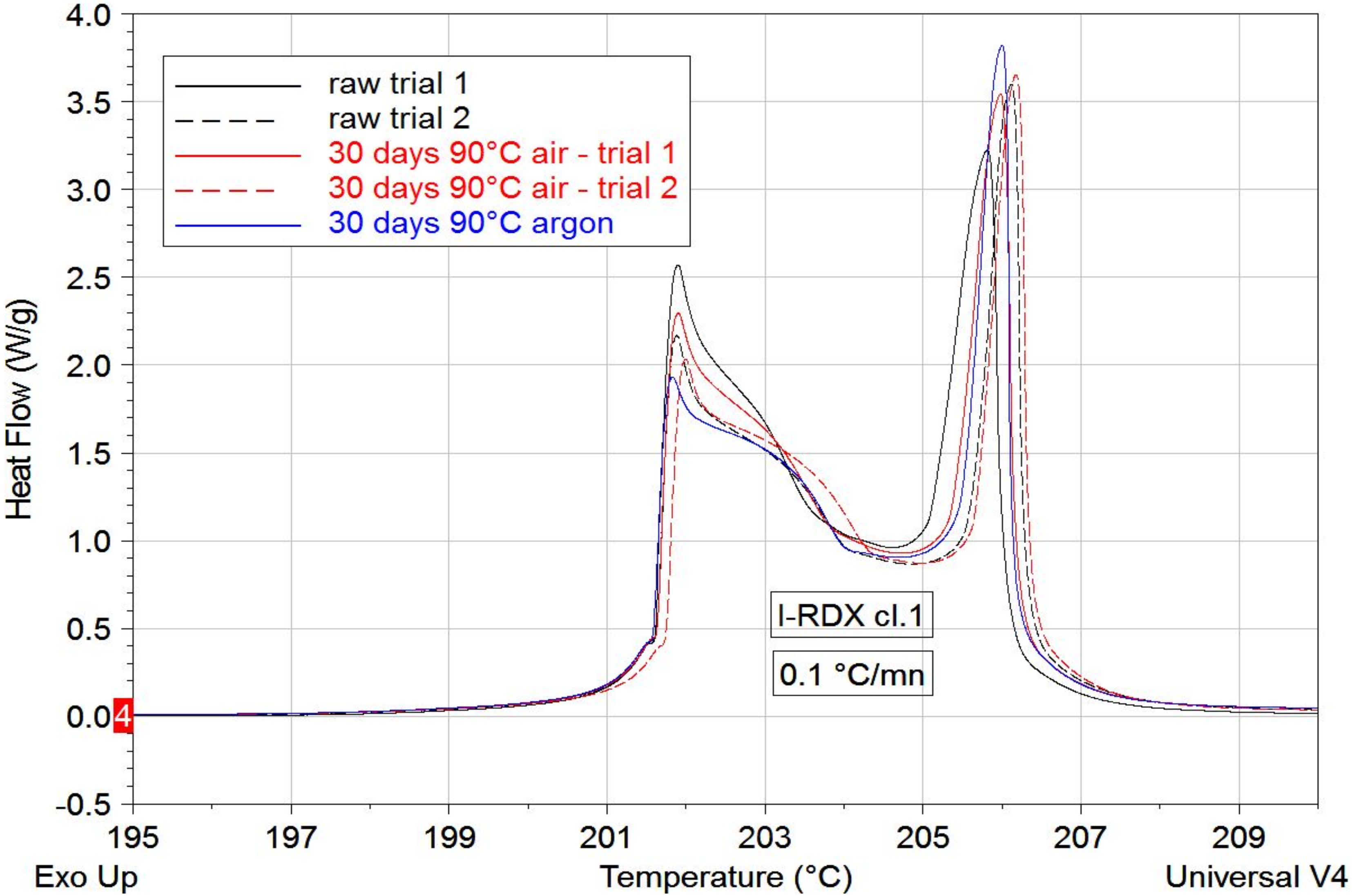
No ageing influence

DSC results: Ageing effects on S-RDX class 5 (fine particles)



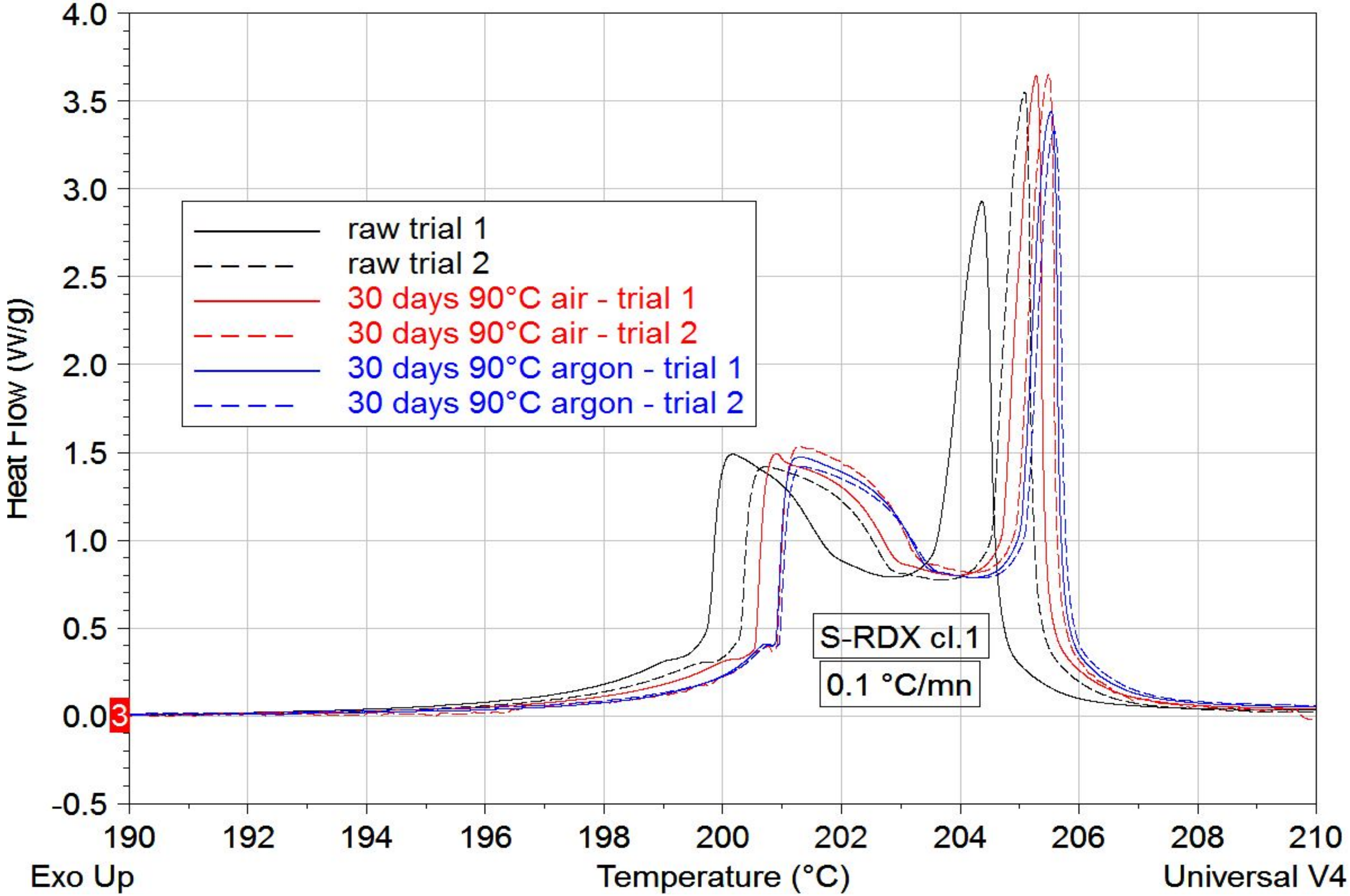
No ageing influence

DSC results: Ageing effects on I-RDX class 1 (coarse particles)



No ageing influence

DSC results: Ageing effect on S-RDX class 1 (coarse particles)



Slight ageing influence

Shift of peaks to higher temp.

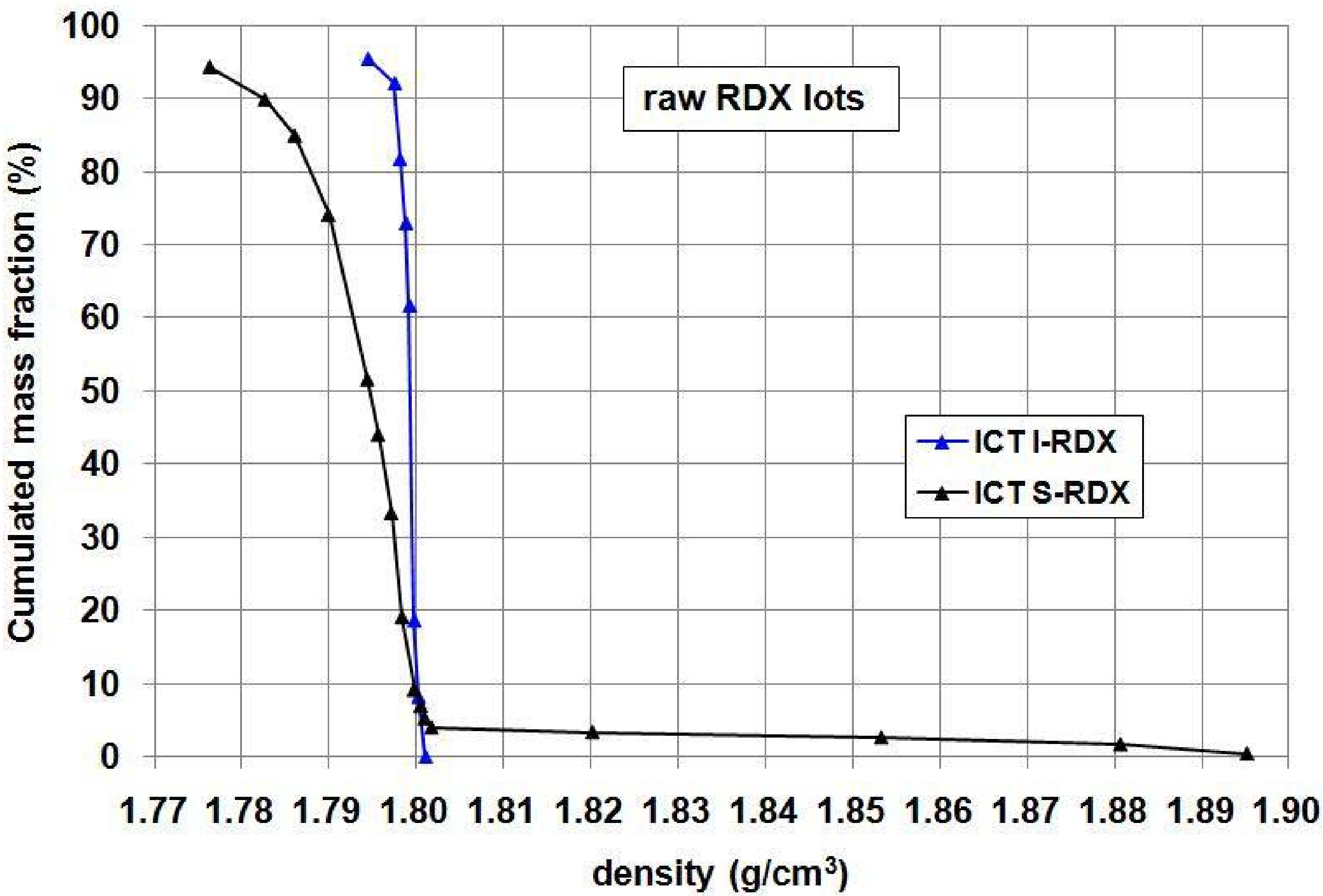
Improving by ageing?

Conclusions from DSC measurements

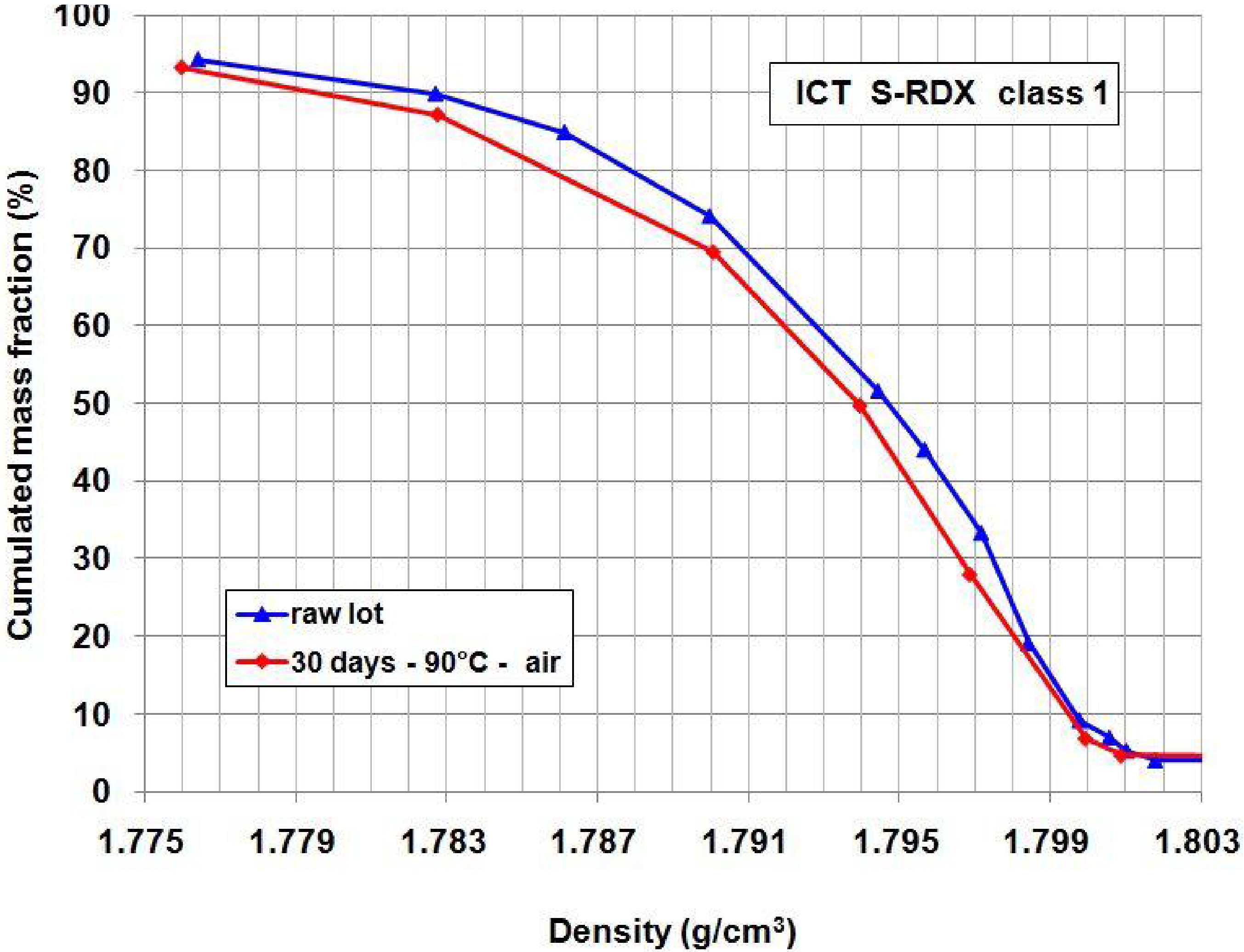
- No effects of accelerated ageing on I-RDX particles (fine and coarse) (90°C, 30 days under air or argon) revealed by DSC measurements at 0.1 °C/min

- presumably only a very small effect of accelerated ageing on S-RDX particles class 1 (90°C -30 days under air or argon) on DSC measurements at 0.1°C/mn.
Ageing results in a small delay of the thermal decomposition.

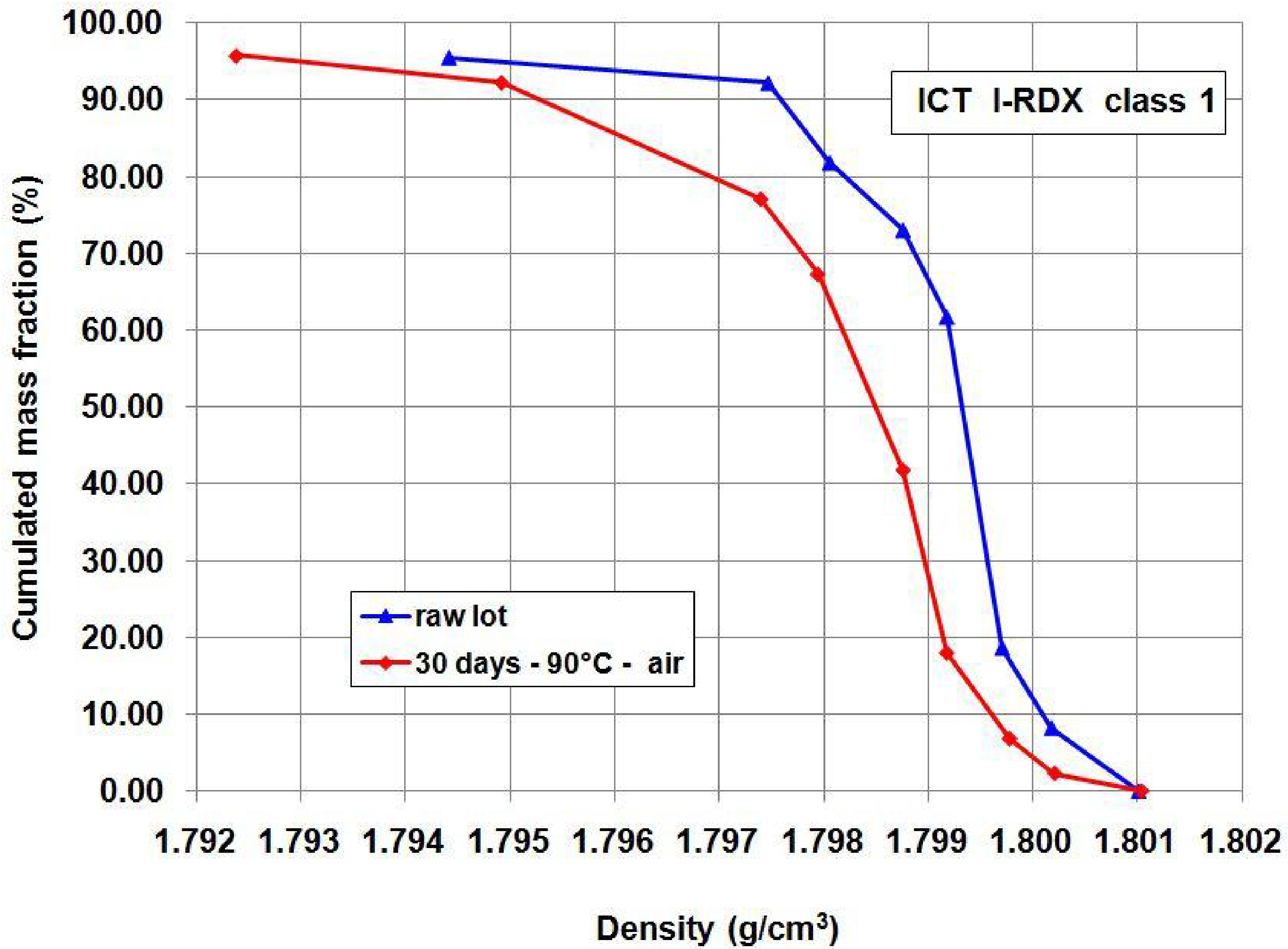
Density distribution of unaged RDX samples – comparison of I-RDX and S-RDX



Density distribution in S-RDX unaged and aged (ISL, Lionel Borne)



Density distribution in I-RDX unaged and aged (ISL, Lionel Borne)

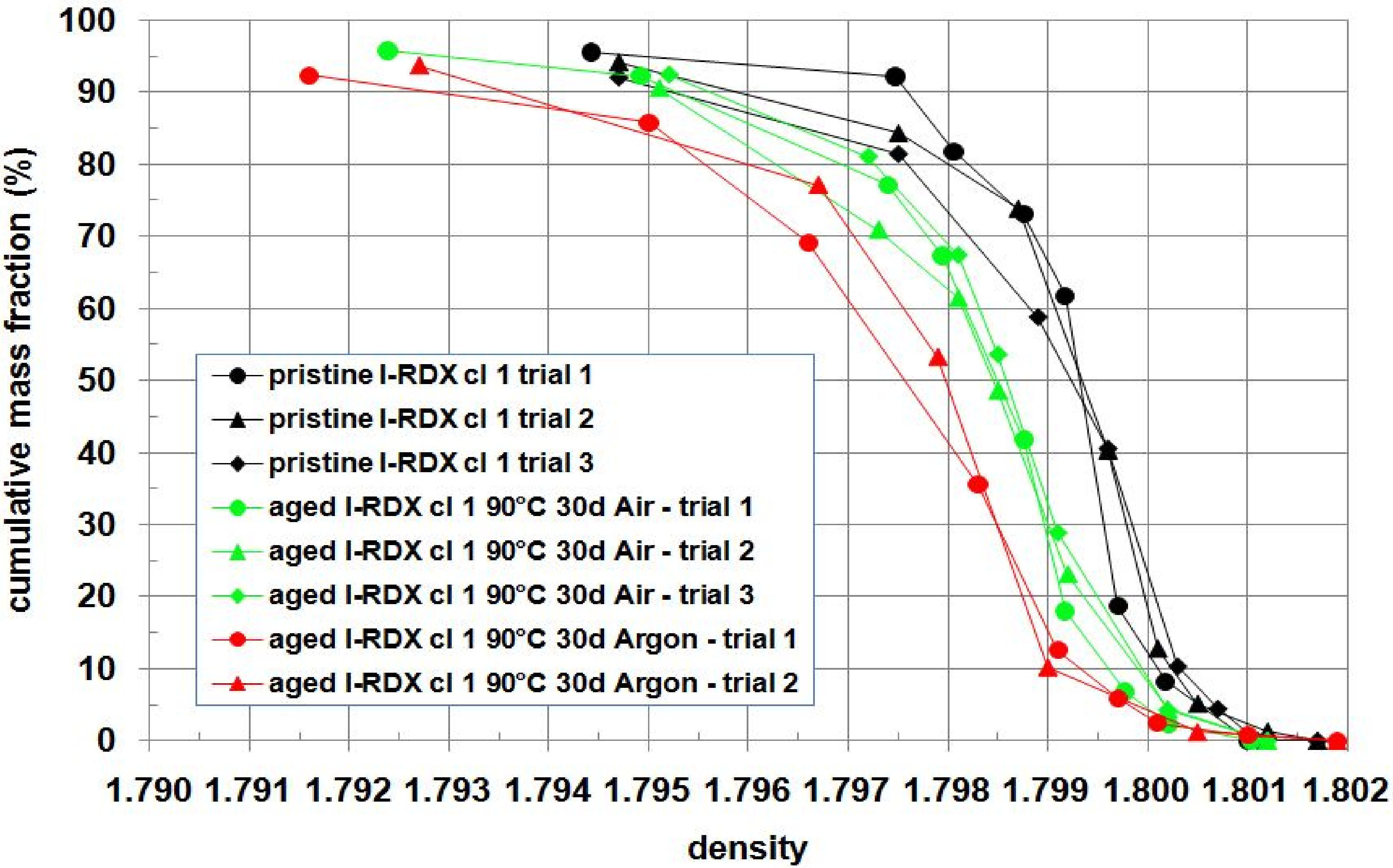


I-RDX particle density distribution measurements

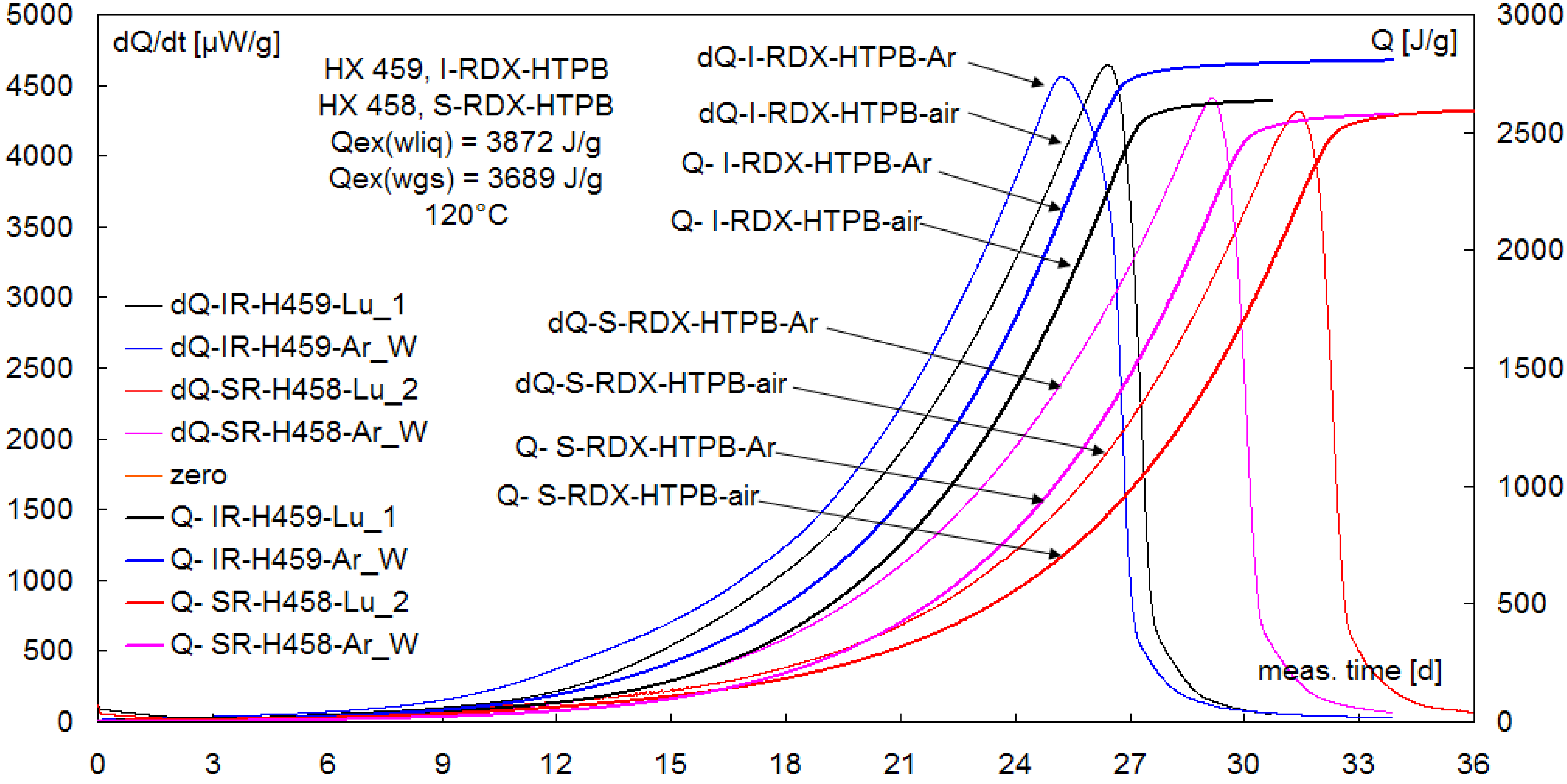
I-RDX particle density variations

Assumption
The process liquor trapped in particle inclusions during the crystallization process is removed by diffusion during the accelerated ageing.

Diffusion kinetics seems different in air and argon.



HGR and HG at 120°C, in air and in argon
comparison of HTPB-IPDI formulations of I-RDX and S-RDX



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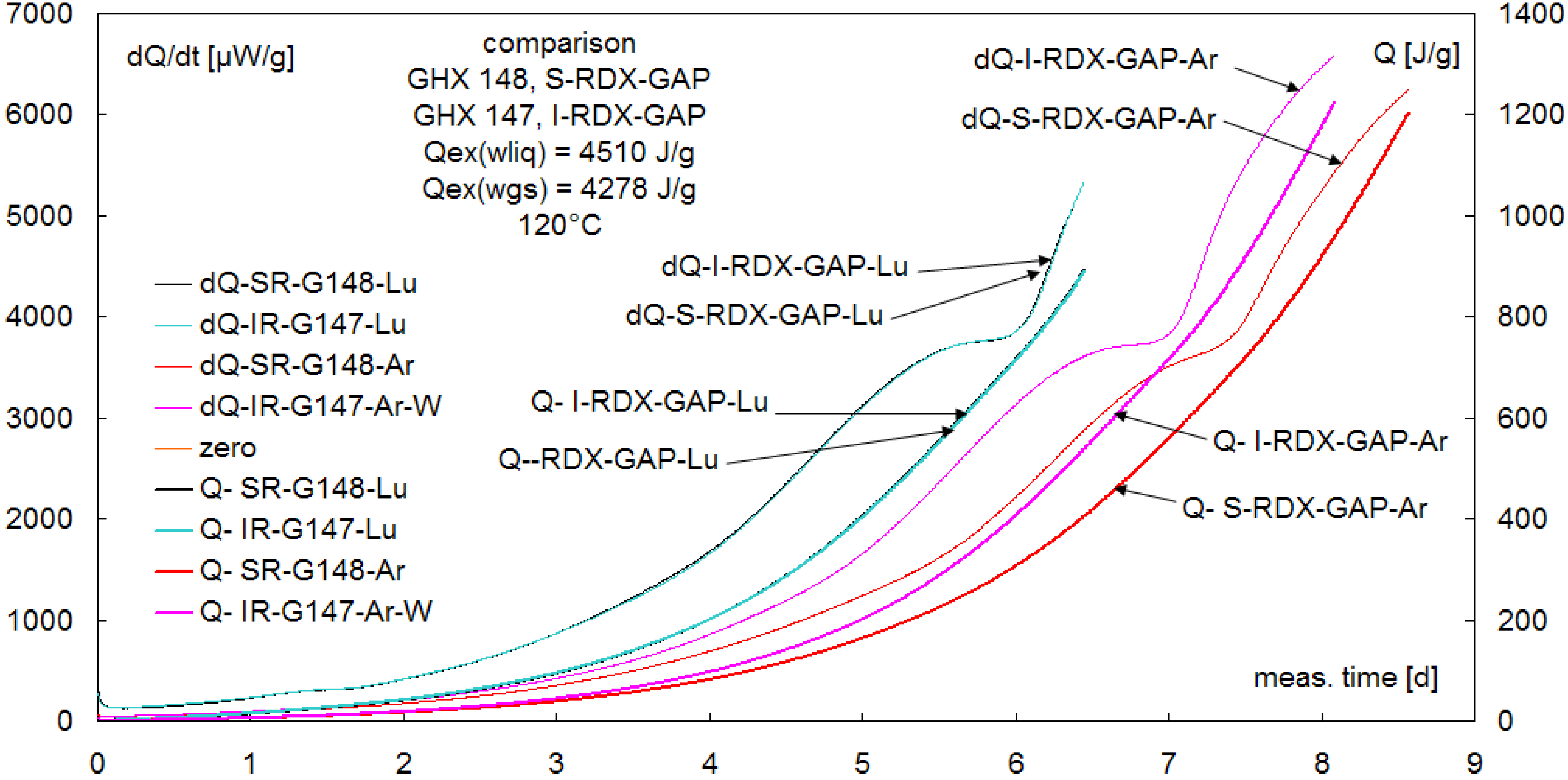
HGR and HG of GAP-N100 formulations with S-RDX and I-RDX at 120°C, in air and in Ar



Summary of micocalorimetric measurements on formulations

HTPB-IPDI-formulations

It seems that in argon the decomposition of HTPB formulations with both RDX types is a little bit faster than in air.

I-RDX formulations react faster than S-RDX formulations.

GAP-N100-formulations

In argon the I-RDX formulation reacts somewhat faster the the S-RDX formulation.

In air the decomposition is faster than in argon.

ARC™ measuring principle of the measuring mode 'heat-wait-search'

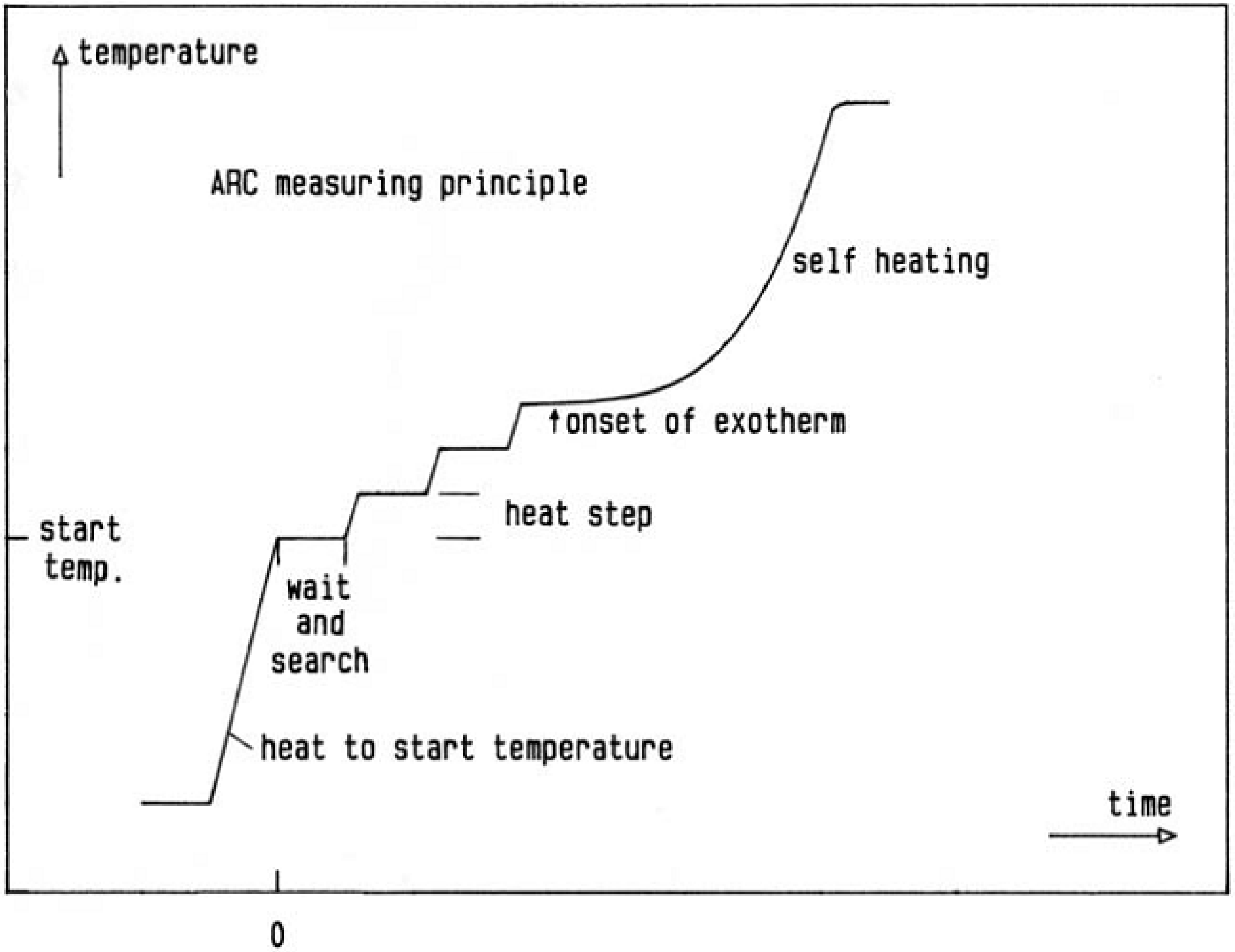
Typical measurement parameters

Wait time period serves as time for temperature equilibration after heating-up
search time period serves as check period if the self heating of the sample is beyond or equal to the sensitivity level

If no self-heating detected the heating up by the preset heat step is started

Wait time: 15 min
Heat step: 4 to 5 °C
Sensitivity: 0.02°C/min

Search time is situation dependend and adjusted by the search algorithm. During selheating the machine works in adiabatic mode. Means the oven is just heated-up to follow the temperature of the sample



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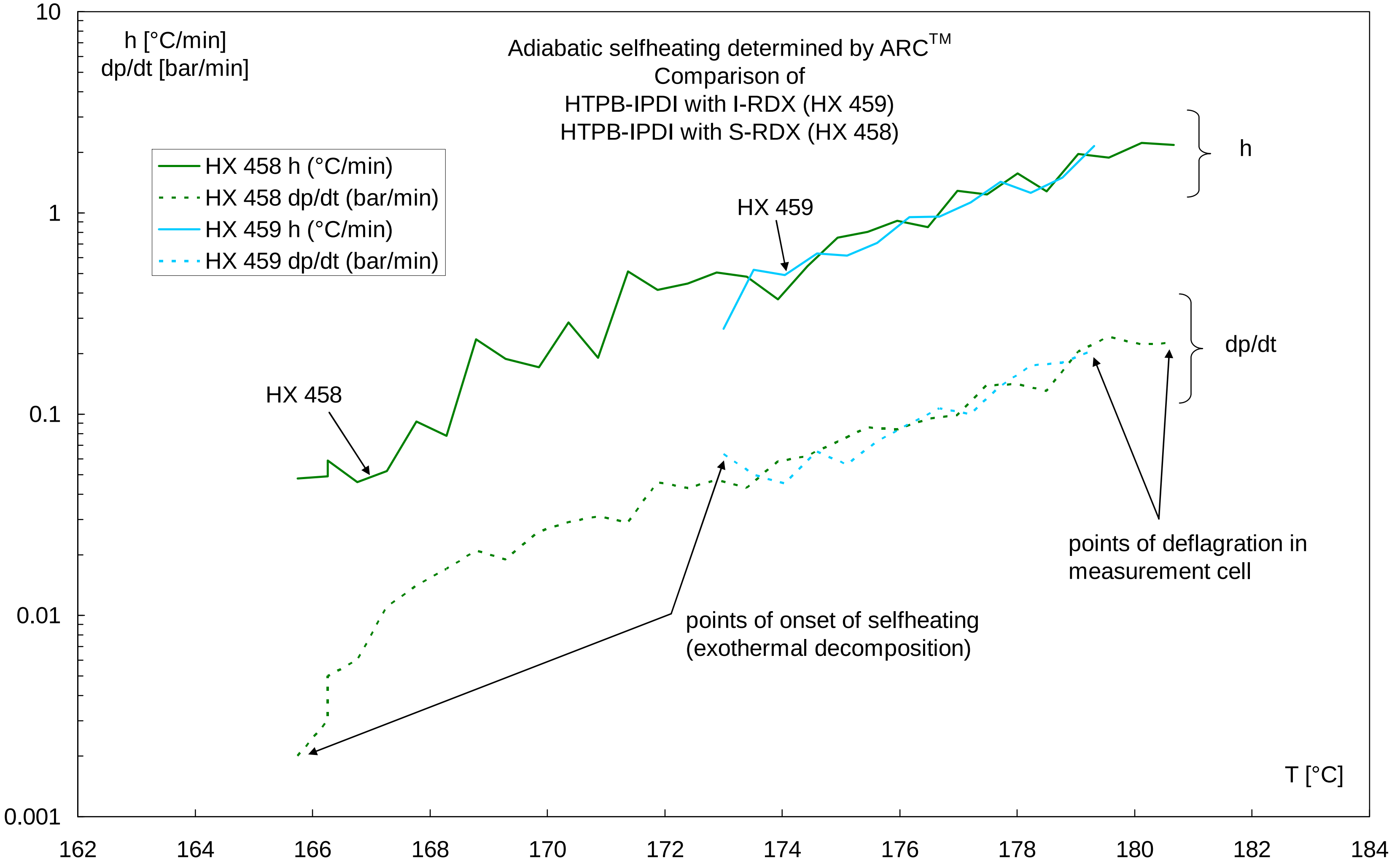
Adiabatic selfheating of HX 458 and HX 459



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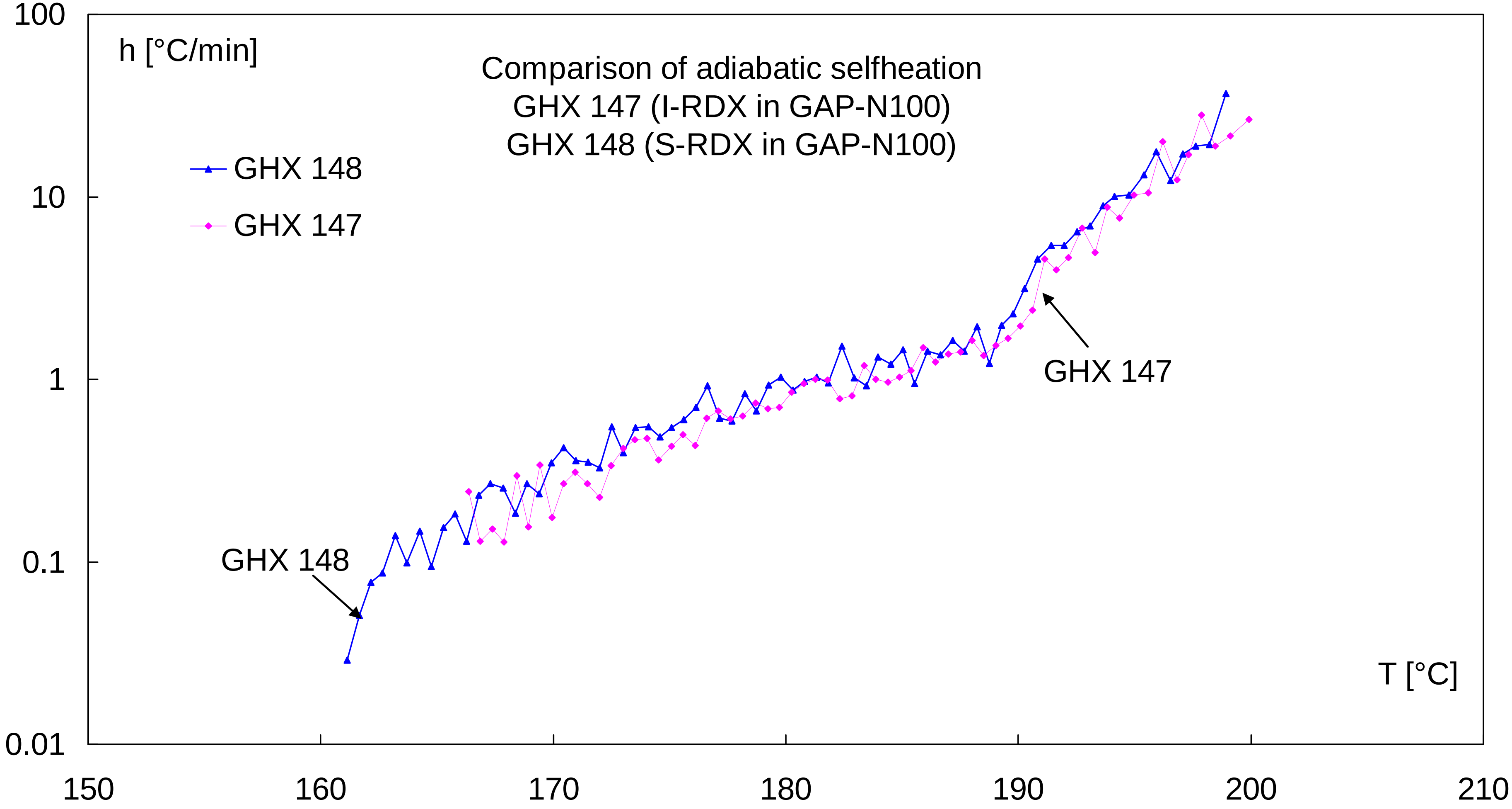
Adiabatic selfheating of GHX 147 and GHX 148



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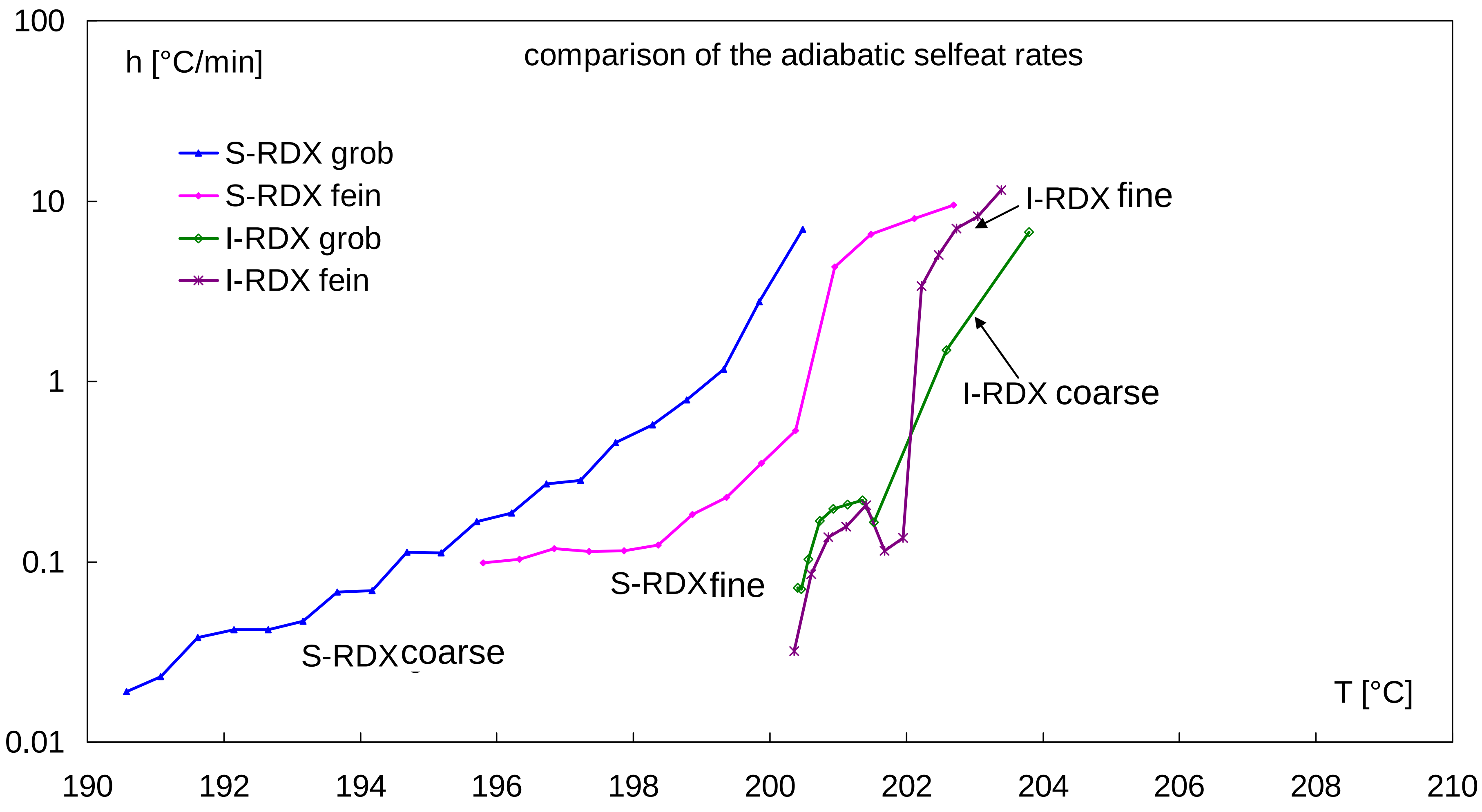
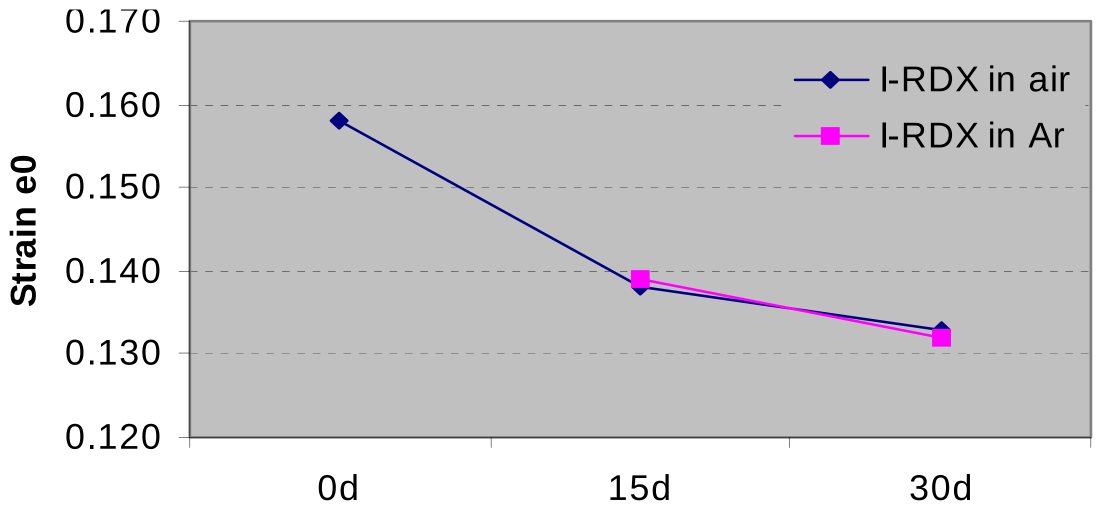
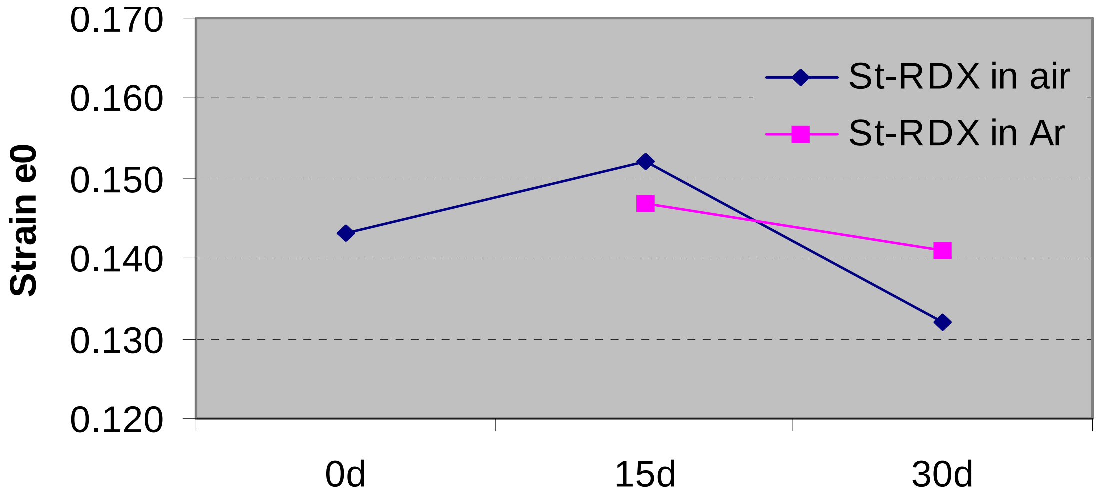
Adiabatic selfheating of the RDX sample by ARC™



Results of Size / Strain-Analysis by X-ray diffraction (ICT, Michael Herrmann)





I-RDX (class 5, fine):
Reduced microstrain on aging,
no differences between air and Argon

S-RDX (class 5, fine):
Increased strain after 15 d
but reduced strain after 30 d.

Comparison:
Different behavior of I-RDX and S-RDX;
> significantly higher starting value in strain for I-RDX, then only decrease in strain
> high strain in S-RDX after 15 d

It seems that defect healing happens for
I-RDX and S-RDX beyond 15 d

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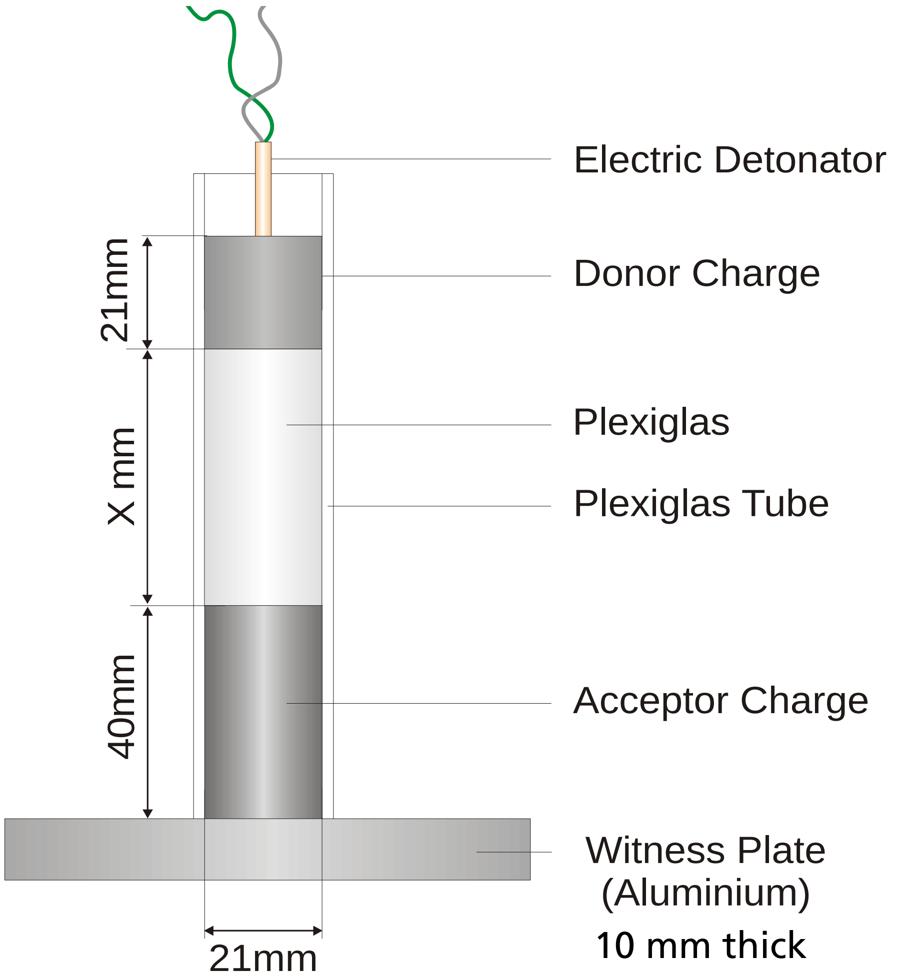
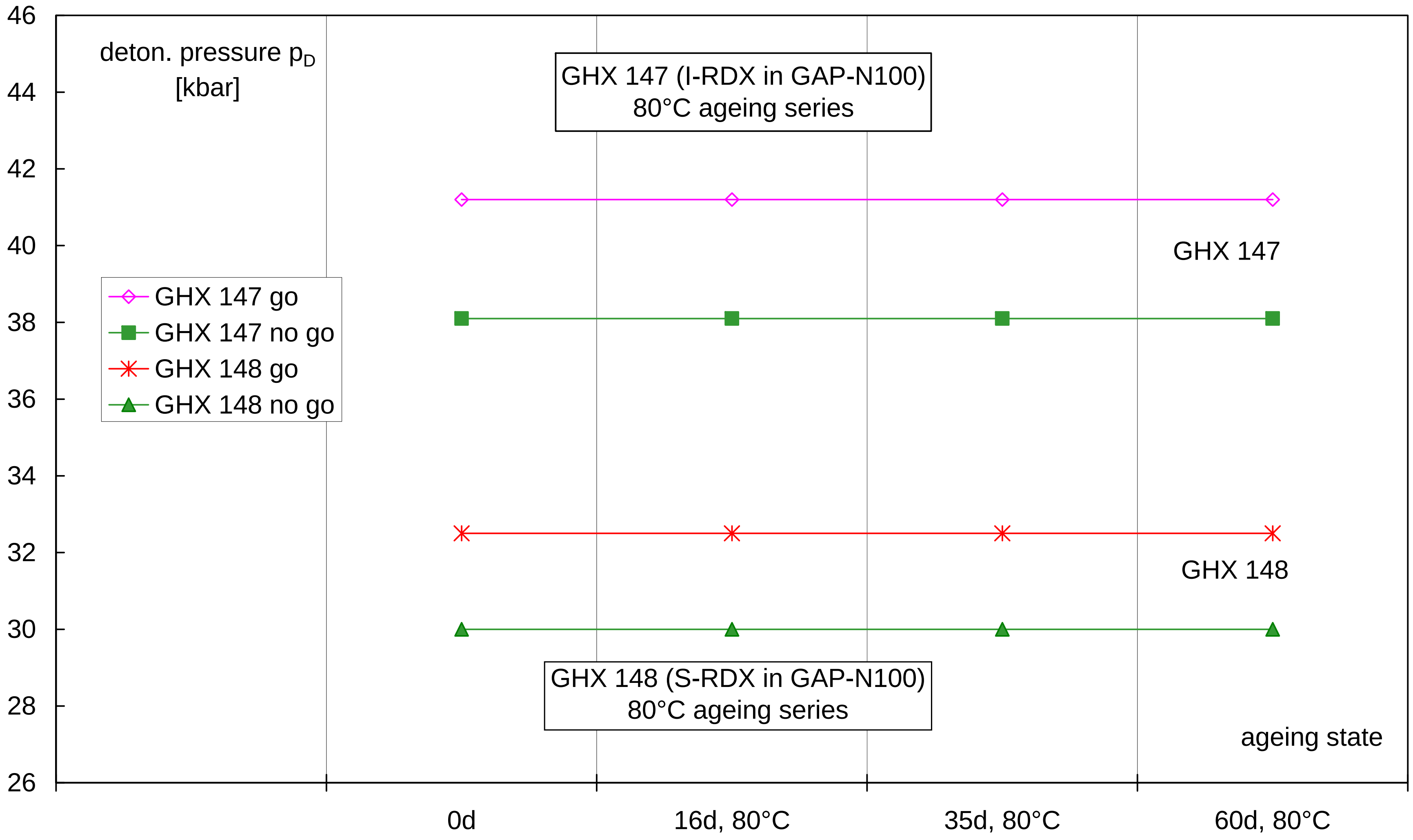
Scheme of ICT-Gap-test, 21mm



Donor with one booster
HX charge:
diam. 21 mm, length 21 mm
RDX / wax / graphite (94.5 % / 4.5 % / 1 %)
pressing force 50 kN
detonator in central bore: T-CU-30-T11U

Actual length of samples were 42 mm

Gap test on GHX 147 and GHX 148, ageing at 80°C



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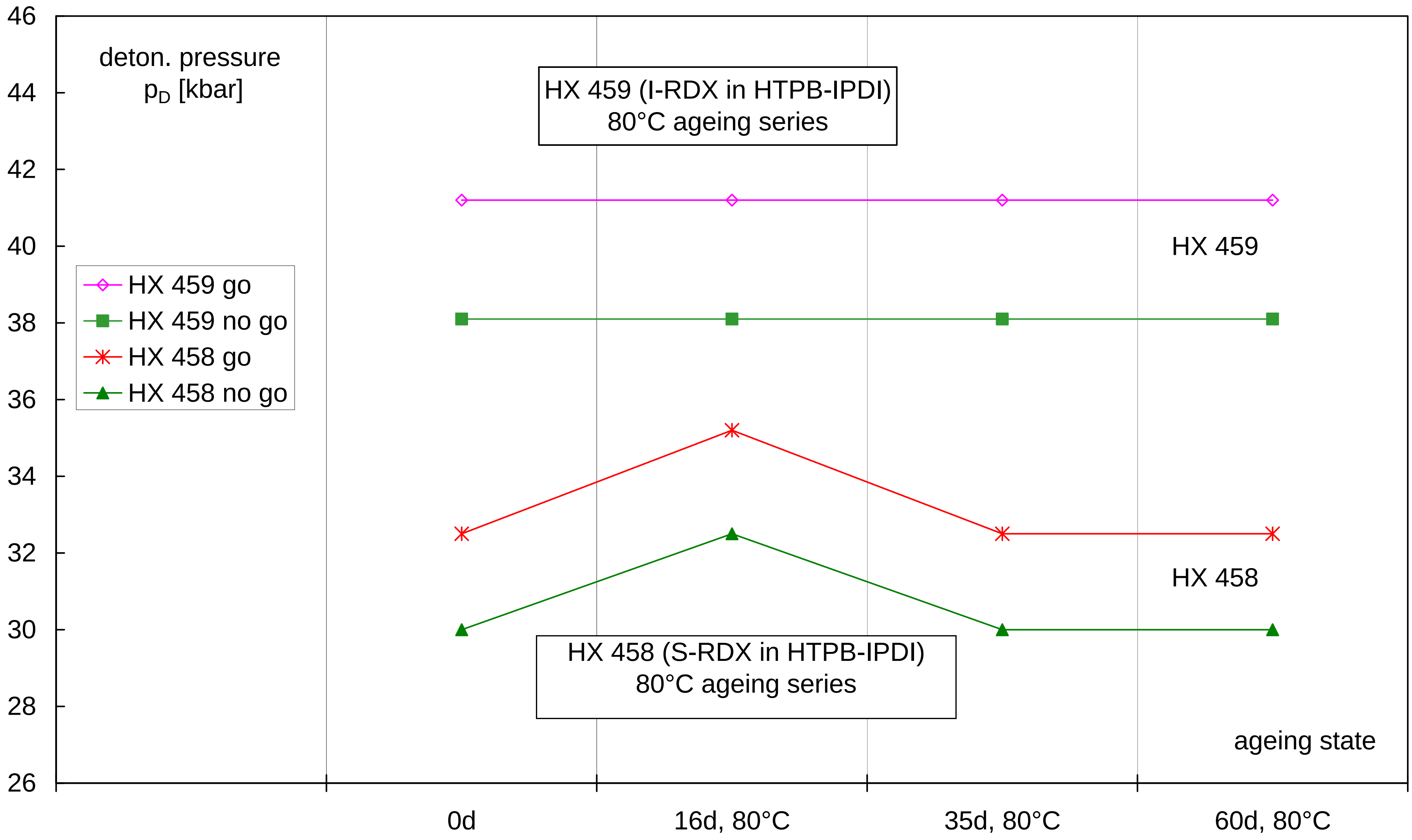
Gap test on HX 458 and HX 459, ageing at 80°C



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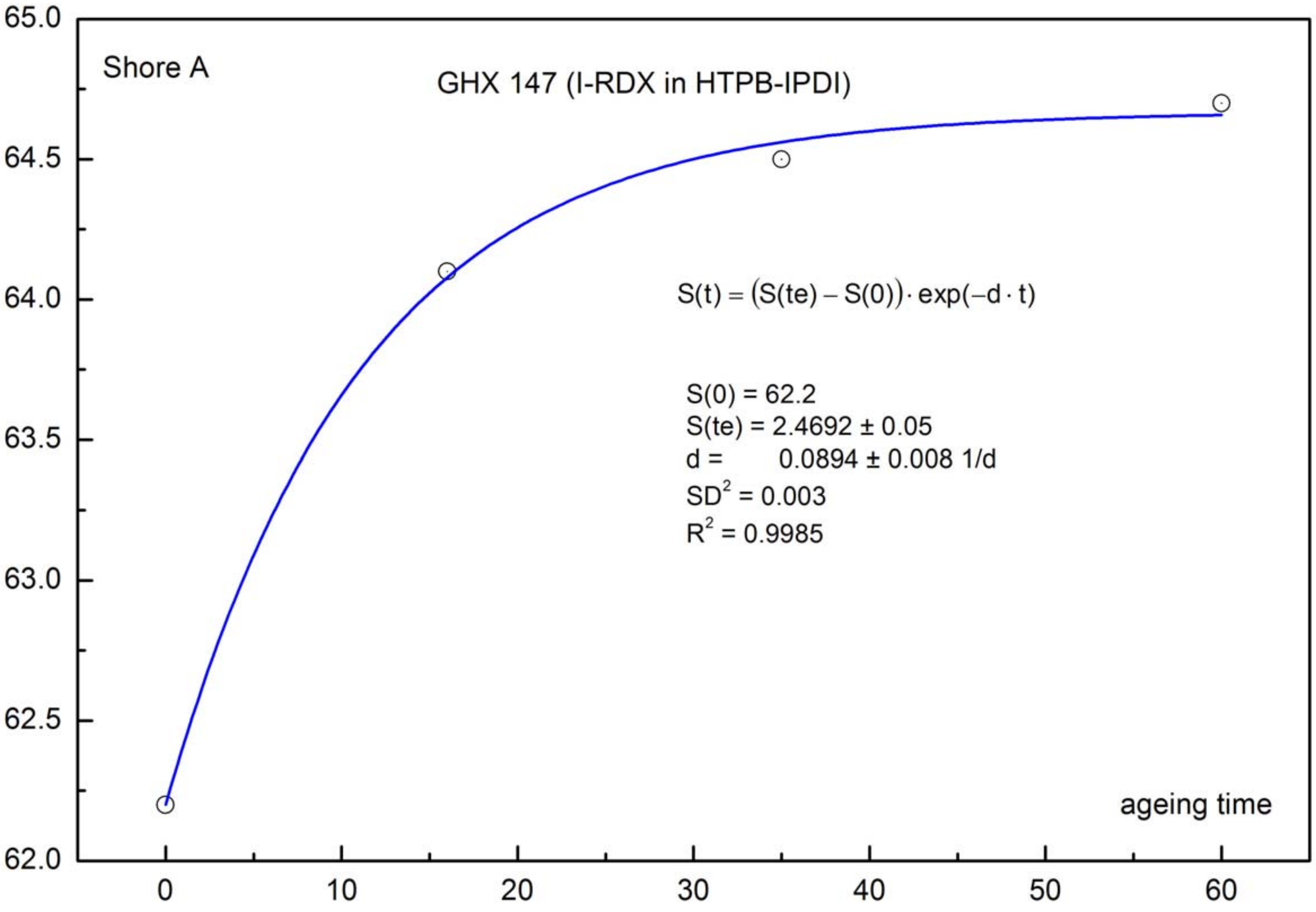
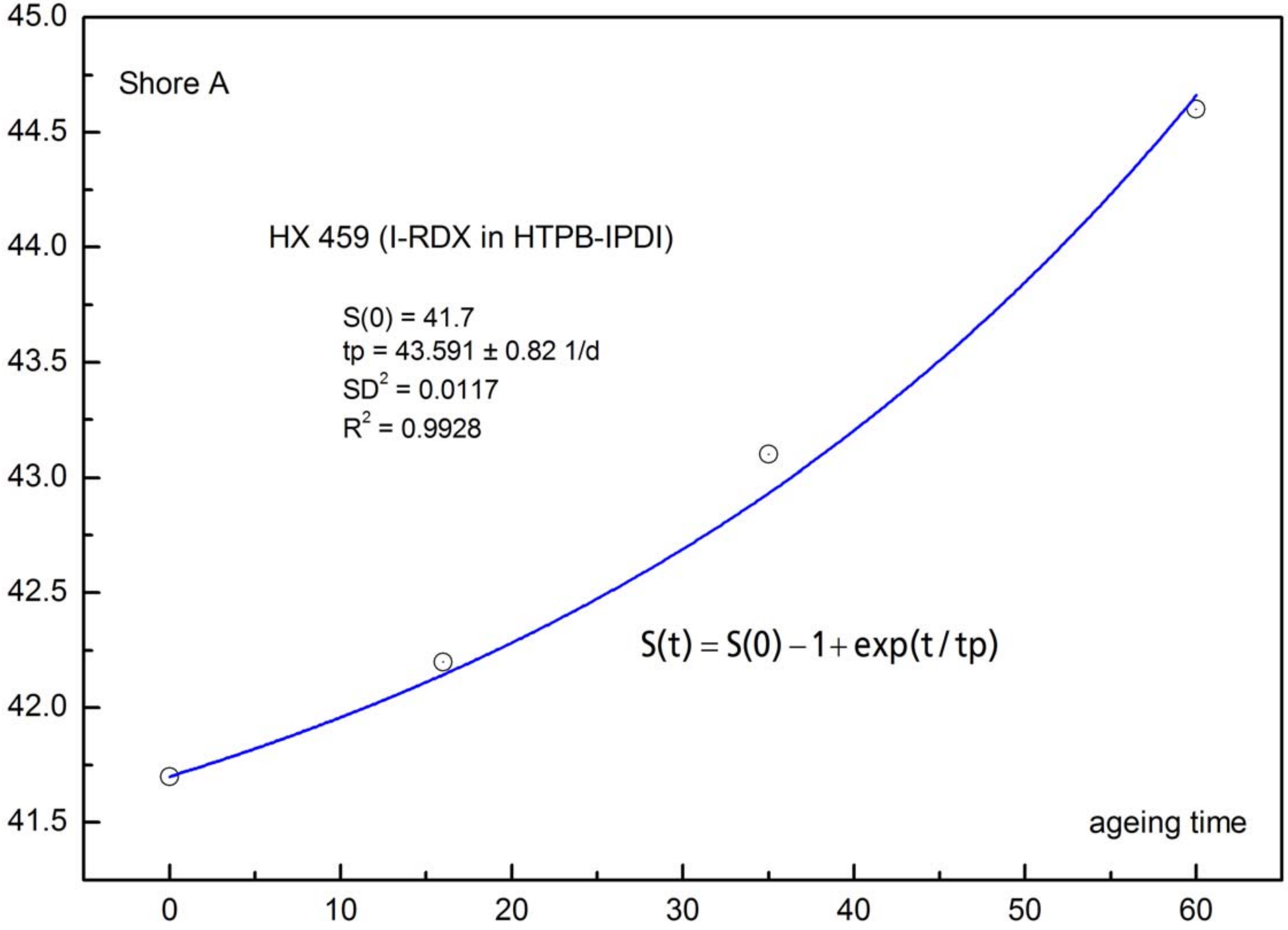
Development of hardness with ageing at 80°C for GHX 147 (I-RDX in GAP-N100)



Development of hardness with ageing at 80°C for HX 459 (I-RDX in HTPB-IPDI)



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Ageing of formulations

80°C:	16 d	35 d	60 d
25°C:	6.8 years	15 years	25 years

HX 459
I-RDX / HTPB-IPDI / DOA
80 : 12 : 8

Pristine | **Aged : 16 days at 80°C** | **Aged : 35 days at 80°C** | **Aged : 60 days at 80°C**

GHX 147
I-RDX / GAP-N100 / BDNPAF
75 : 25 : 10

Pristine | **Aged : 16 days at 80°C** | **Aged : 35 days at 80°C** | **Aged : 60 days at 80°C**

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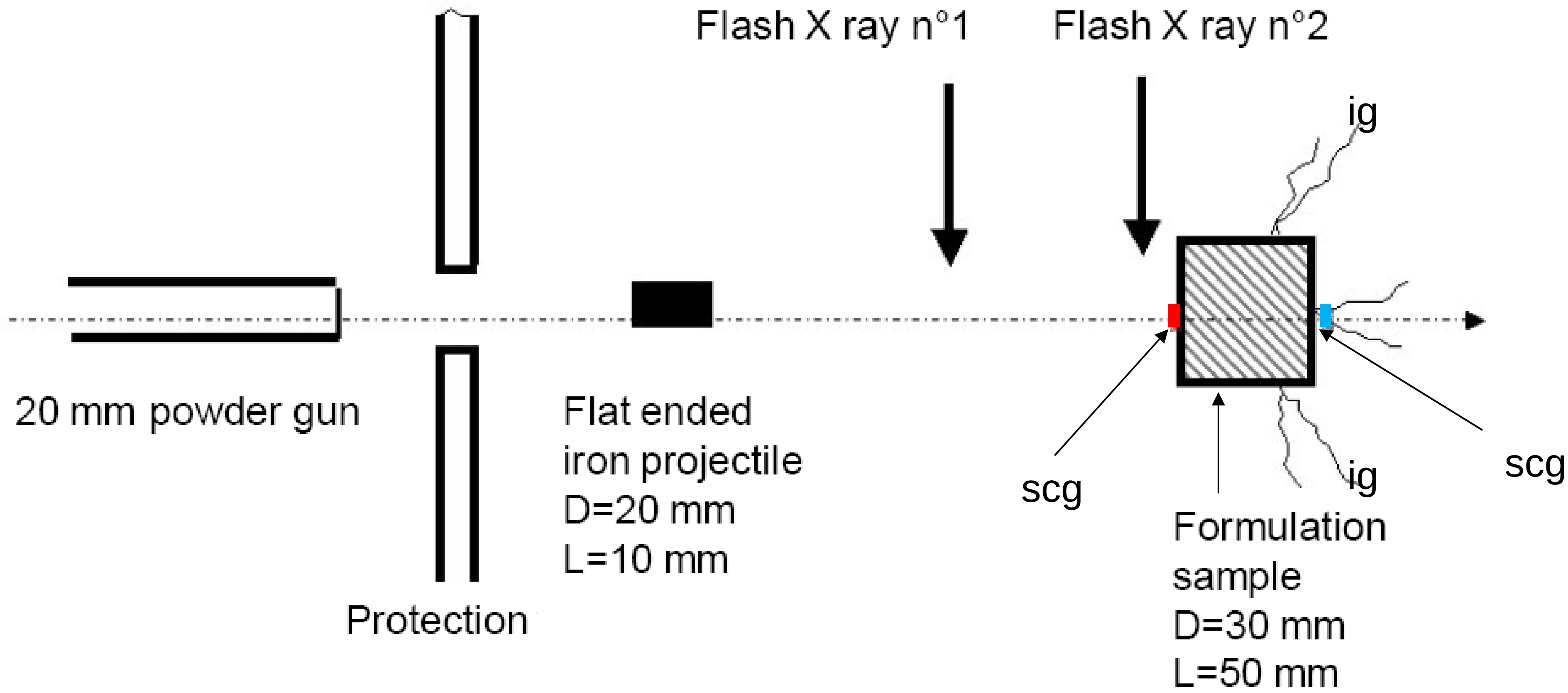
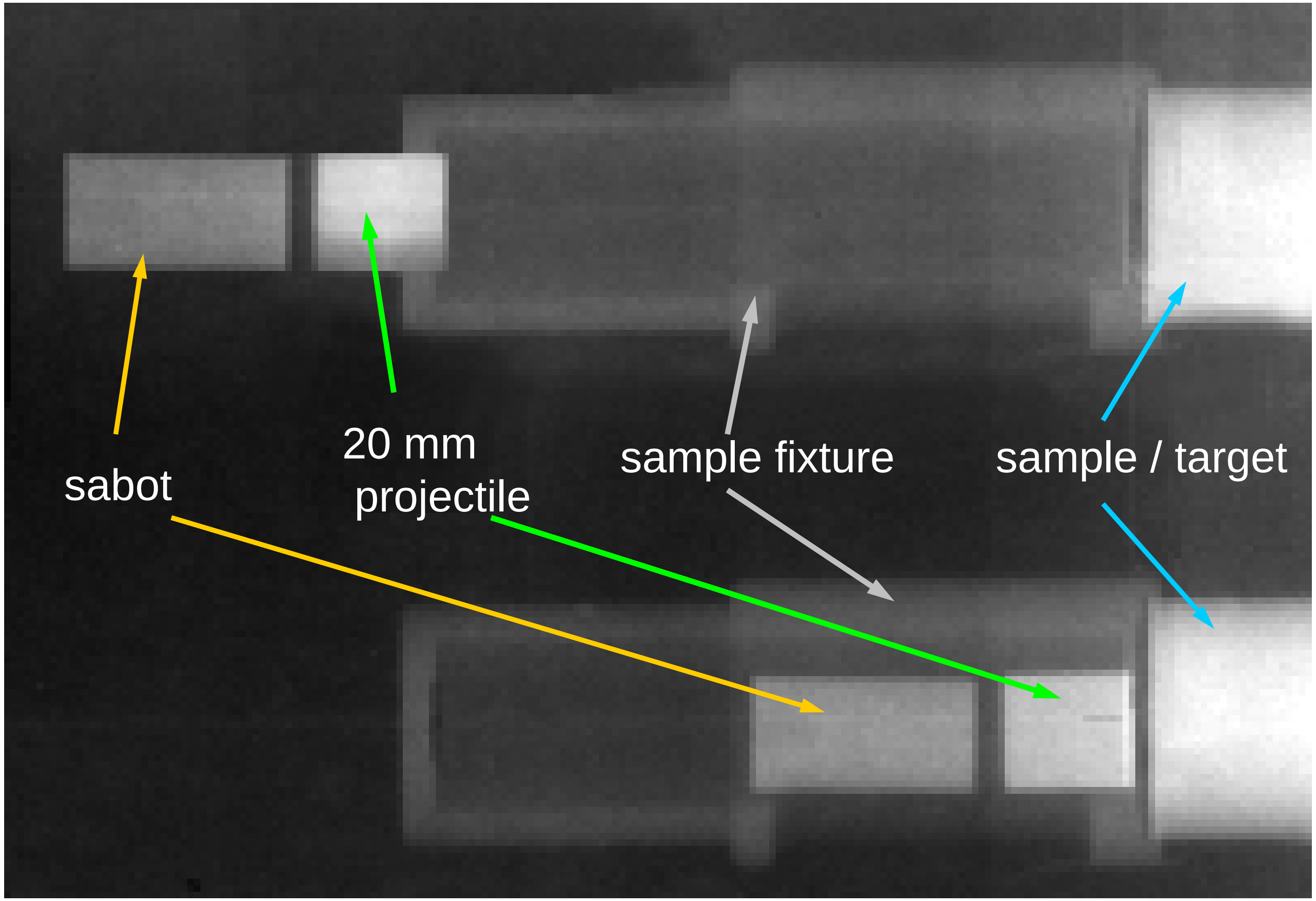
Determination of shock sensitivity by projectile impact on HX and GHX formulations at defined speeds done by ISL

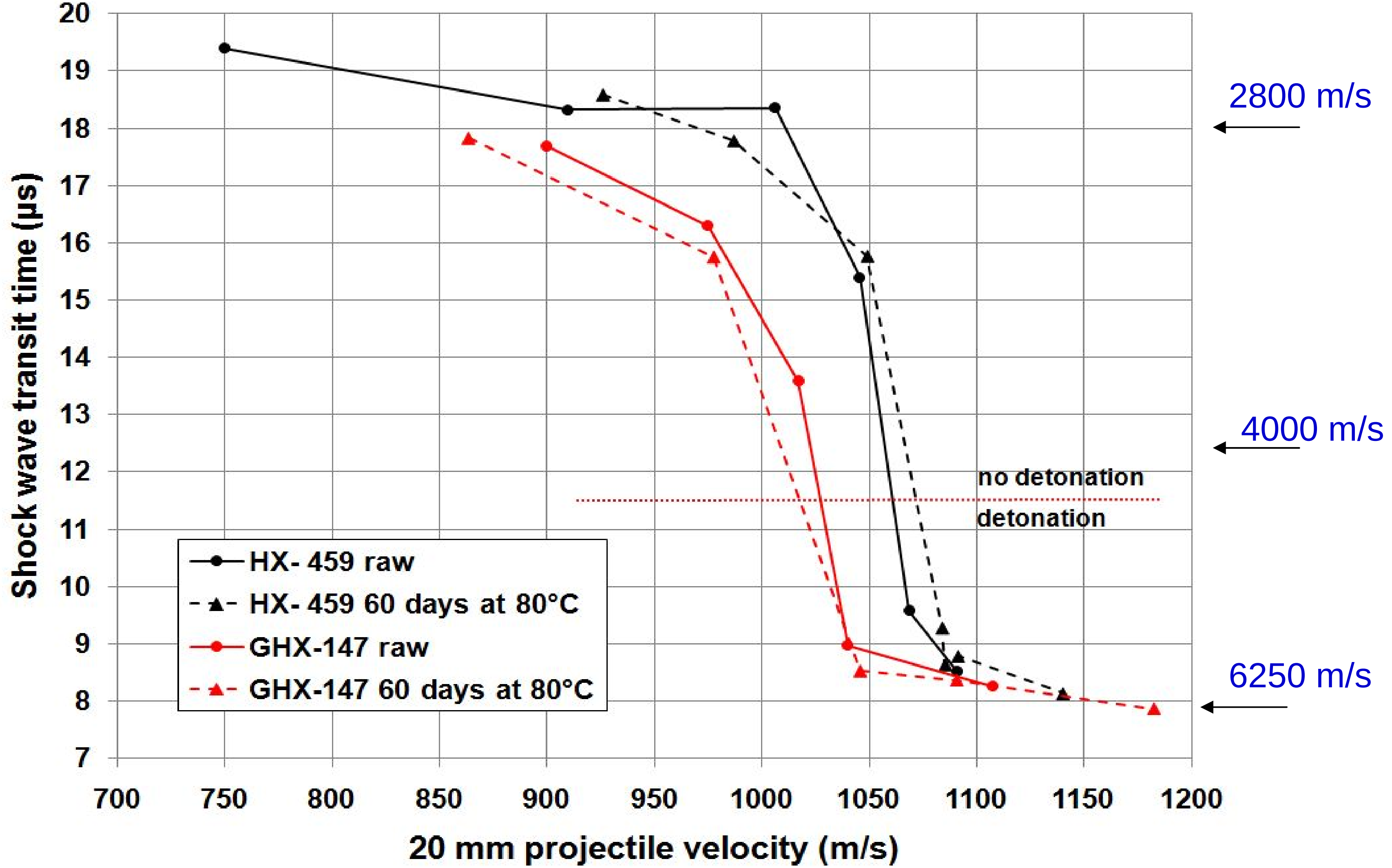


scg: short circuit gauge
ig: ionisation gage

Determination of shock sensitivity by projectile impact on HX and GHX formulations at defined speeds - X-ray photograph



Shock sensitivity by projectile impact of HX-459 and GHX-147 determined at ISL



Summary and conclusions - 1

Ageing of RDX samples in air and argon

with I-RDX changes in colour in both atmospheres, aged samples become significantly darker;
S-RDX samples change colour only slightly they show a little darkening.

Results on thermal sensitivity with DSC at low heating rate

no changes with I-RDX;
slight change with S-RDX coarse, but decomposition shifts to higher temperatures.

Results on adiabatic selfheating (ARC) of used RDX samples

clear differences between S-RDX and I-RDX;
the two S-RDX samples (coarse and fine) have lower onset temperatures.

Results on adiabatic selfheating (ARC) of the formulations

HTPB-binder: differences in formulations with I-RDX and S-RDX,
with I-RDX decomposition starts at higher temperatures;
GAP-binder differences in formulations with I-RDX and S-RDX are small.

Shore A hardness of gap samples and projectile impact samples

general difference in hardness between GAP-N100 and HTPB-IPDI samples;
GAP-N100 formulations have higher hardness;
trend in ageing behaviour seems different between the two binders.

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Summary and conclusions - 2

Shock sensitivity of the four formulation types

21 mm gap test samples (ICT) — no ageing influence found
30 mm projectile impact test (ISL) — no ageing influence found

from gap tests
S-RDX formulations are more sensitive than I-RDX formulations;
Difference is about 10 kbar in initiation shock pressure in 21 mm gap test.

Microcalorimetric measurements

decomposition of I-RDX is in argon a bit faster than in air;
same holds for the I-RDX- HTPB-formulations;
S-RDX-HTPB formulation reacts slower than I-RDX-HTPB-formulation

Density distributions

no severe change in distribution with I-RDX, but by ageing the densities shift somewhat to lower values.
Assumption: trapped process liquid diffuses out of the particles during ageing.
The diffusion kinetics seems to be different by ageing in air or in argon.

Fraunhofer ICT

Thank you for your attention

Questions ?