Investigation of ageing behaviour of plasticised nitrocellulose – accelerated ageing and real ageing

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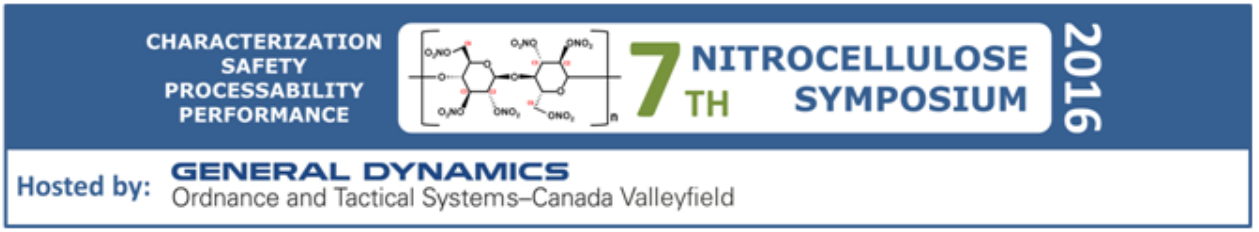
Hosted and organized by
General Dynamics - Ordnance and Tactical Systems (GD-OTS), Valleyfield, Canada



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Outline

- Motivation and objectives
- Material
- Results of investigation on chemical stability 24 years ago
- Results on chemical stability after 24 years of natural ageing
- Comparison
- Conclusion

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Motivations and Objectives

- At Fraunhofer ICT years ago an extended study on the chemical stability of lacquer NC was performed in collaboration with former company Wolff Walsrode, now belonging to Dow Chemical.
- One type was investigated in more detailed: NC Chips type 24E.
- A sample of these NC Chips was kept as control in one bunker of ICT, from the investigations in 1991 and 1992 on up to 2015 / 2016.

- The true prediction of real ageing with data of accelerated ageing is steadily on the agenda.
- Determination of chemical stability after 24 years at natural ageing at about 15°C, in part stored in original card board container, in part in a 2 liter PE bottle.
- Comparison of stability state after 24 years with former prediction.

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Investigated material

The used NC material is so-called plasticized nitrocellulose, a lacquer type NC.
It is of type 24E.
It was produced by former company Wolff Walsrode in Walsrode, Germany.
The company name for E24 type is E510.
E stands for solubility in esters as ethyl acetate.
24 is a characterizing number for the viscosity determined in standardized procedure.

The plasticization substance was dibutyl phthalate (DBP) (today others are used as DOA, SAIB, Nepplast,…)
Added is normally between 15 and 24 mass-%, here it was 18 mass-% of DBP.
The nitrogen content of this E-type is between 11.8 and 12.4 mass-% (regarding NC).

Investigated was the material NC Chips E510 Mi063, N-content of NC alone was 12.3 mass-%.
The chips are irregular flakes typically 12 mm to 12 mm in size, about 0.6 mm thick. It has stabilizer added.

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Stability results from 1992

method	unit	1992	limit values	
			for NC-chips	for non-stab. NC
autoignition in Wood bath, 5°C/min, 0.2g	°C	176	> 170	> 170
Bergmann-Junk values, 132°C, 2 h, 2.44g	0.01 n NaOH in ml/g	4.3	≤ 12.5	≤ 12.5
	NOx in ml/g	0.96	≤ 2.81	≤ 2.81
	N_2 in ml/g	0.48	≤ 1.40	≤ 1.40
time to fast increase of mass loss (ML)				
at 70°C	d	277	90	27
at 80°C	d	92.3	30	9
at 90°C	d	23.5	10	3
Activ. energy from ML by 'time to event'	kJ/mol	130	114	114

Methodology and results published:

M.A. Bohn, F. Volk, O. Brauer

Determining the Safe Lifetime of a Plasticized Nitrocellulose.

Pages 483 to 494 in Proceedings of the 8th international Symposium on 'Loss Prevention and Safety Promotion in the Process Industries'. Antwerp, Belgium, June 6 to 9, 1995.

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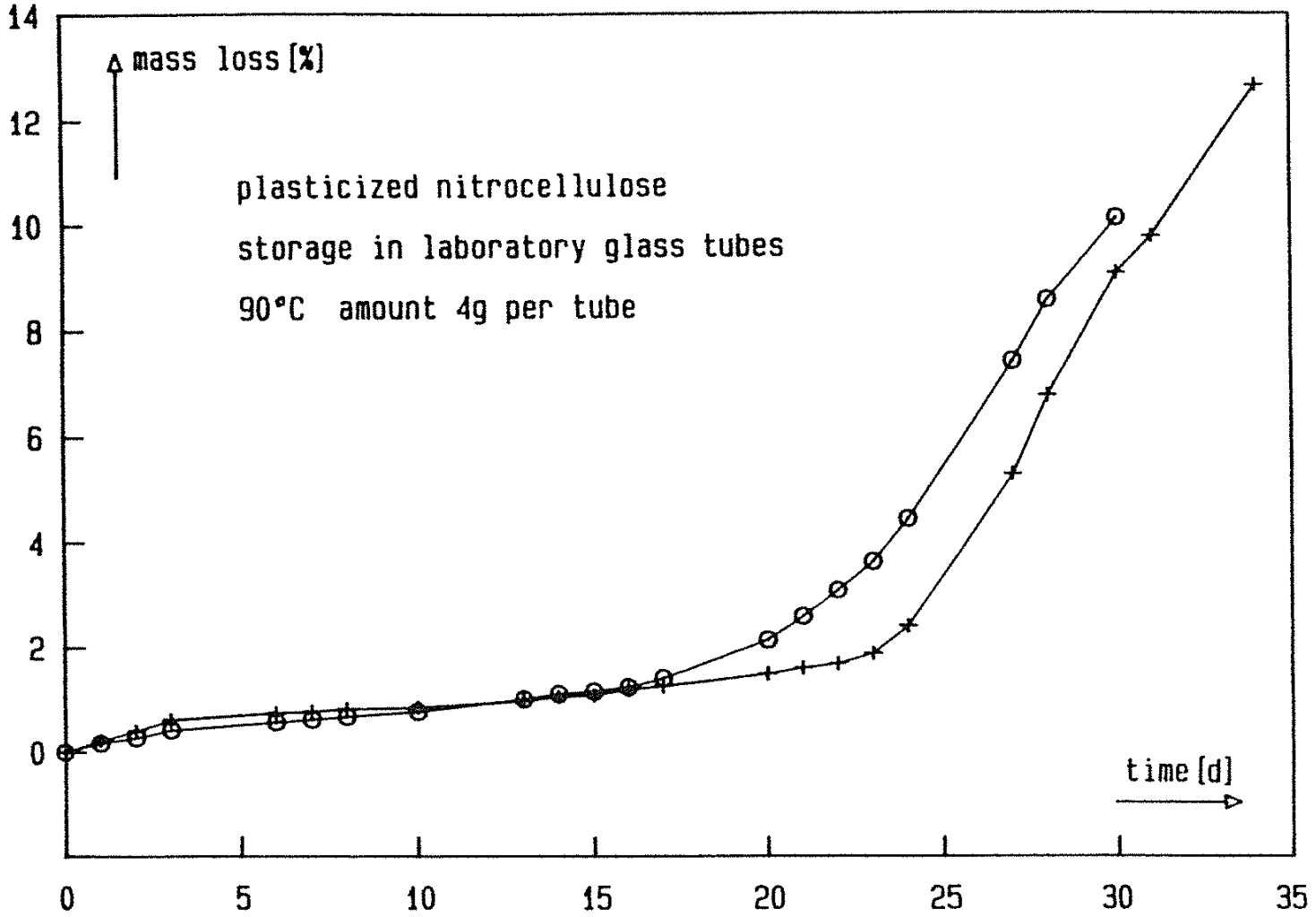
Typical mass loss curve in baseline investigation of 1992



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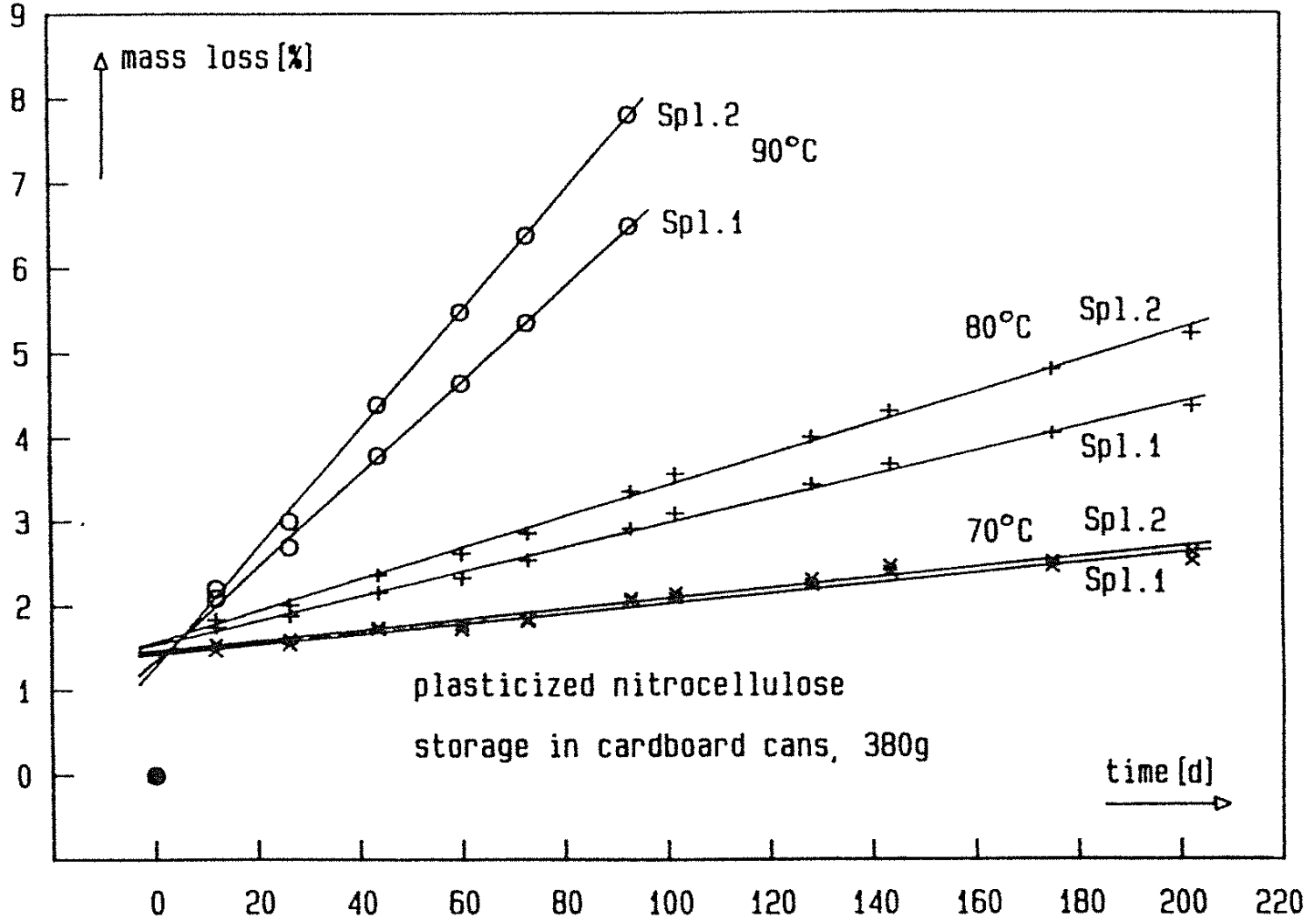
Mass loss data obtained from 380g samples in card board cans



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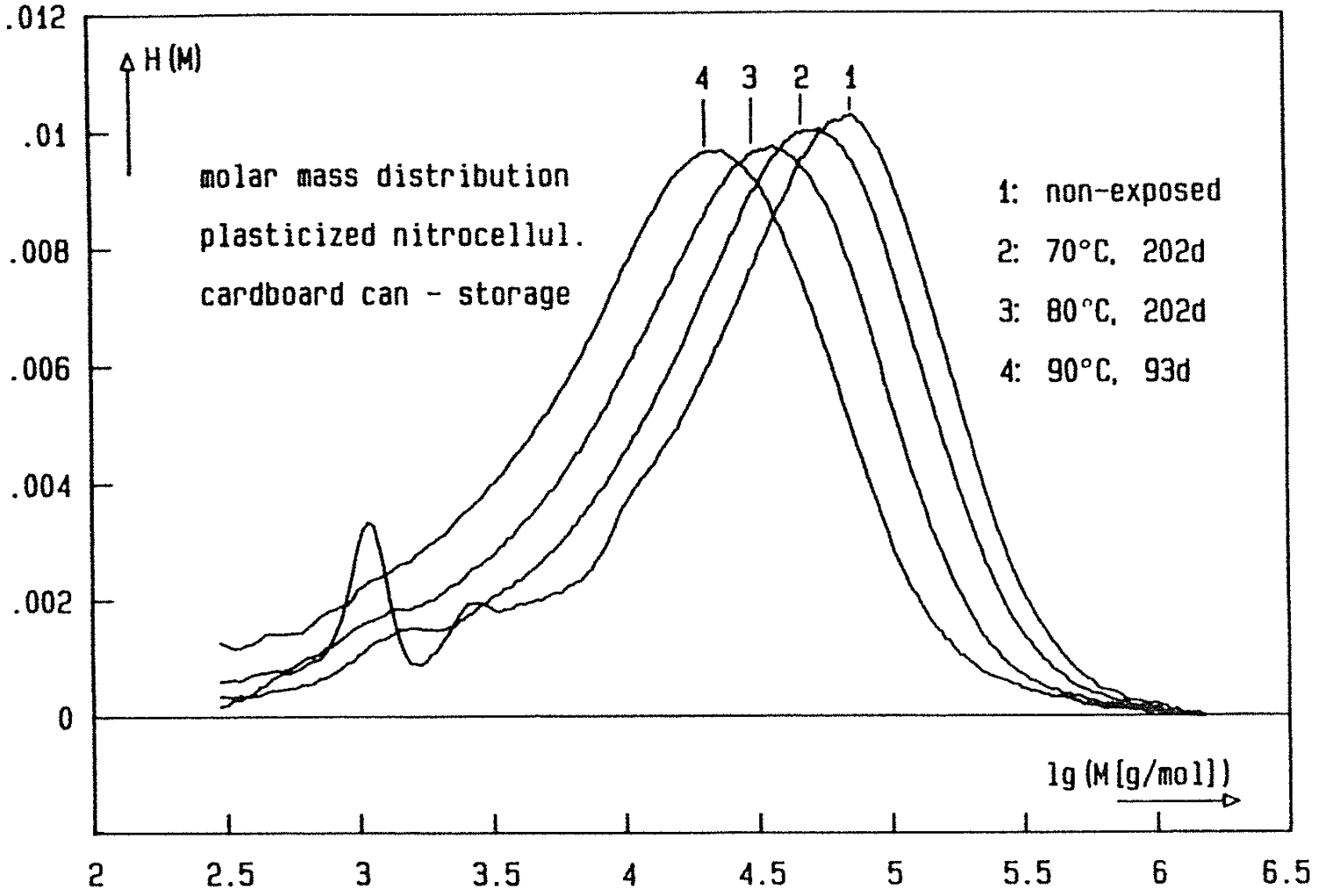
Molar mass distributions from 1992



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Compilation of all results from 1992

Comparison of the Arrhenius parameters

	Laboratory glass tubes 2g	4g	cardboard cans 380g
Ea [kJ/mol]	130.6±4.3	126.8±3.7	122.8±7.8
ln(Z)	40.05±1.5	38.84±1.3	37.93±2.66
Z	$2.475 \cdot 10^{17}$	$7.379 \cdot 10^{16}$	$2.970 \cdot 10^{16}$
[Z]	1/d	1/d	%/d

Values of the mean molar masses of non-exposed and exposed NC chips

Stress (Exposure)	Mp	Mn	Mw	Mz
	in kg/mol			
non-exposed	70.8	10.2	73.9	194.0
70 °C, 202 d	53.1	11.5	61.5	166.5
80 °C, 202 d	37.0	8.3	46.2	146.6
90 °C, 93 d	22.5	5.9	33.7	128.9

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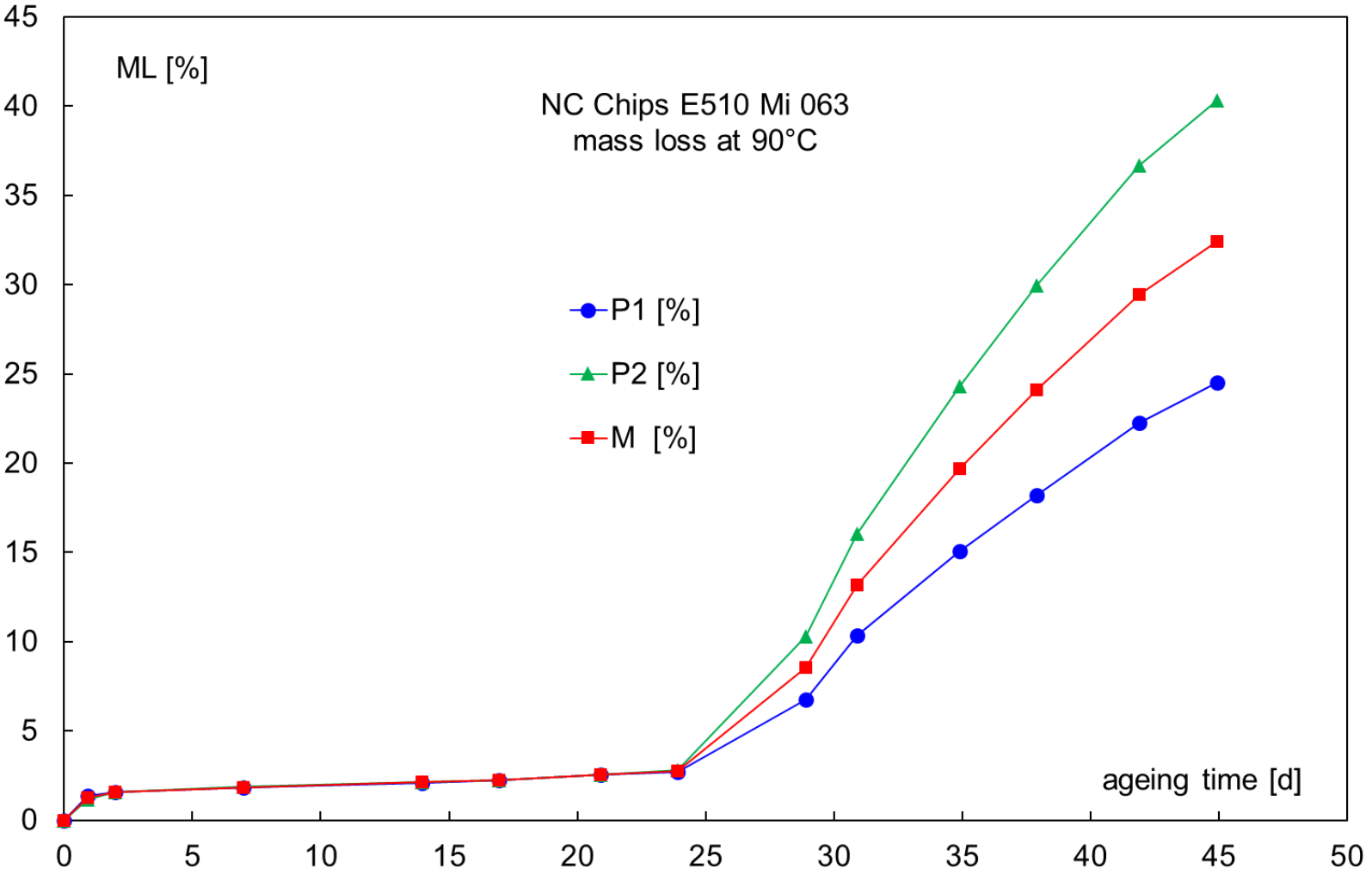
Example of mass loss of naturally aged material



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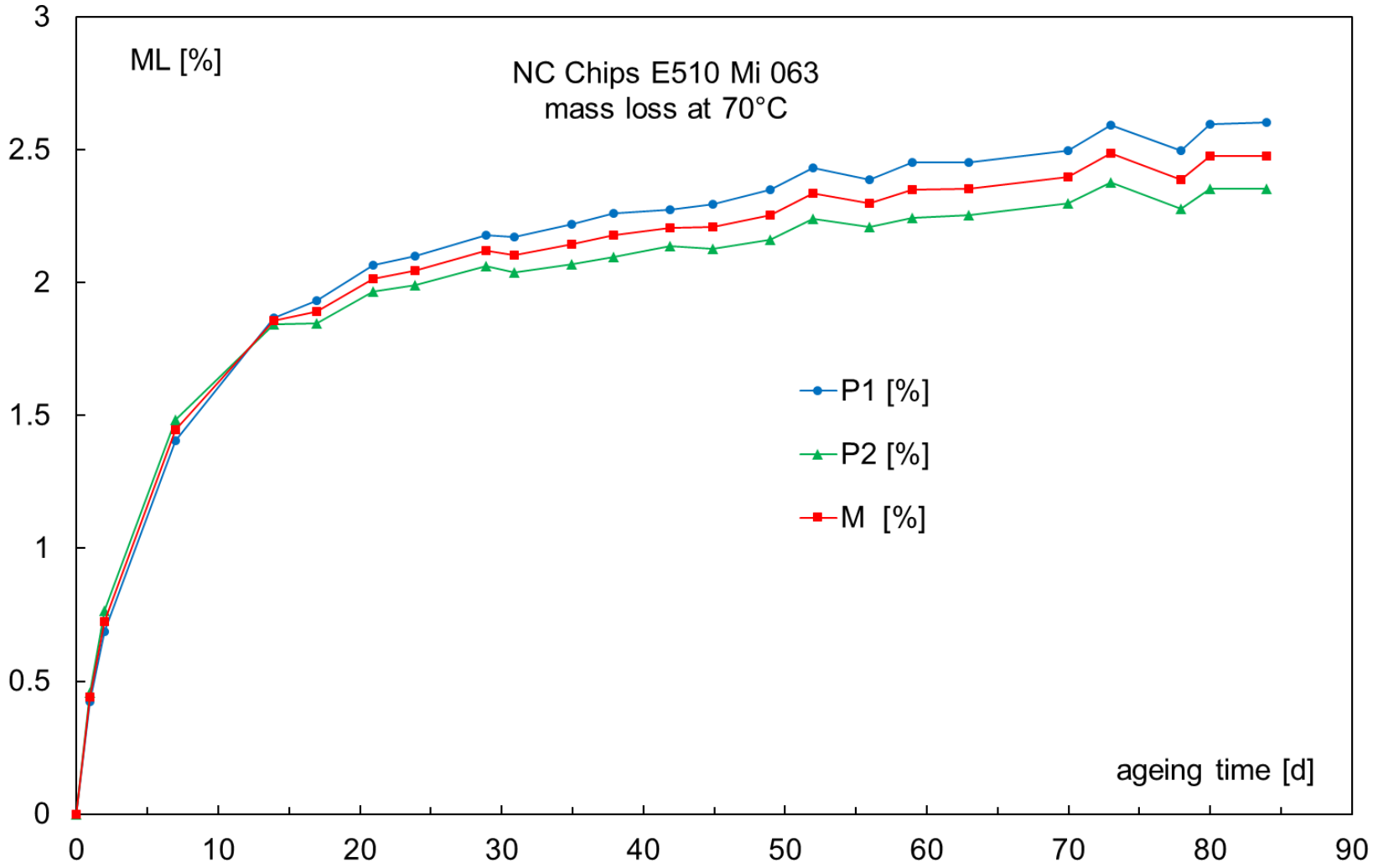
Mass loss data of naturally aged material at 70°C



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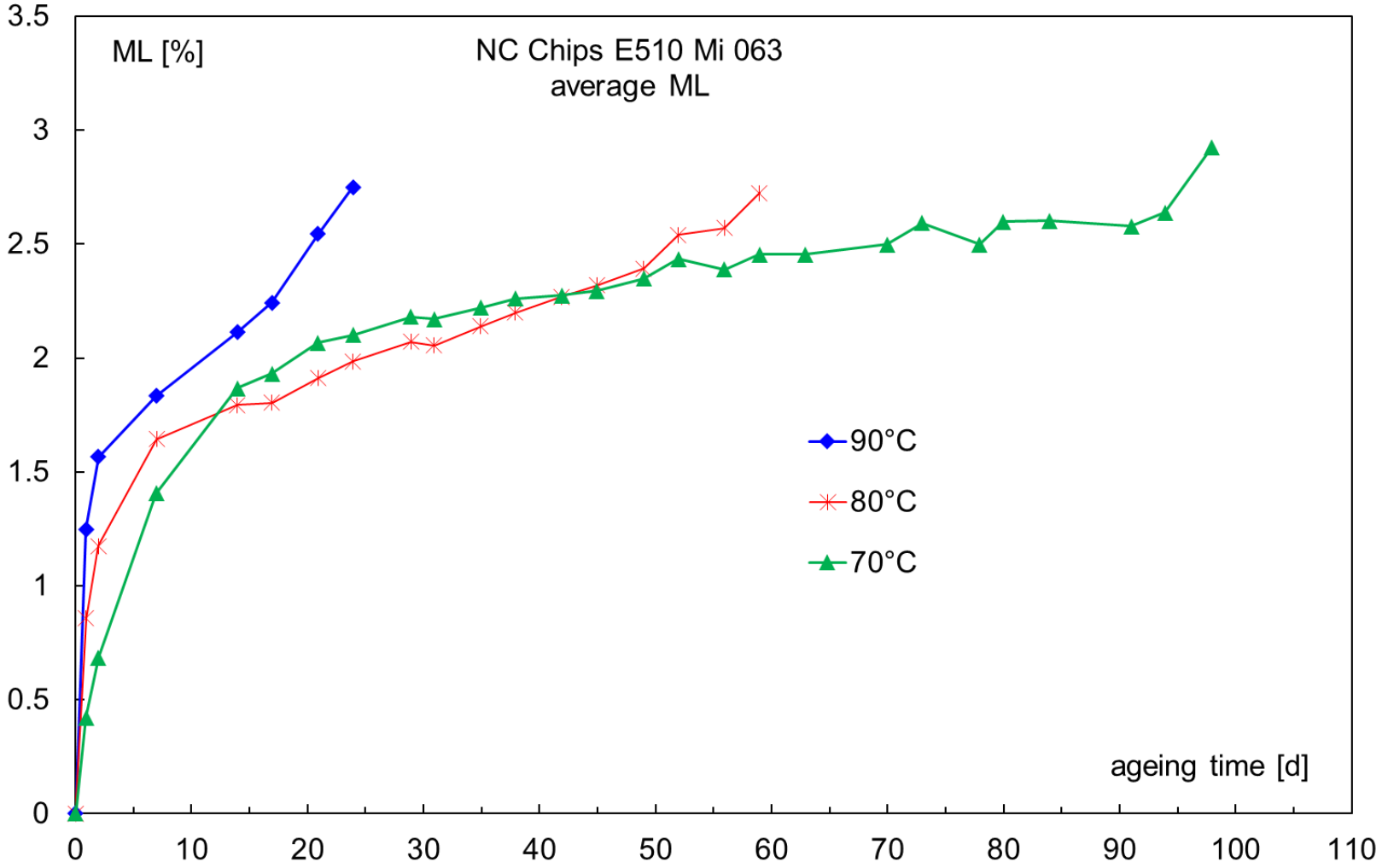
Mass loss data using the range of linear increase and up to strong increase



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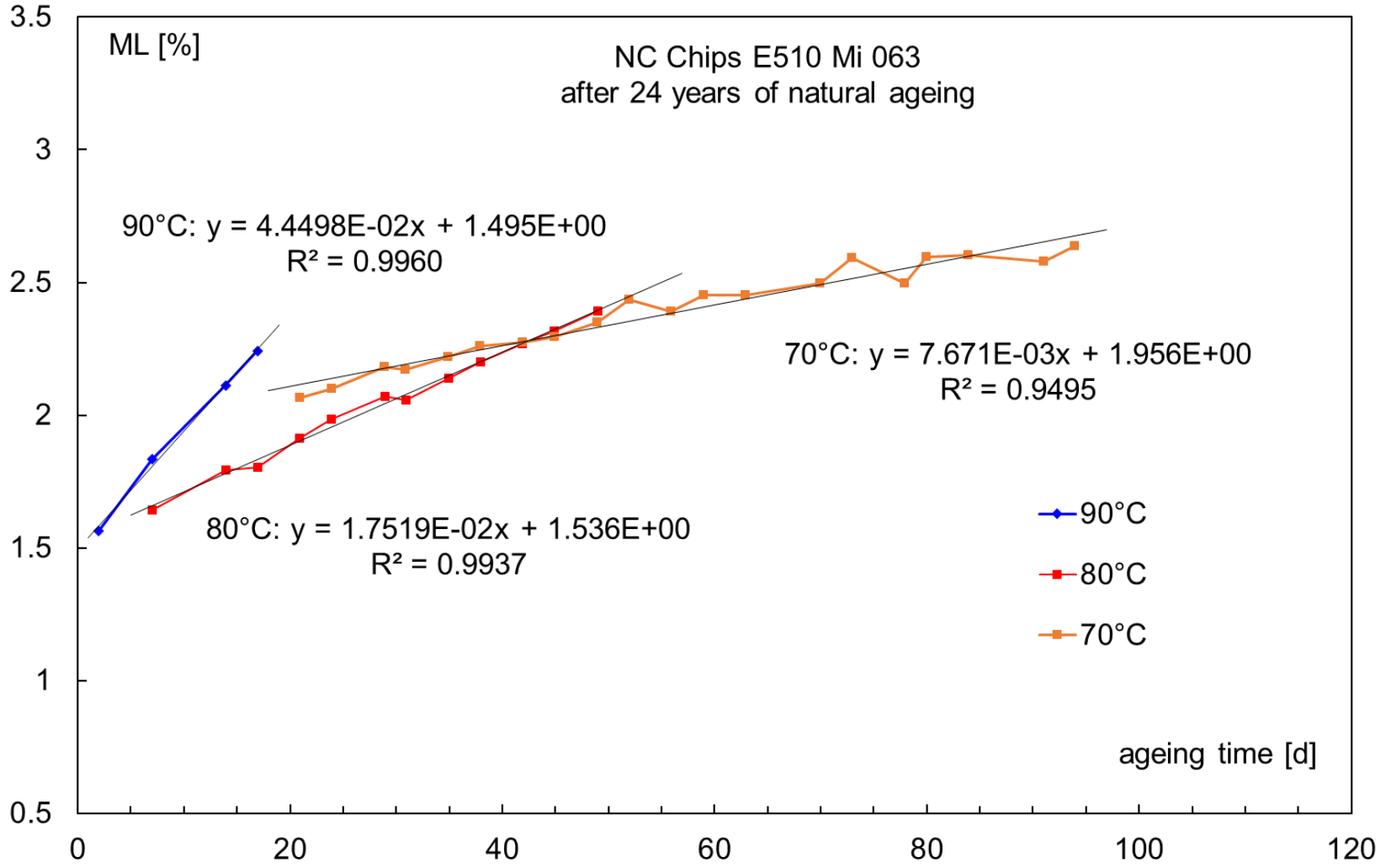
Evaluation of mass loss data – kinetically by linear increase of ML



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Activ. energy from ML by 'time to event'	kJ/mol	130	**91**	114	114

Conclusion

all basic stability data are still fulfilled.

some surprise: the low value of activation energy with 91 kJ/mol compared with 1992.

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Preparation and separation of the NC solutions by GPC (SEC)

Solution in THF, solution time 20h at room temperature
Concentration 1.5 mg /ml THF
All solution have been filtrated by 0.45 teflon syringe filter
Injection volume: 100µl
Eluent: THF, flow 1ml/min

The instrumentation of the GPC apparatus:

Agilent Series 1100
consisting of isocratic pump, injection block, auto-sampler,
refractive index detector, column oven
Solvent degasser from company PSS, Mainz, Germany

Columns from company PSS, 8 mm in diameter, 300 mm long, 10µm SDV particles

SDV: modified styrene-divinylbenzene copolymer network

separation column 1	PSS SDV 10 µm, pore size	100 Å
separation column 2	PSS SDV 10 µm, pore size	1000 Å
separation column 2	PSS SDV 10 µm, pore size	100 000 Å

Columns in oven on 35°C, detector cell on 35°C

Calibration of apparatus with narrowly distributed polystyrene standards (means Mn ≈ Mw ≈ Mp)

Data evaluation with software PSS WinGPCUniChrom.

PSS: Company Polymer Standards Service GmbH, Mainz, Germany.

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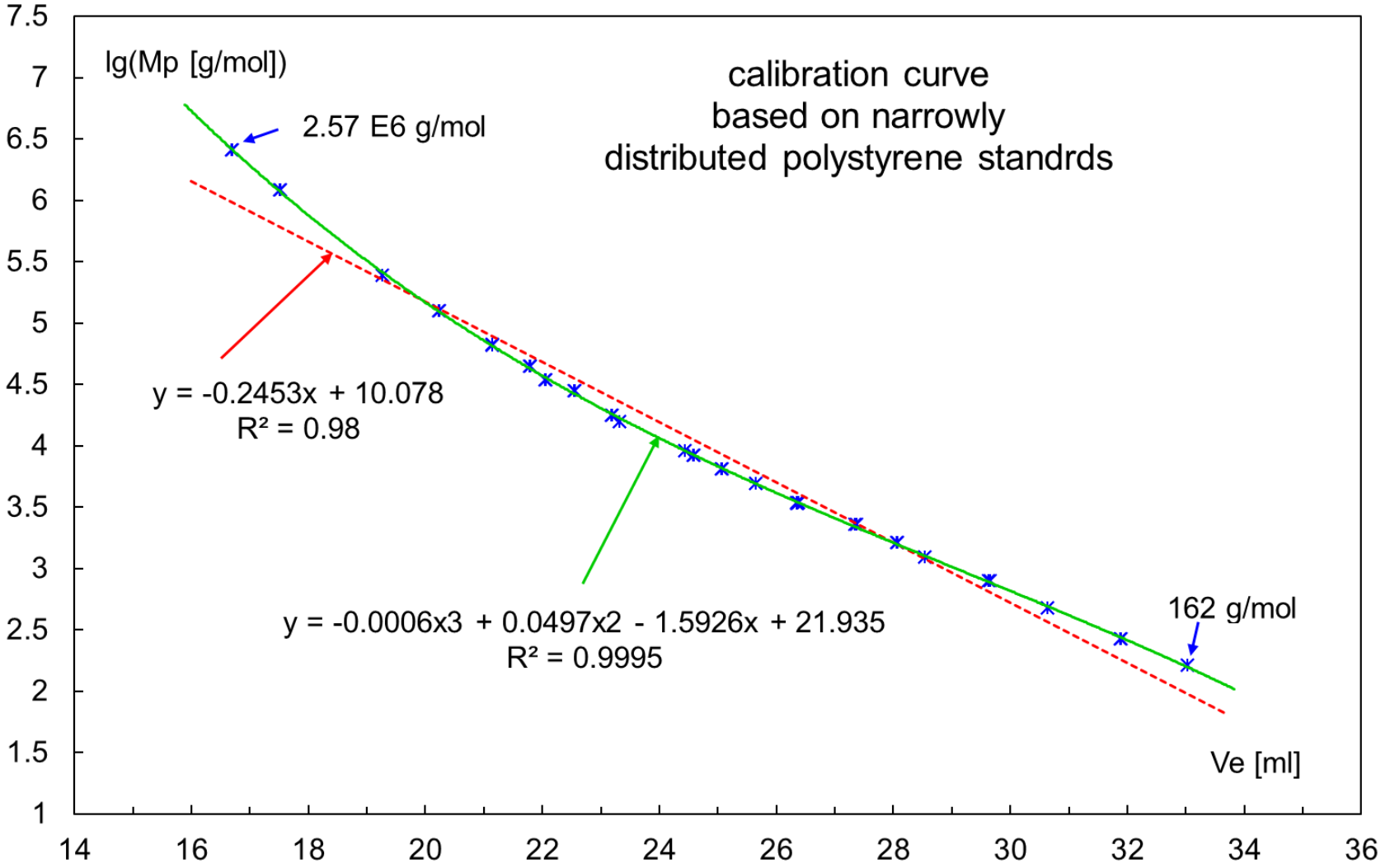
Calibration curve of the GPC column set with 22 PS standards



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Evaluation of GPC-data – calculation of MMD and mean molar masses

The separation of the polymeric solution is with GPC (SEC) according to the size of the so-called hydrodynamic volume of the polymer molecules.

This is proportional to the polymer length and the coiling behaviour of the polymer in the used solvent.

If one calibrates with another polymer than the analysed one, a principal error is introduced, because the coiling behaviour and formation of solvent shell are different.

But comparisons of the results from ageing series are still possible, if the ageing is not to strong and the principle character of the analysed polymer will not be changed.

The elugram is via calibration curve converted into the molar mass distribution function.

Because the signal of RI detector is proportional to concentration or mass (mass of polymer in the elution fraction in detector cell) on gets the mass weighted MMD hm.
The mean molar masses are calculated as so-named moments of the MMD.

In kinetics the molar number averaged MMD hn is the correct function and correspondingly the molar number averaged mean molar mass Mn.
But sometimes Mn is difficult to use – see later.

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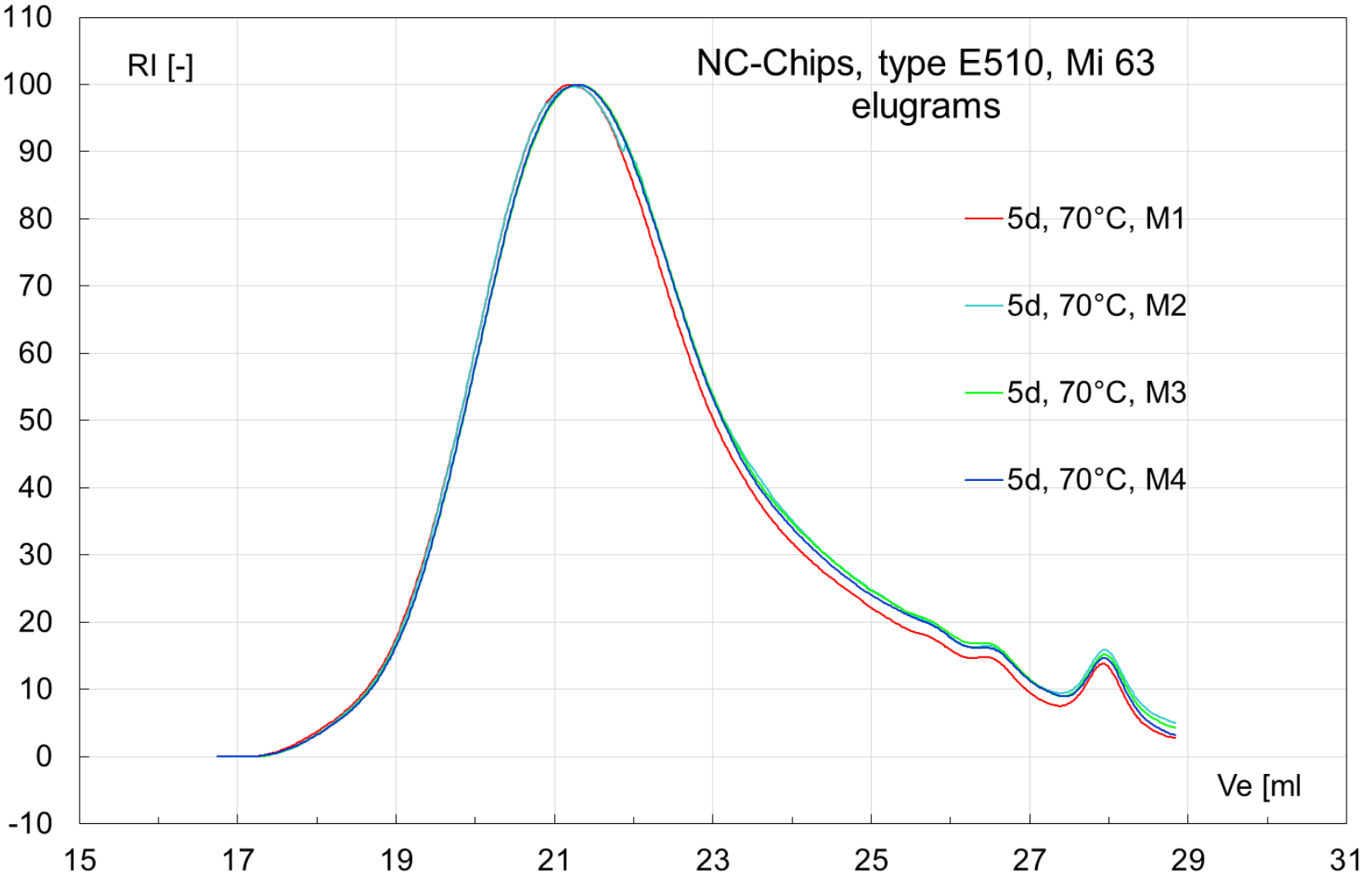
Example of elugrams



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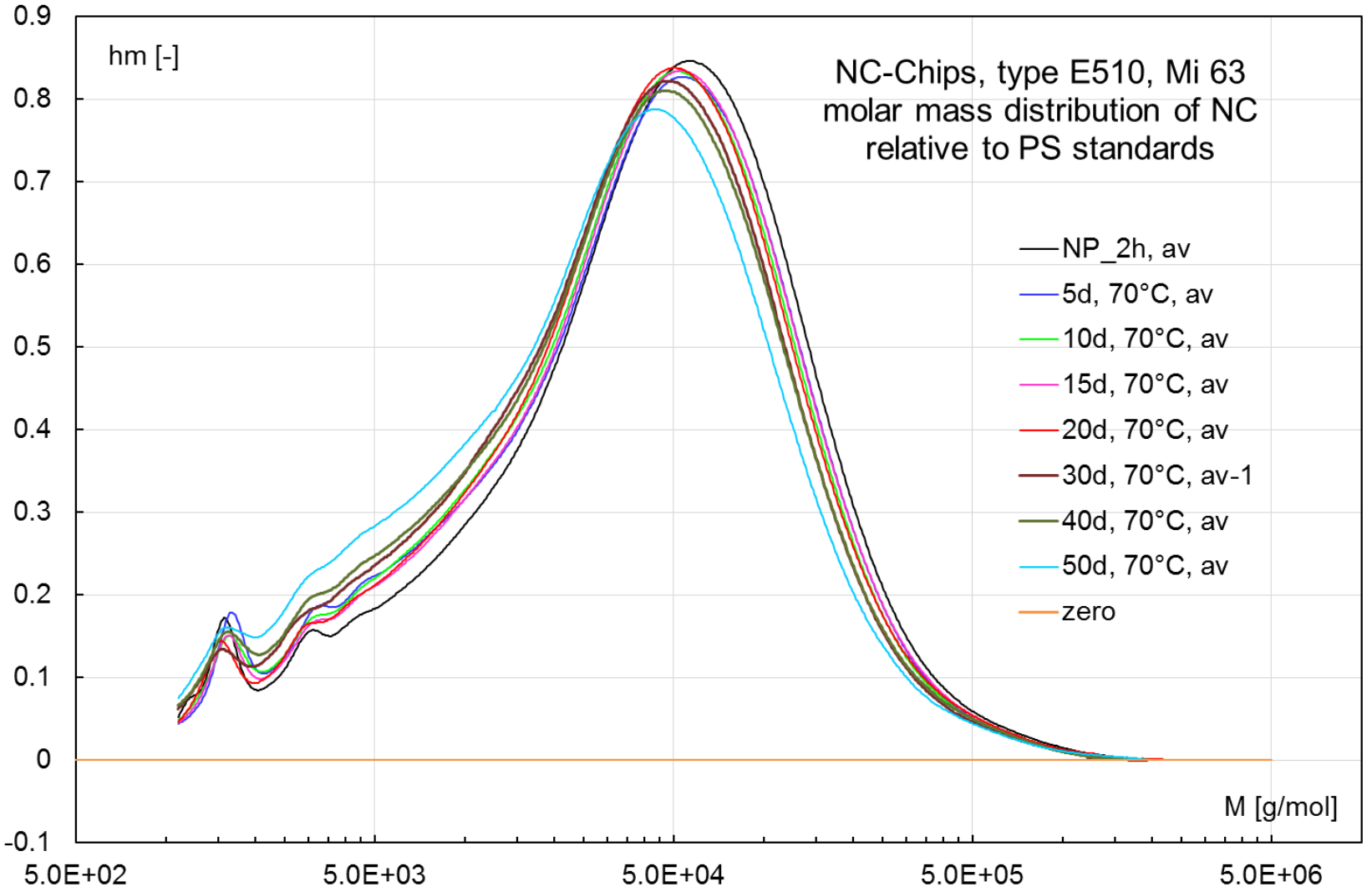
Molar mass distribution of type hm ageing series 70°C



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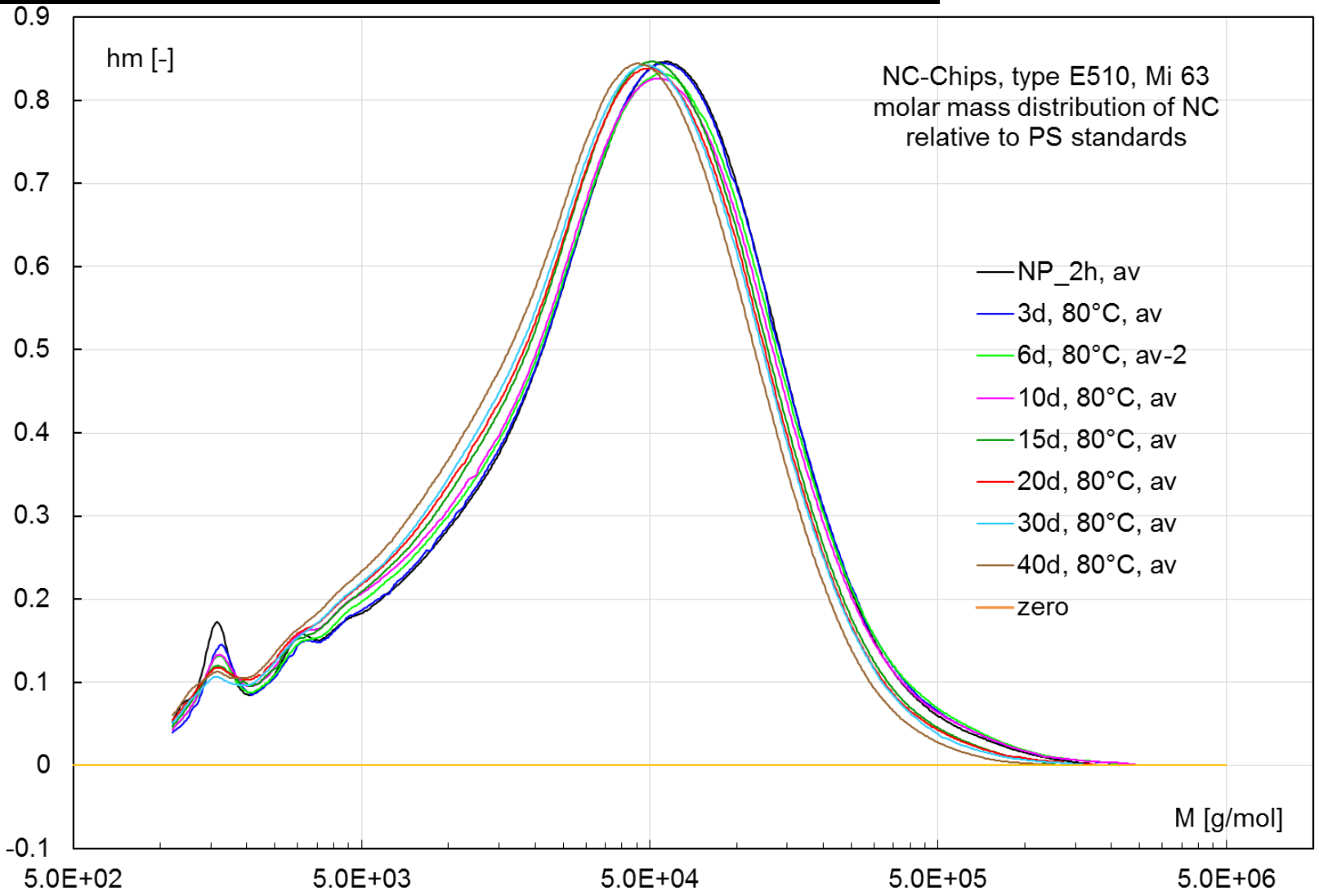
Molar mass distribution of type hm ageing series 80°C



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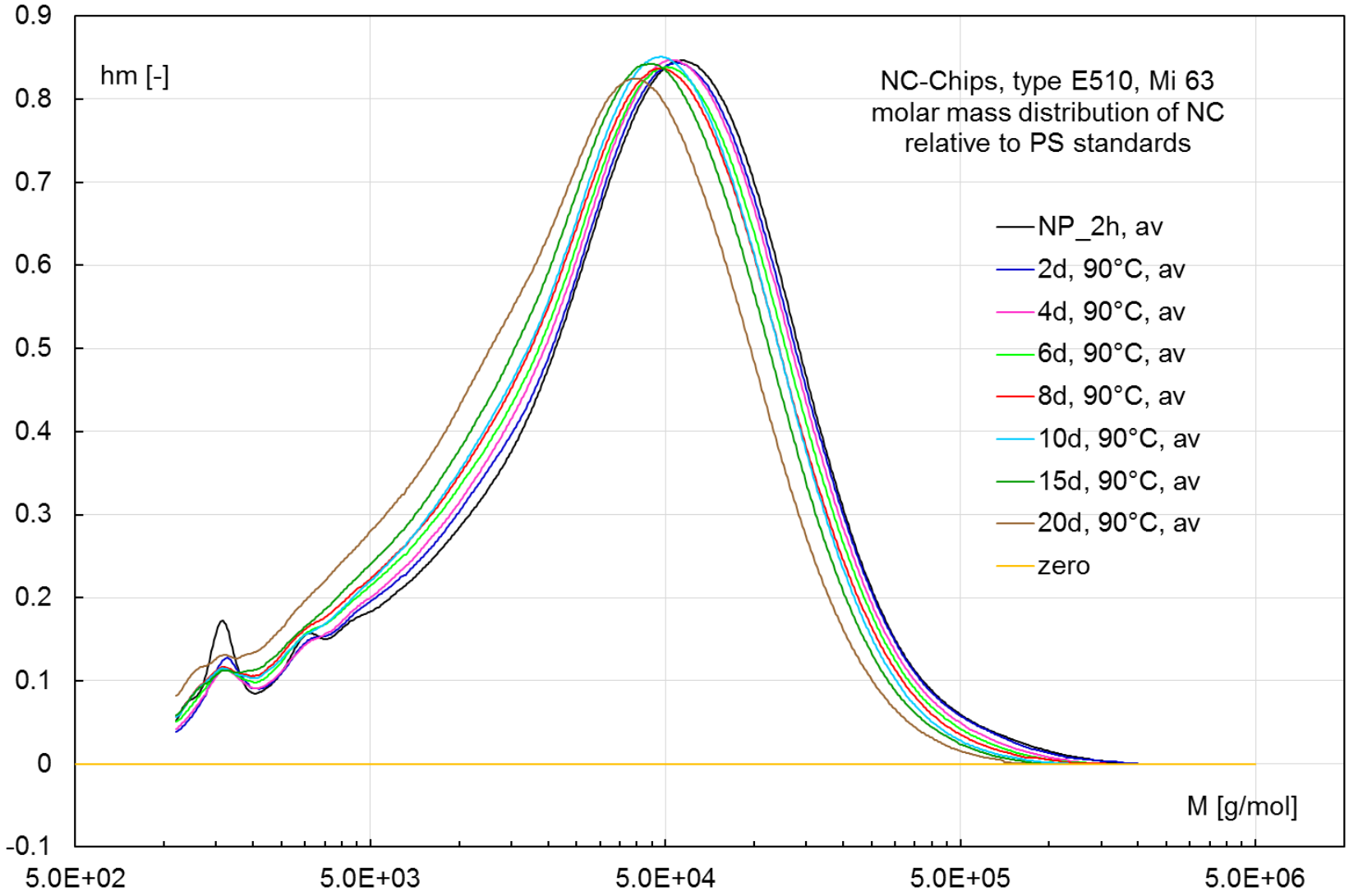
Molar mass distribution of type hm ageing series 90°C



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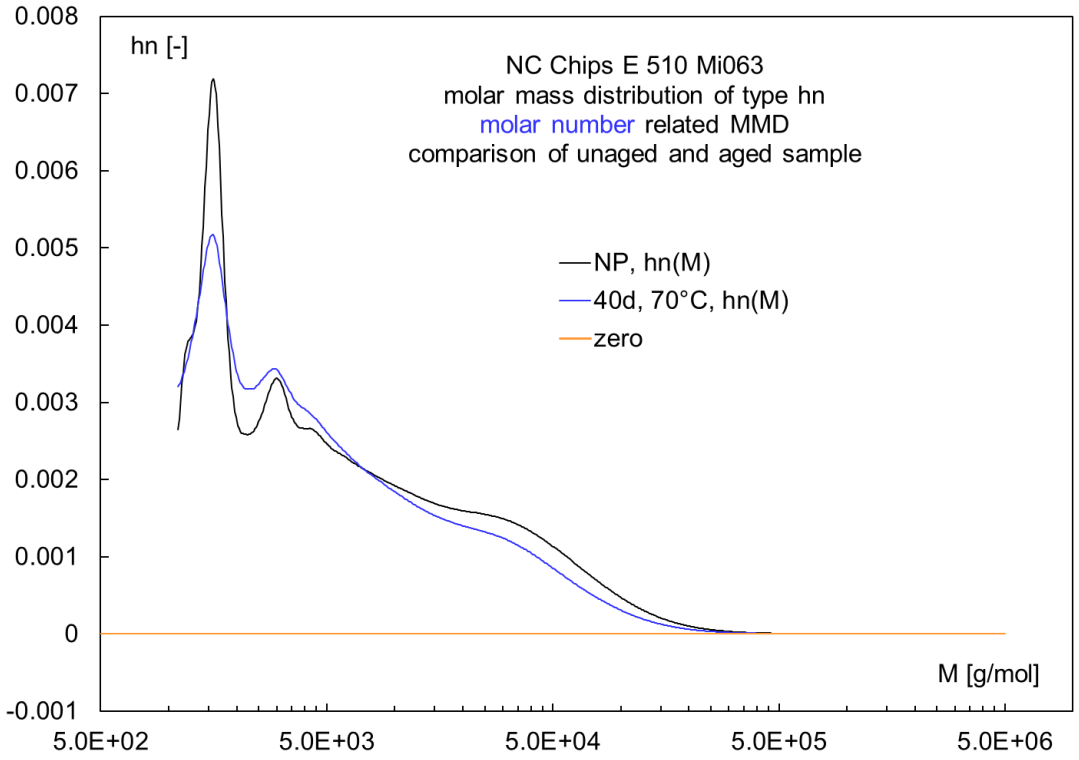
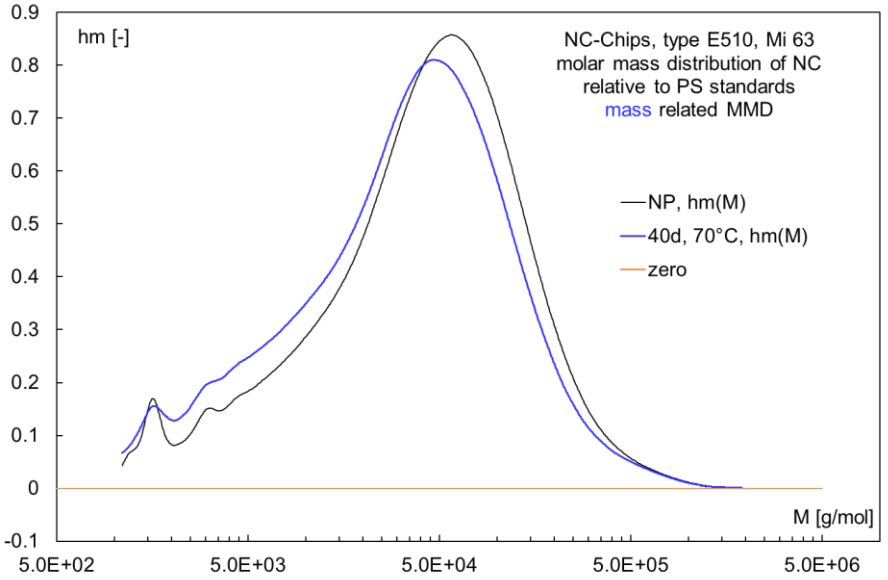
Comparison of the MMD types hn and hm



$$hn_i(M) = \frac{hn_{u,i}(M)}{\sum_i hn_{u,i}(M)} = \frac{\frac{hm_{u,i}(M)}{M_i}}{\sum_i \frac{hm_{u,i}(M)}{M_i}}$$

Formally this fraction mass related MMD **hm(M)** is used to calculate the fraction mass averaged mean molar mass Mw



Formally this fraction molar number related MMD **hn(M)** is used to calculate the fraction molar number averaged mean molar mass Mn

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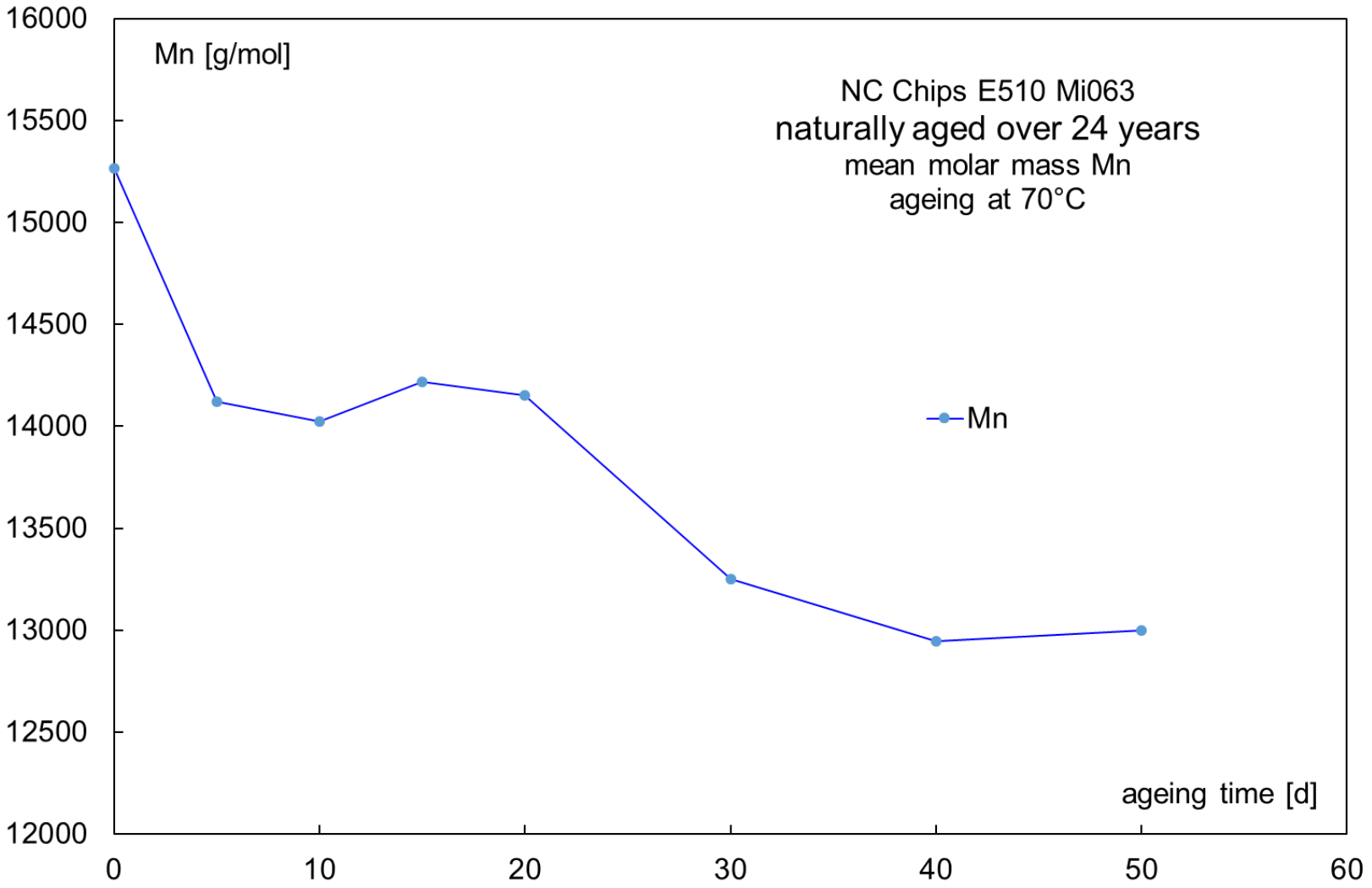
Decrease of mean molar mass Mn of NC in the chips at 70°C ageing



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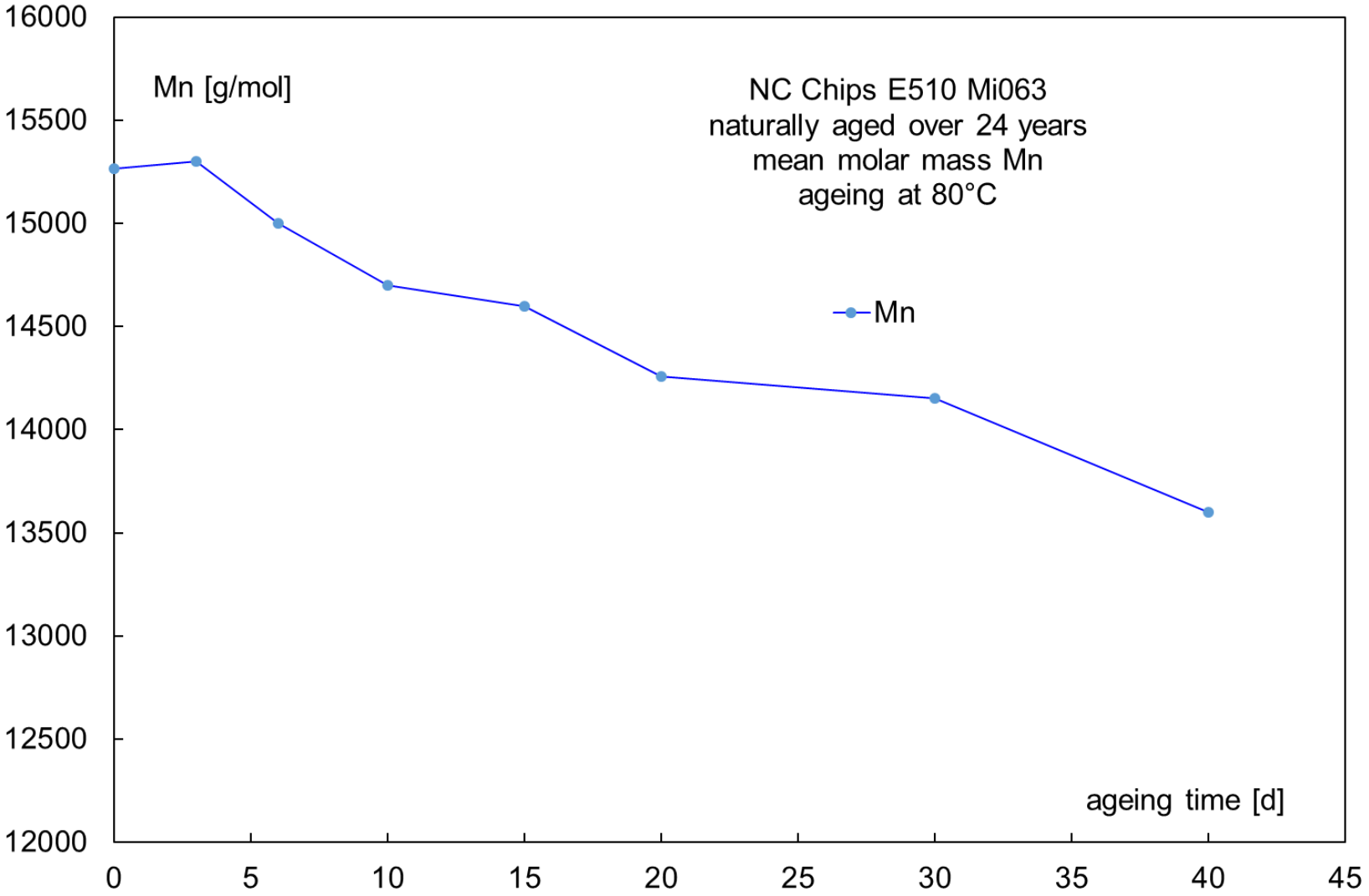
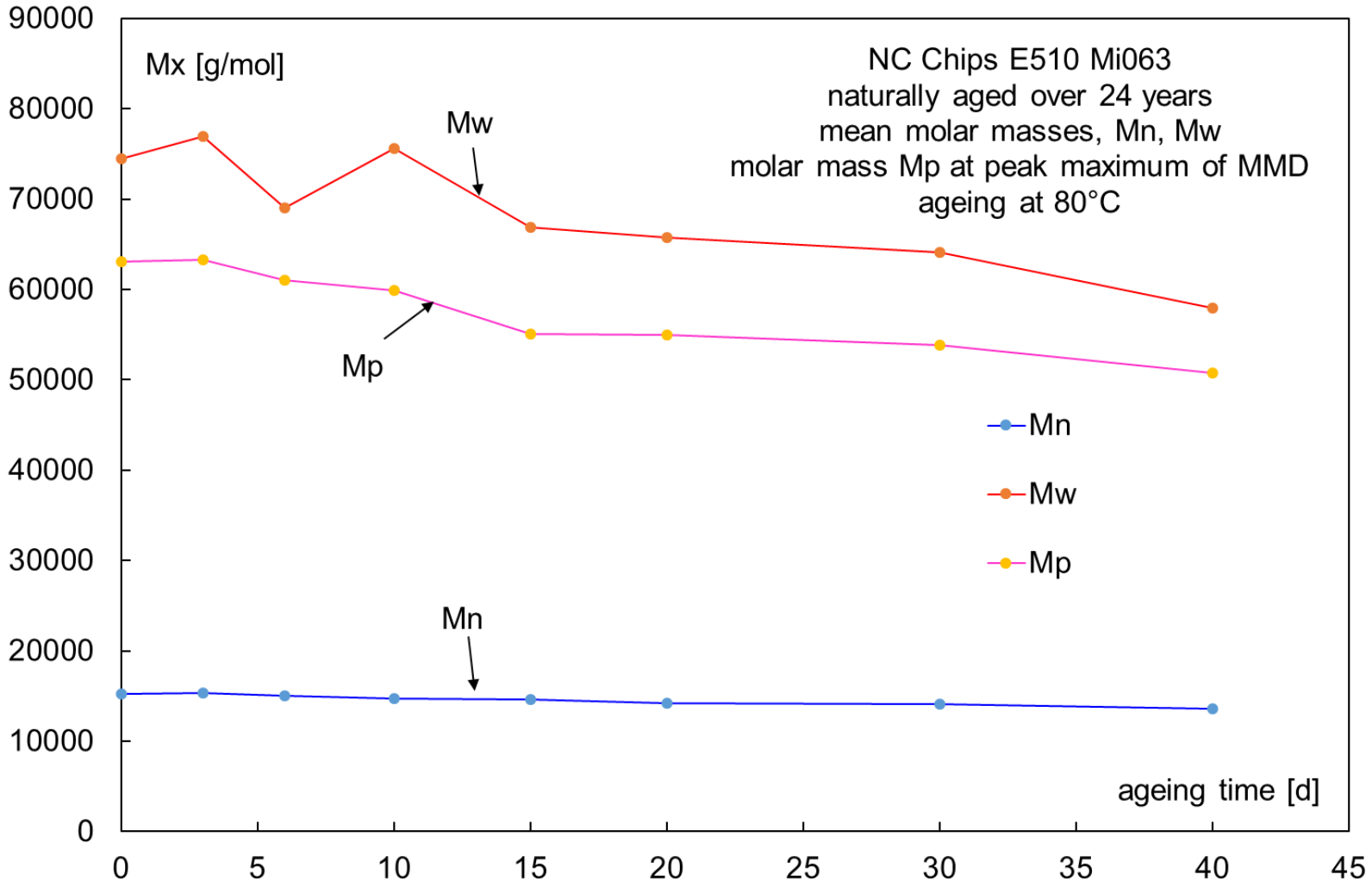
Decrease of mean molar mass Mn of NC in the chips at 80°C ageing



Fraunhofer ICT

Decrease of mean molar masses Mn, Mw and Mp of NC in the chips at 80°C ageing



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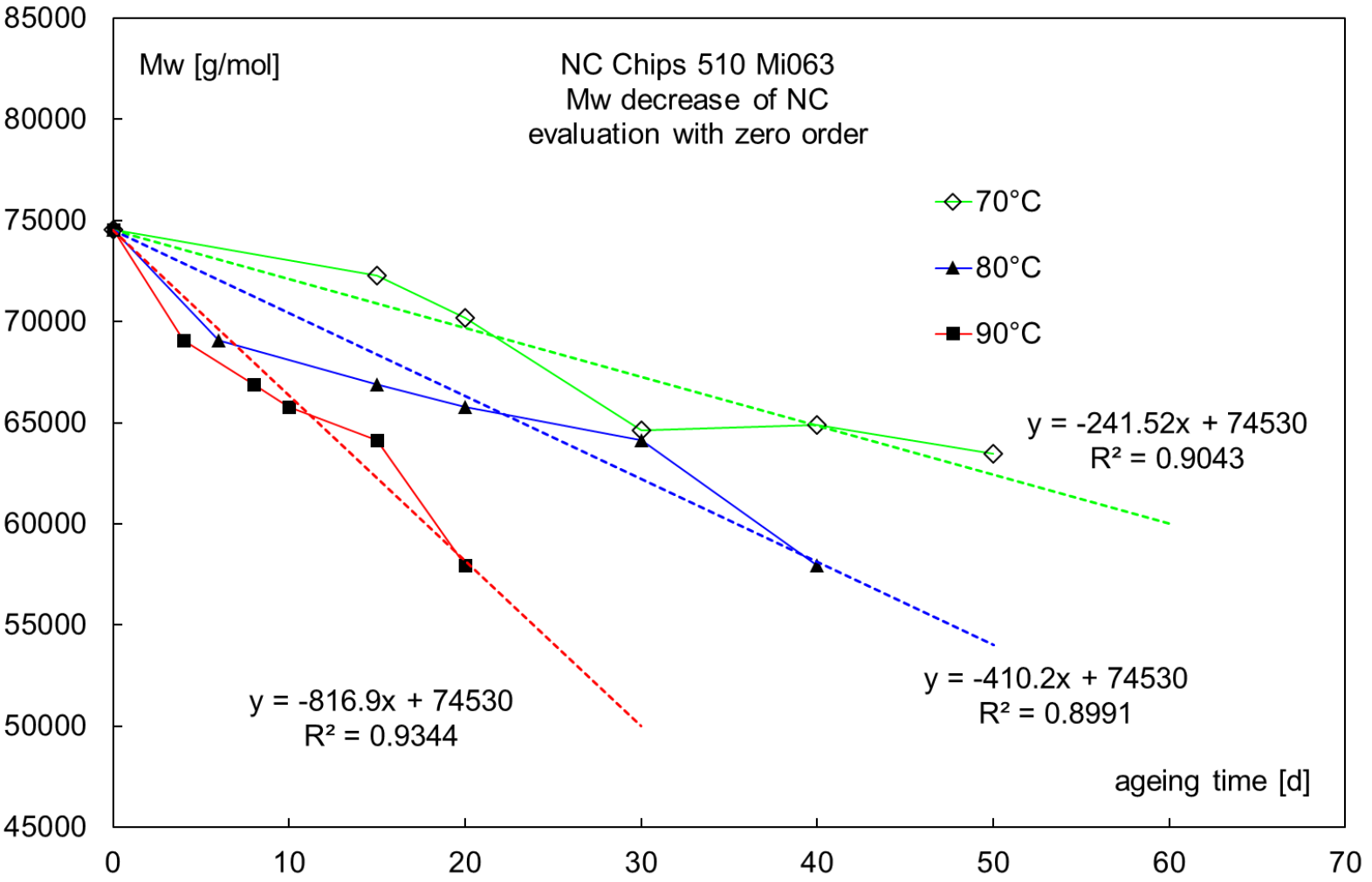
Evaluation of the Mw data by zero order decrease



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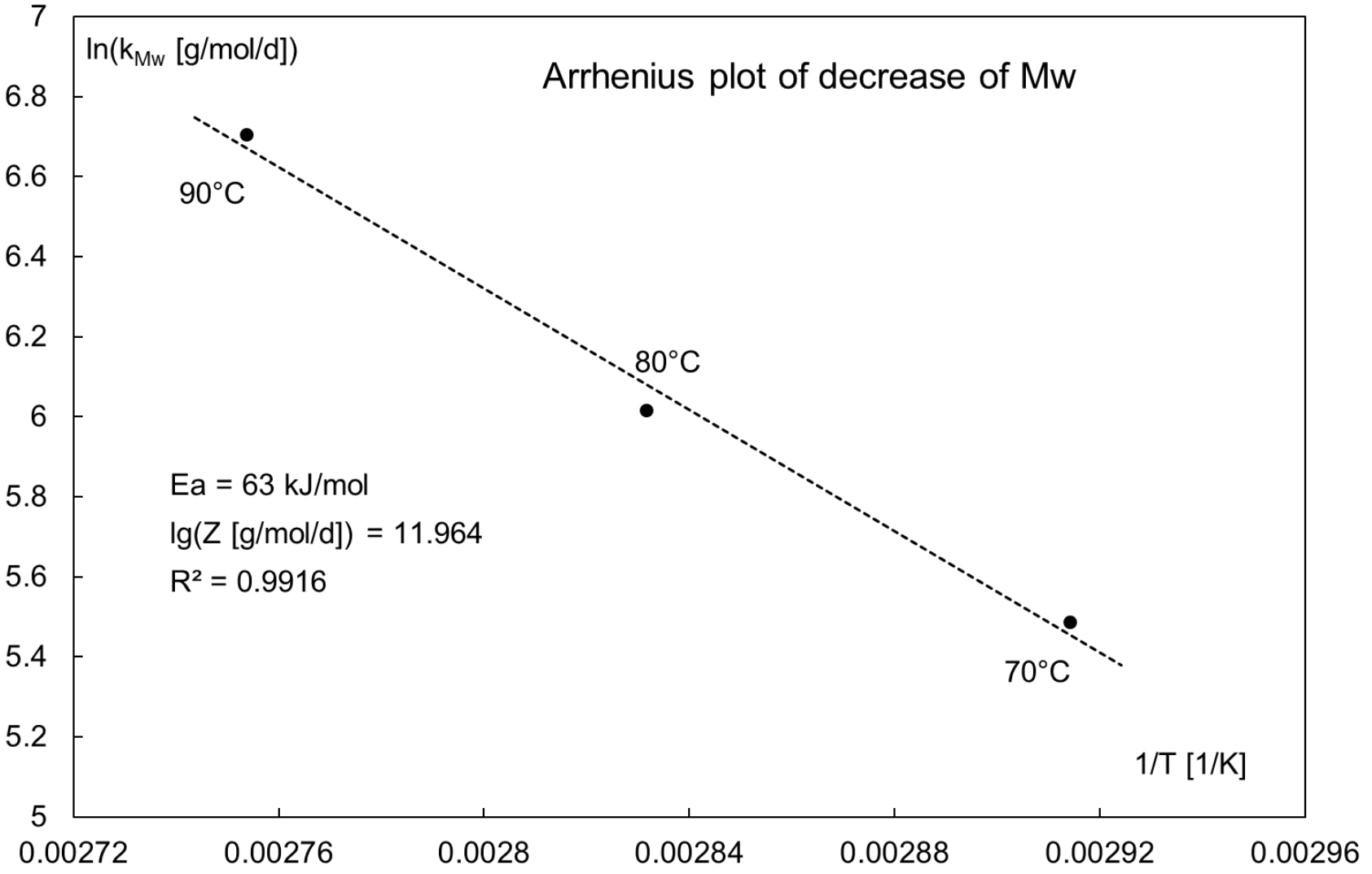
Arrhenuis plot for decrease of Mw



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Compilation of activation parameters fom Mn, Mw and Mp decrease

With quantity	Ea [kJ/mol]	lg(Z [g/mol/d])	R^2
Mn	65	11.402	0.9022
Mw	63	11.964	0.9916
Mp	70	12.96	0.8786

Low activation energies;
Probably caused by a greater part of hydrolytic chain scission.
Molar mass degradation is sensitive to hydrolytic cleavage of NC backbone

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Comparison by adiabatic self heating performed with an ARC™

ARC: Accelerated Rate Calorimeter

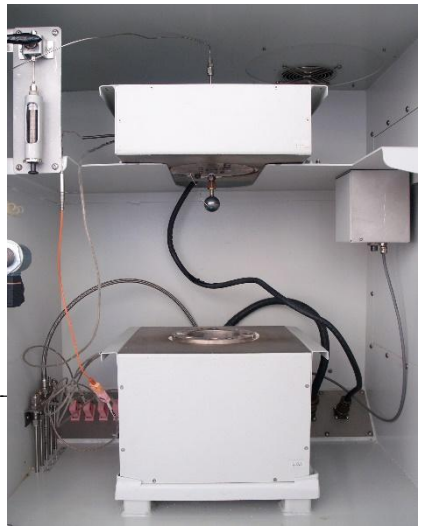
ARC follows the self-heating of the substance by keeping the oven temperature on the same temperature as of the substance, which was reached by the exothermal decomposition of it.

A pseudo-adiabatic environment is established for the sample.
This causes increasingly decomposition.

Typically one determines the adiabatic self-heat rate of the sample against the temperature, which was adiabatically reached by the sample itself.

Important quantity: the phi-factor which determines the inert masses around the sample which have to be heated also.
This causes a retardation of the decomposition rate of the sample.
Phi = 1 means no inert mass has to be heated.

ARC can be used also in isothermal mode.



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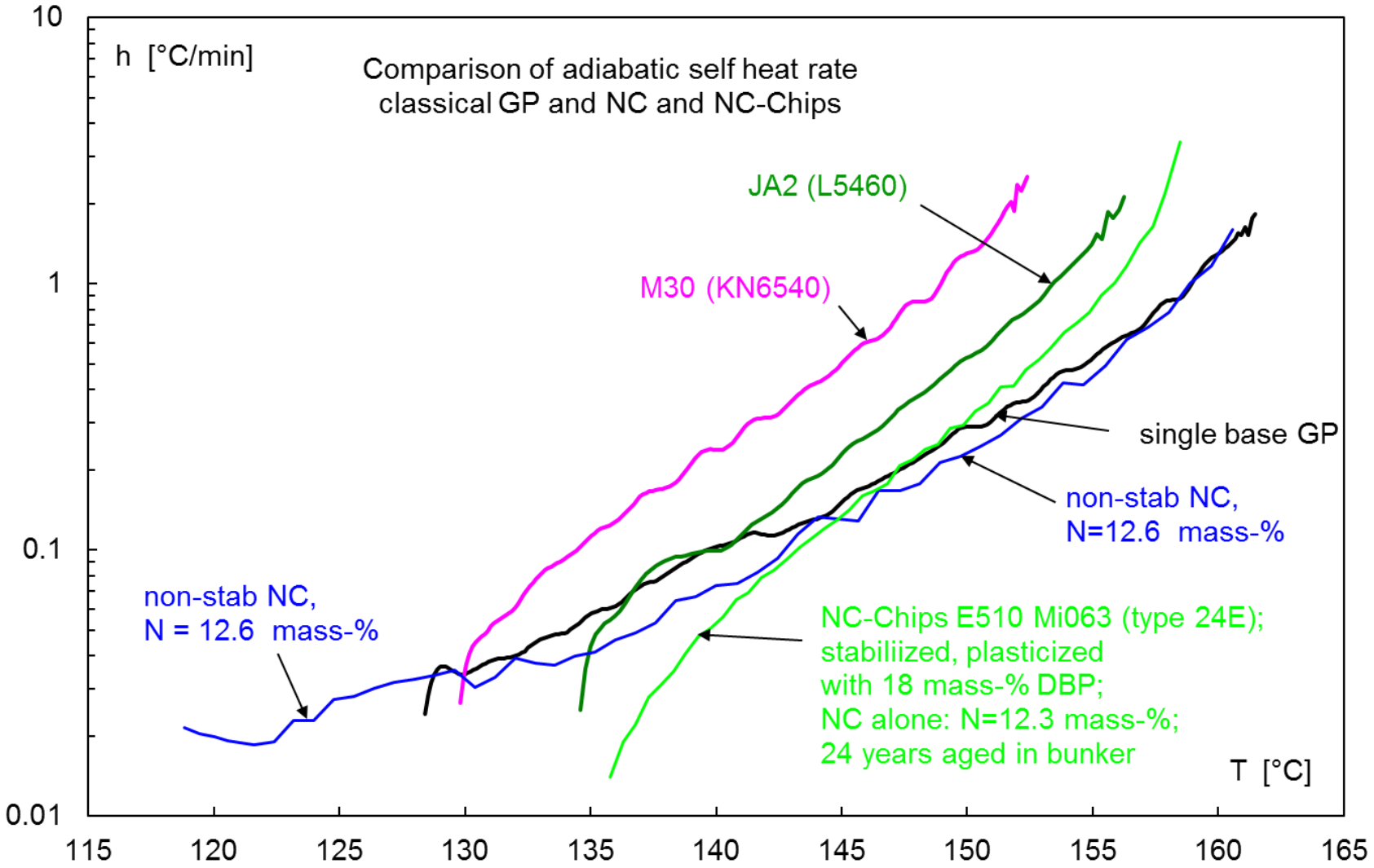
Adiabatic selfheating determined with ARC™ – comparison with NC Chips



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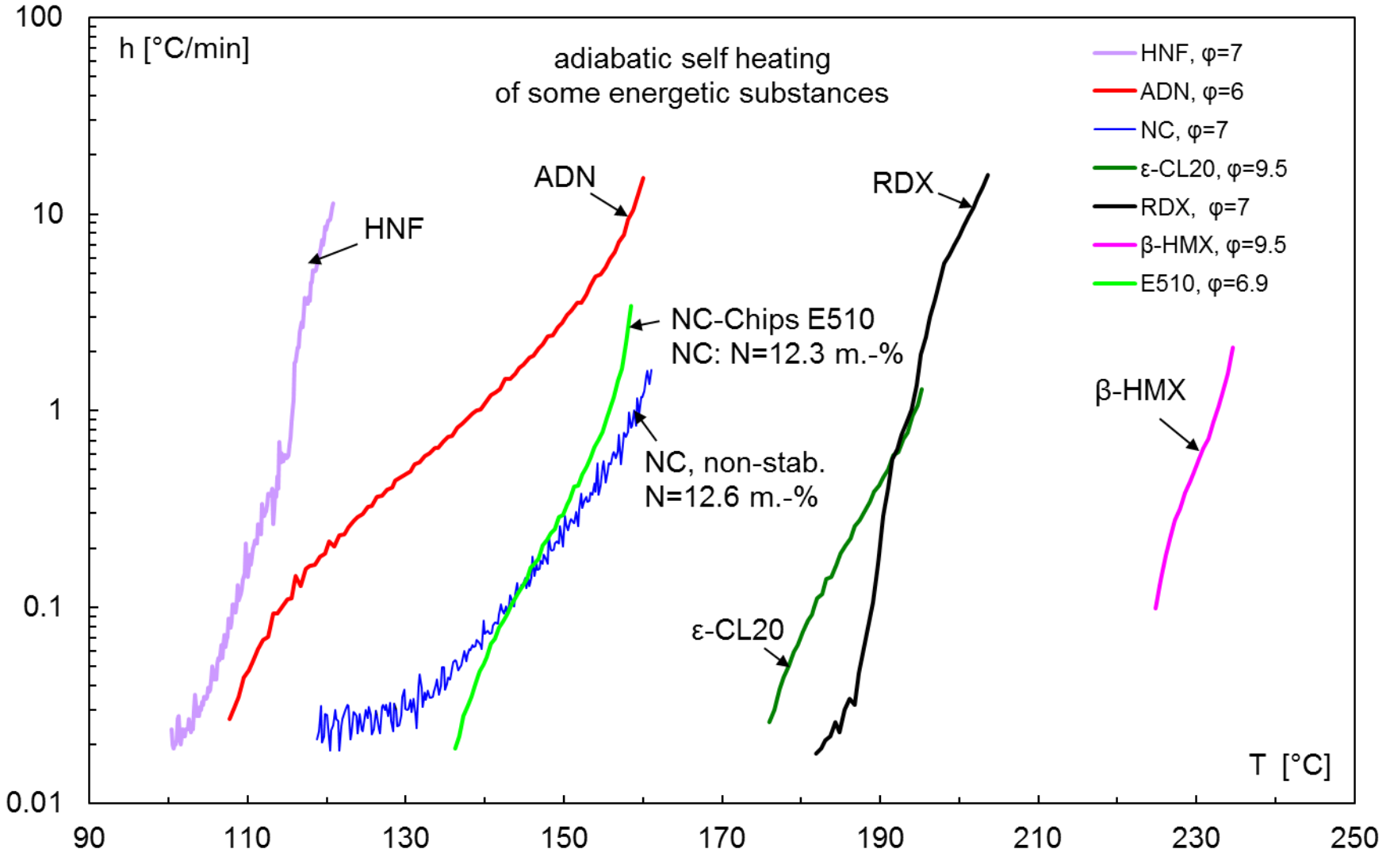

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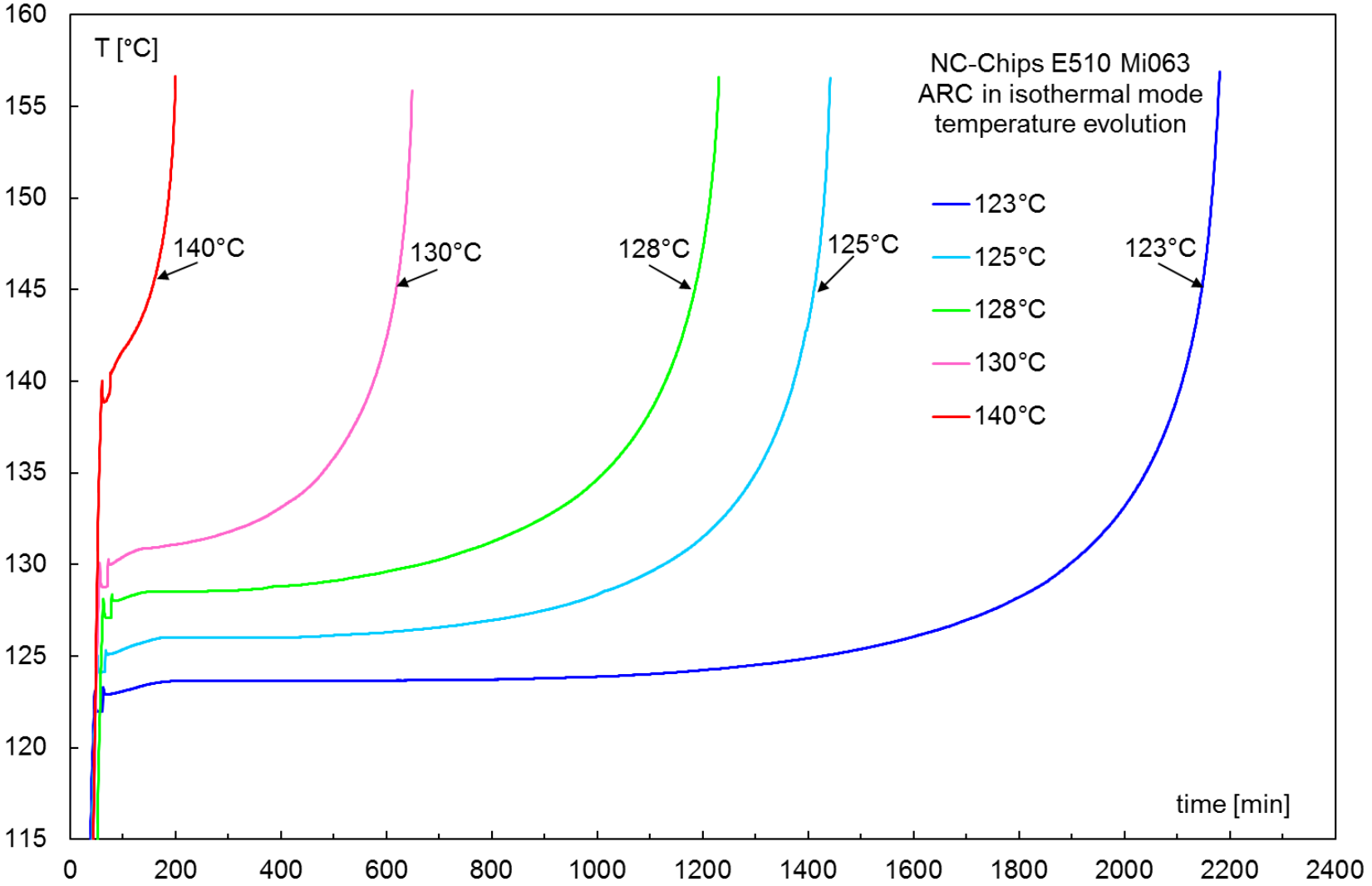
Isothermal ARC™ – evaluation the data with time to reach 156°C



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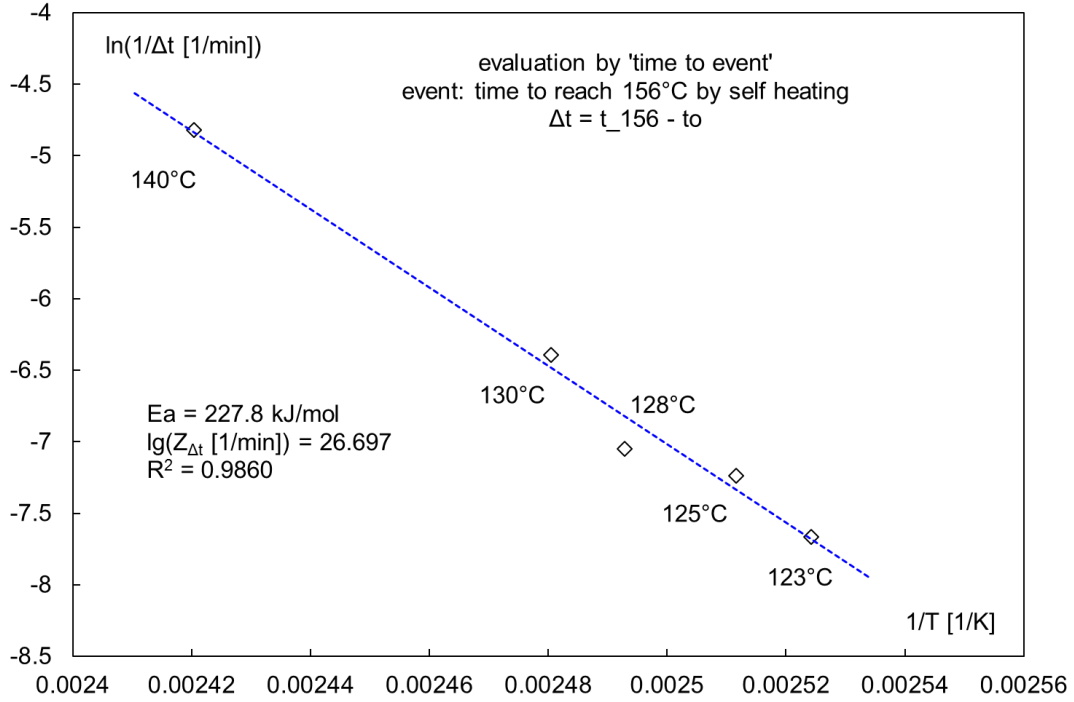
Evaluation of the data time to event Δt = t_156°C – to



Relatively high activation energy.
Oxidative degradation of cellulose backbone

T [°C]	to [min]	t-156°C [min]	Δt [min]	1/Δt [1/min]	1/T [1/K]	ln(1/Δt [1/min])
123	47.7	2180	2132.3	0.00046898	0.0025243	-7.664956488
125	49.2	1441.7	1392.5	0.00071813	0.00251162	-7.238855972
128	81.7	1230.7	1149	0.00087032	0.00249283	-7.046647278
130	51.7	648.5	596.8	0.0016756	0.00248047	-6.391582049
140	75.7	199.7	124	0.00806452	0.00242043	-4.820281566

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Microcalorimetry

Measurement of heat generation rate dQ/dt (heat flow) at several temperatures.

By integration over time the released heat Q (heat generation) is obtained.

Because microcalorimeter have a very high sensitivity, measurements at relatively low temperatures are possible.

The instruments used here are

TAM (thermal Activity Monitor) of type II, manufactured by former Thermometric AB, Sweden.

TAM of type III, developed by Thermometric AB, later manufactured by TA Instruments.

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Microcalorimetric instrumentation

Measurement ampoules

Stainless steel, glass with sample, empty glass ampoule

microcalorimeter
type TAM II,
high temperature version

From Thermometric AB

microcalorimeter
type TAM III

TA Instruments version

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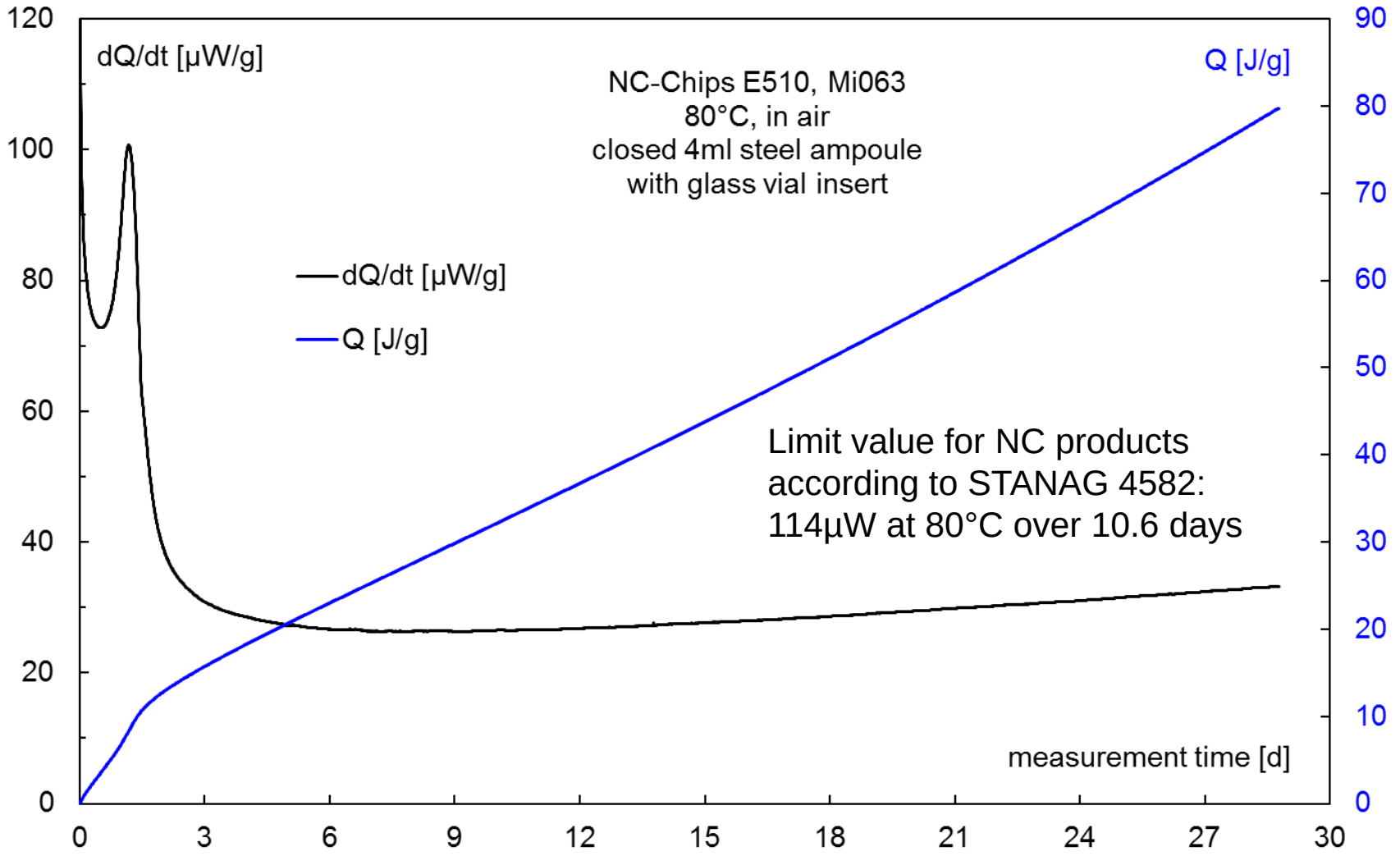
Heat generation rate dQ/dt and heat generation Q at 80°C



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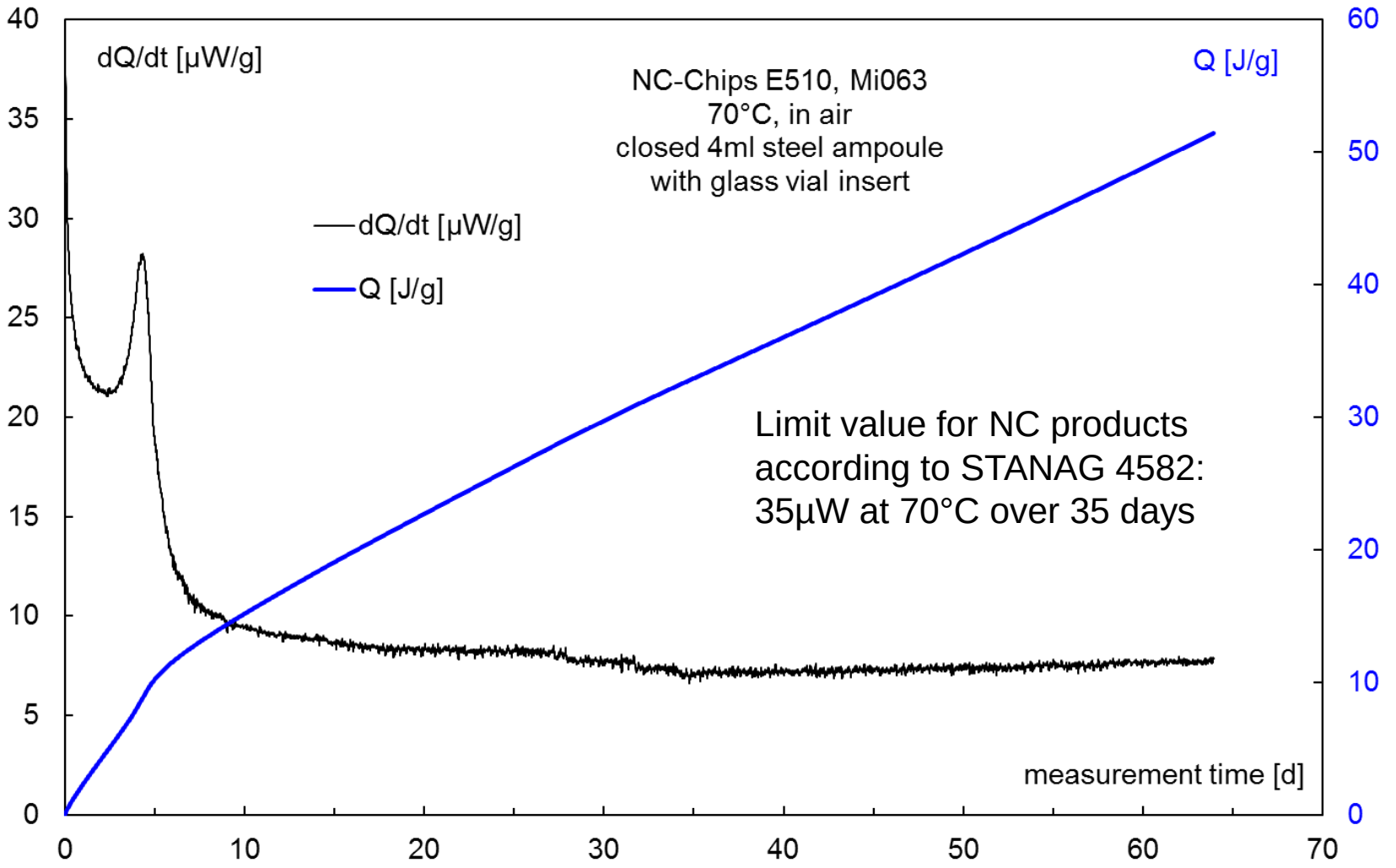
Heat generation rate dQ/dt and heat generation Q at 70°C



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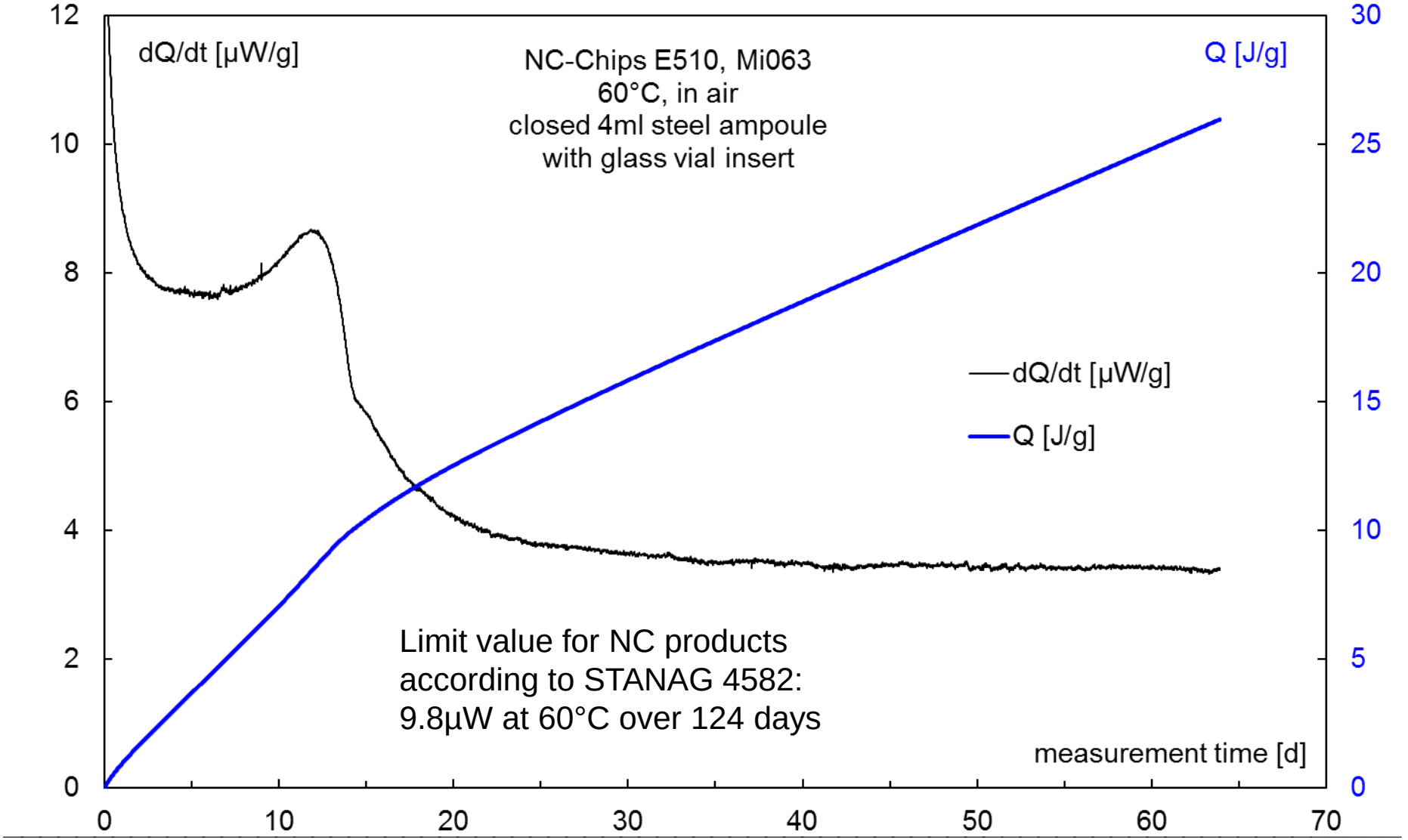
Heat generation rate dQ/dt and heat generation Q at 60°C



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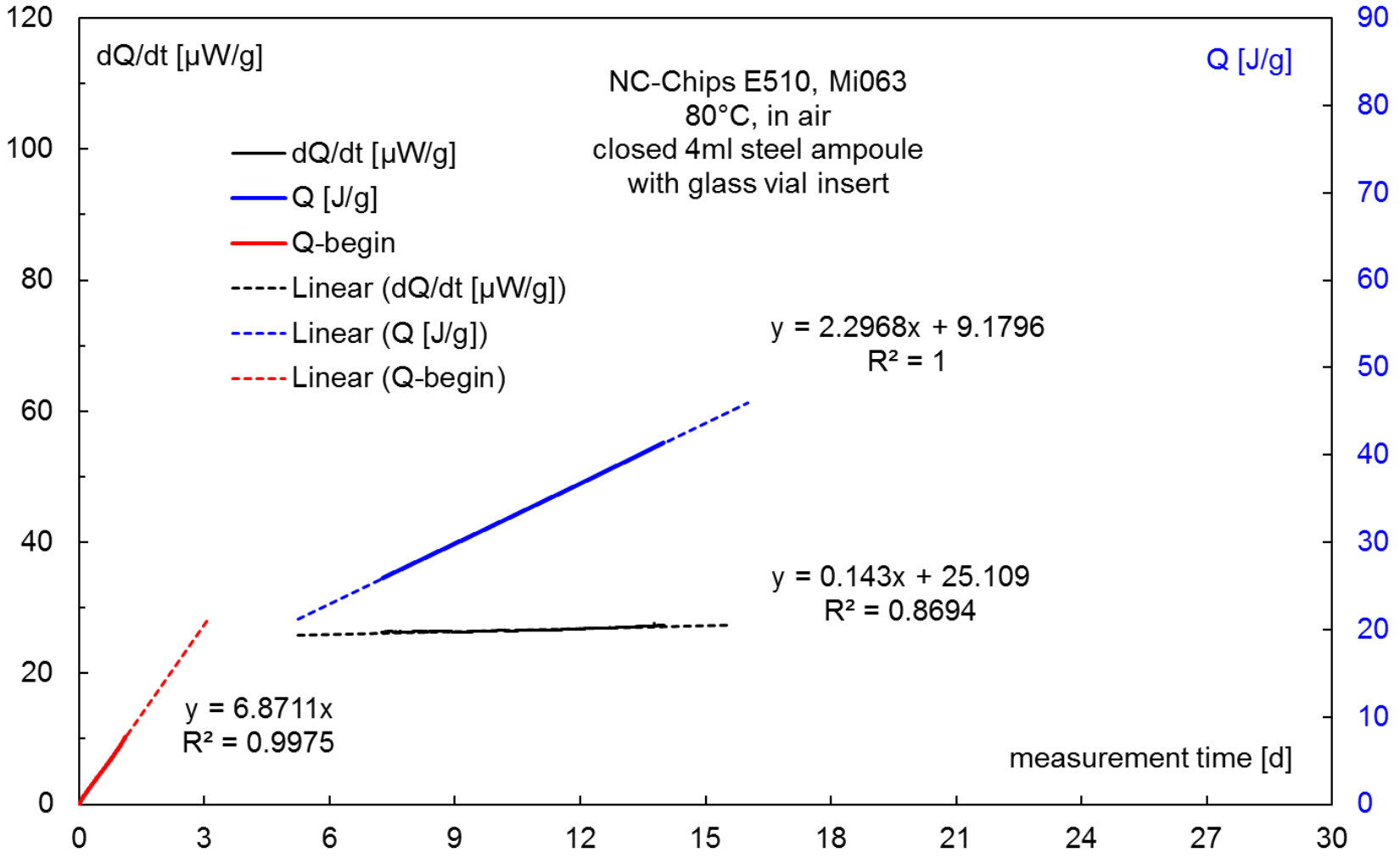
Data evaluation at 80°C

three types of evaluation Q at end Q at begin and dQ/dt at end



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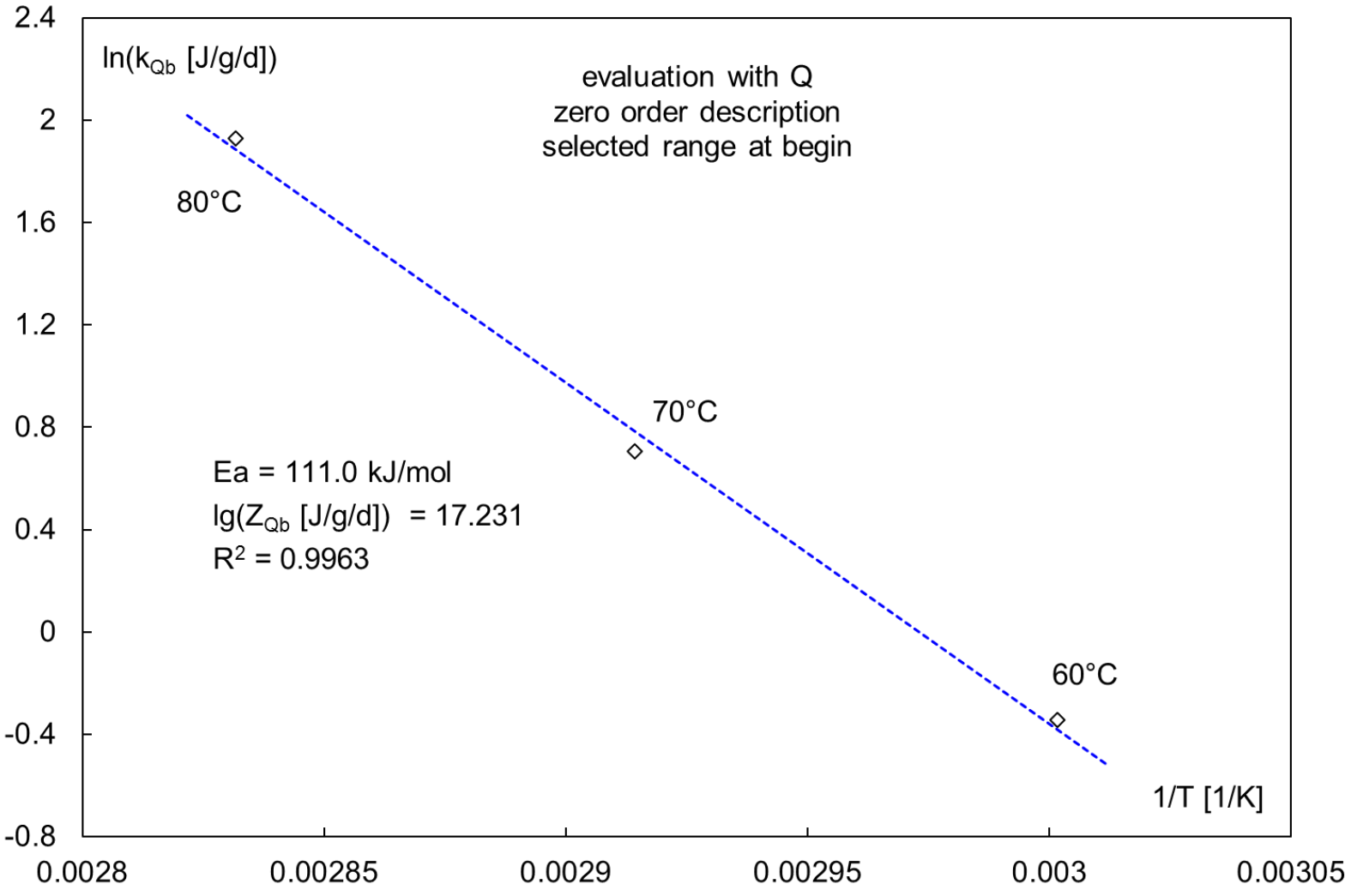
Arrhenius plot from Q-begin evaluation



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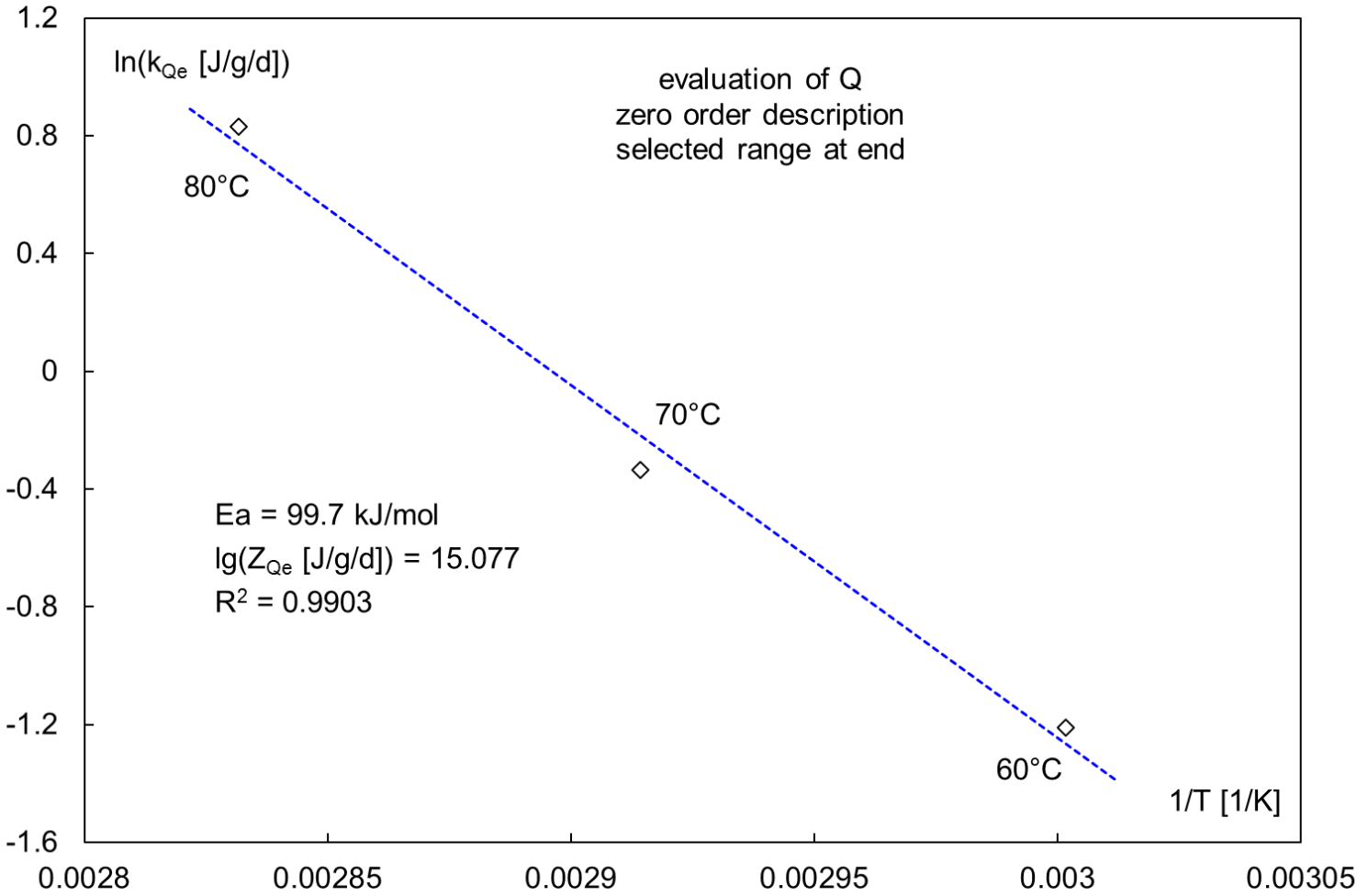
Arrhenius plot from Q-end evaluation



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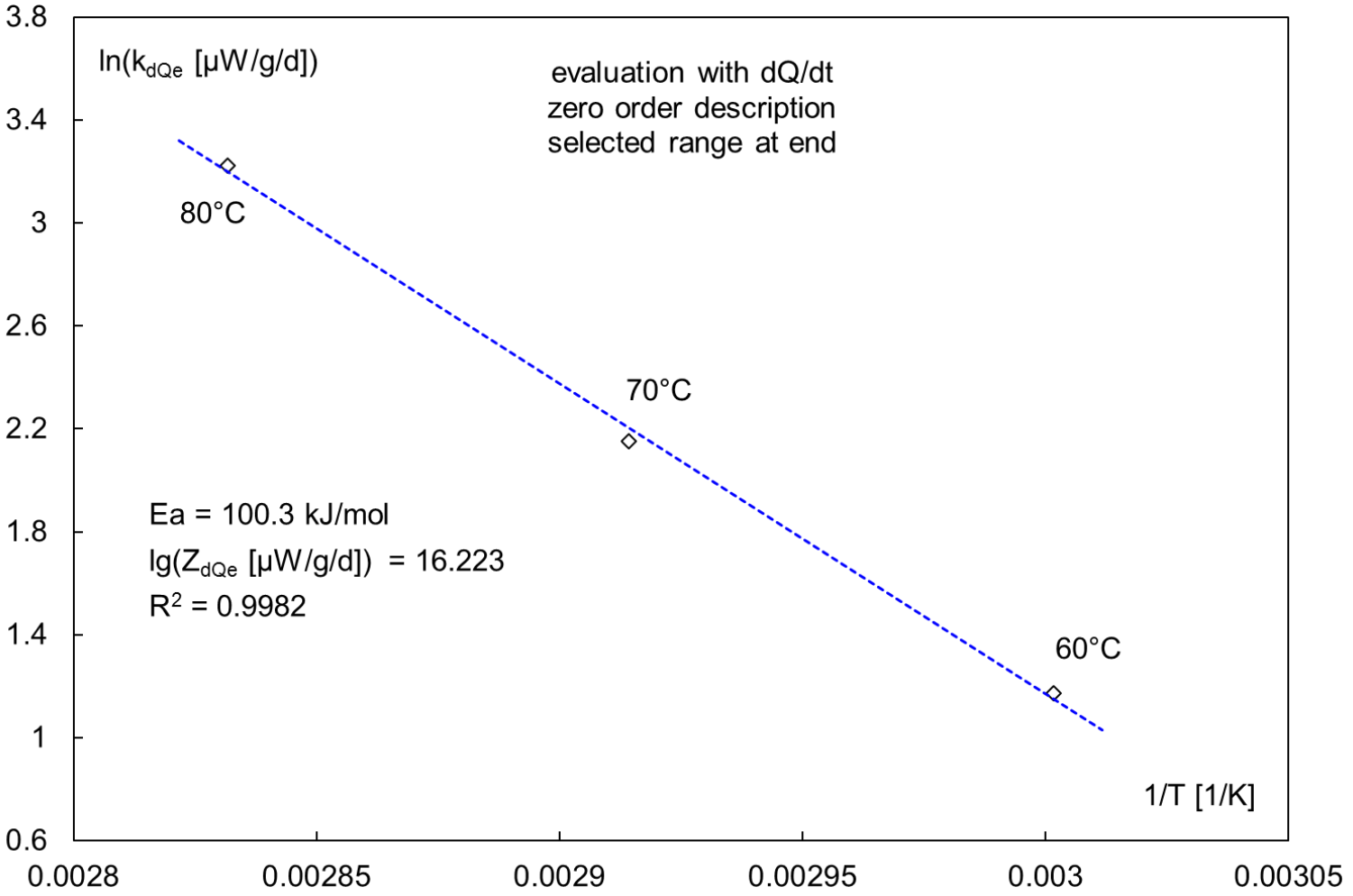
Arrhenius plot from dQ/dt-end evaluation



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	NOx in ml/g	0.96	**1.24**	≤ 2.81	≤ 2.81
	N_2 in ml/g	0.48	**0.62**	≤ 1.40	≤ 1.40
time to fast increase of mass loss (ML)					
at 70°C	d	277	**139**	90	27
at 80°C	d	92.3	**62.9**	30	9
at 90°C	d	23.5	**23.9**	10	3
Activ. energy from ML by 'time to event'	kJ/mol	130	**91**	114	114
Activ. energy from ML-beginn by zero order	kJ/mol		**67**	evaporation	
Activ. energy from HGR by dQ/dt-e zero order	kJ/mol		**100.3**		
Activ. energy from HG by Q-end zero order	kJ/mol		**99.7**		
Activ. energy from HG by Q-begin zero order	kJ/mol		**111**		
Activ. energy Mw decrease, zero order	kJ/mol		**63**	in part hydrolysis of backbone	
Activ. energy isothermal ARC, 'time to event'	kJ/mol		**227.8**	high temperature decomposition, oxidation of backbone	

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Comparison of results – molar mass of NC

sample	Mn [g/mol]	Mw [g/mol]	Mz [g/mol]	Mp [g/mol]	pore size in Å of column set
after 24 years of ageing	15267	74530	206193	63044	100, 1000, 100000
1992, unaged	10200	73900	194000	70800	100, 1000, 100000

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Conclusion

The fresh material manufactured in 1991 was chemically stable.
This was proven with mass loss measurements in vials and in card board cans with 380g samples.

The material was kept in an ICT bunker over 24 years.

All investigations made with this aged material,
- adiabatic selfheating by ARC™
- mass loss
- heat generation rate by microcalorimetry

confirm that this material is still chemically stable.

Some degradation has occurred, recognizable by the lower activation energies obtained with mass loss, which were confirmed by microcalorimetry.
The reason could be the influence of humidity, which increases the decomposition rate especially at lower temperatures.

The objective, to conclude from measurements 24 years ago on the present stability is not directly achievable because of not ‘calculable’ influences.

It stays a task to develop methods to achieve this objective.

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Thank you for your attention

Questions ?

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