International Atomic Energy Agency
RER/8/010 Regional Workshop on Harmonization,
Implementation and Use of Quality Assurance & Quality Control Methods
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CHEMICAL TESTS FOR PRODUCT QUALIFICATION

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Physical and Chemical Tests related to Irradiation

Products Involved

- Medical Devices
- Packaging Materials
- Others subjected to Radiation Treatment

Materials Involved

- Polymeric Materials of Natural or Synthetic Origin
- Resins, Paints and Varnishes

TARGET PROPERTIES AND COMPOUNDS

Identification, Quantitation & Structural Characterization

- Low-Molecular Weight ('Volatile') Radiolysis Products of Polymers
- Radiolysis Products of Additives
- Degradation Products of Antioxidants

Properties

- Glass transition temperature
- Melting transition temperature
- Thermal decomposition temperature
- Ignition temperature
- Kinetic properties

ANALYTICAL TECHNIQUES INVOLVED

Chromatographic techniques

- Gas Chromatography coupled with Mass Spectrometry (GC-MS)
- Thermal Desorption – GC-MS (TD-GC-MS)

Thermal Analysis

- Thermogravimetric Analysis (TGA) or Thermogravimetry (TG)
- Differential Thermal Analysis (DTA)
- Simultaneous Thermal Analysis (TG-DTA)

GAS CHROMATOGRAPHY / MASS SPECTROMETRY

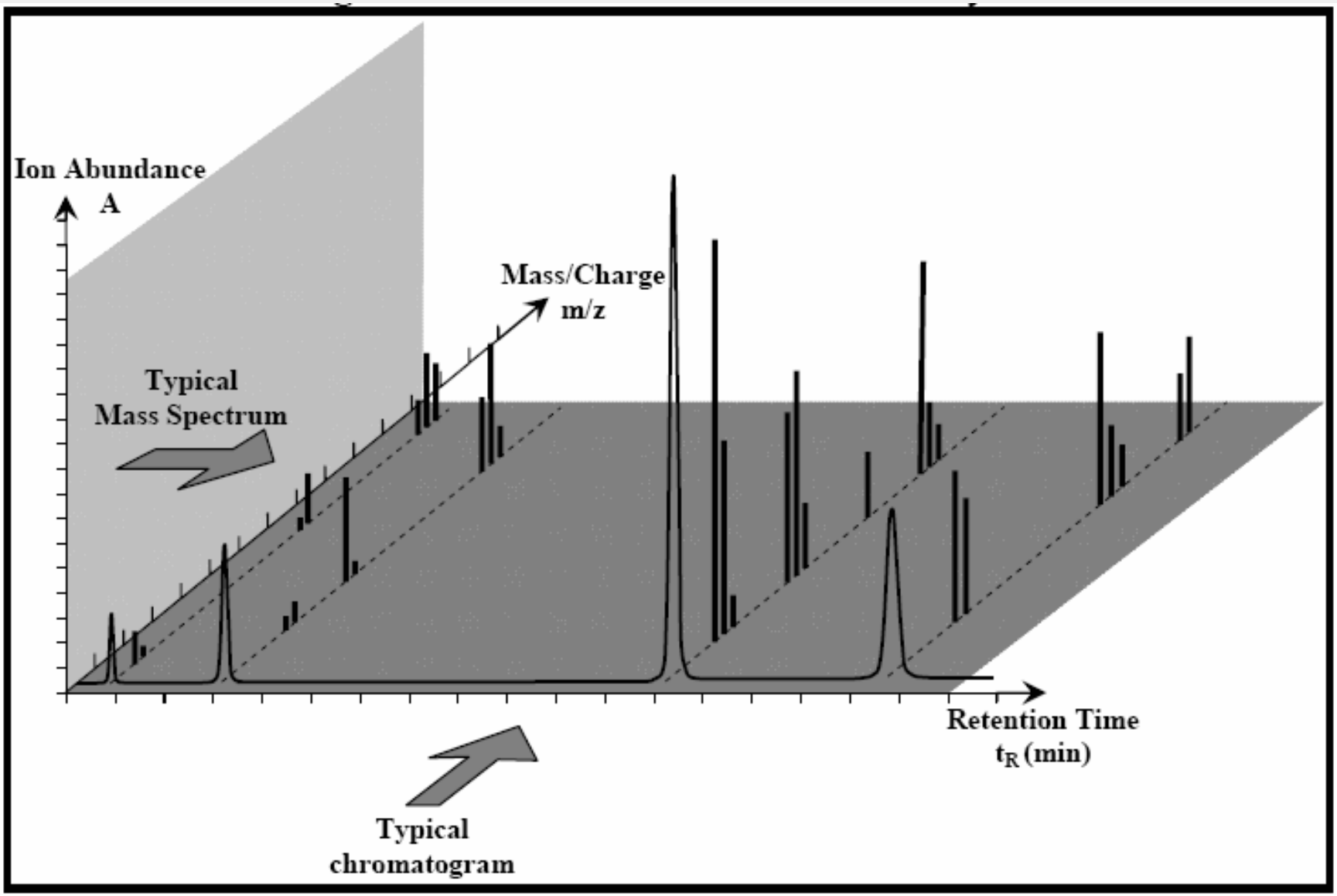
A coupled analytical technique used for the following purposes:

- Confirmation and quantitation of volatile or semi volatile analytes in complex mixtures;
- Determination of molecular weights and / or elemental composition of volatile / semi volatile unknowns;
- Structural determination of volatile / semi volatile unknowns in a mixture by means of spectral matching or spectral interpretation

Parallel between characteristics of GC and MS analytical techniques

#	Chracteristic	GC	MS
1	Ability of handling mixtures	☺	☹
2	Ability to provide structural information	☹	☺
3	Ability to accept vapor state samples	☺	☺
4	Ability to consider ng amount of samples	☺	☺
5	Working pressure	atmospheric (at the column exit)	deep vacuum

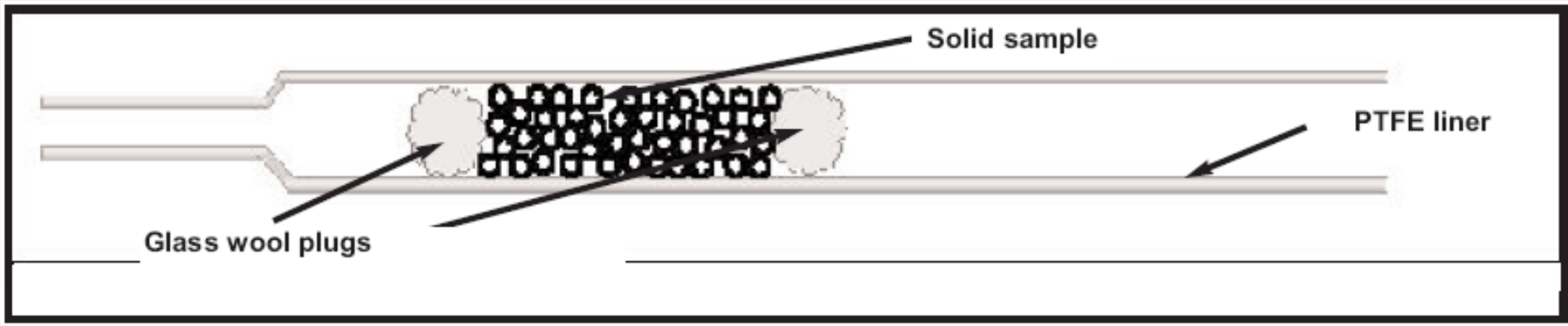
3D result of a GC / MS analysis



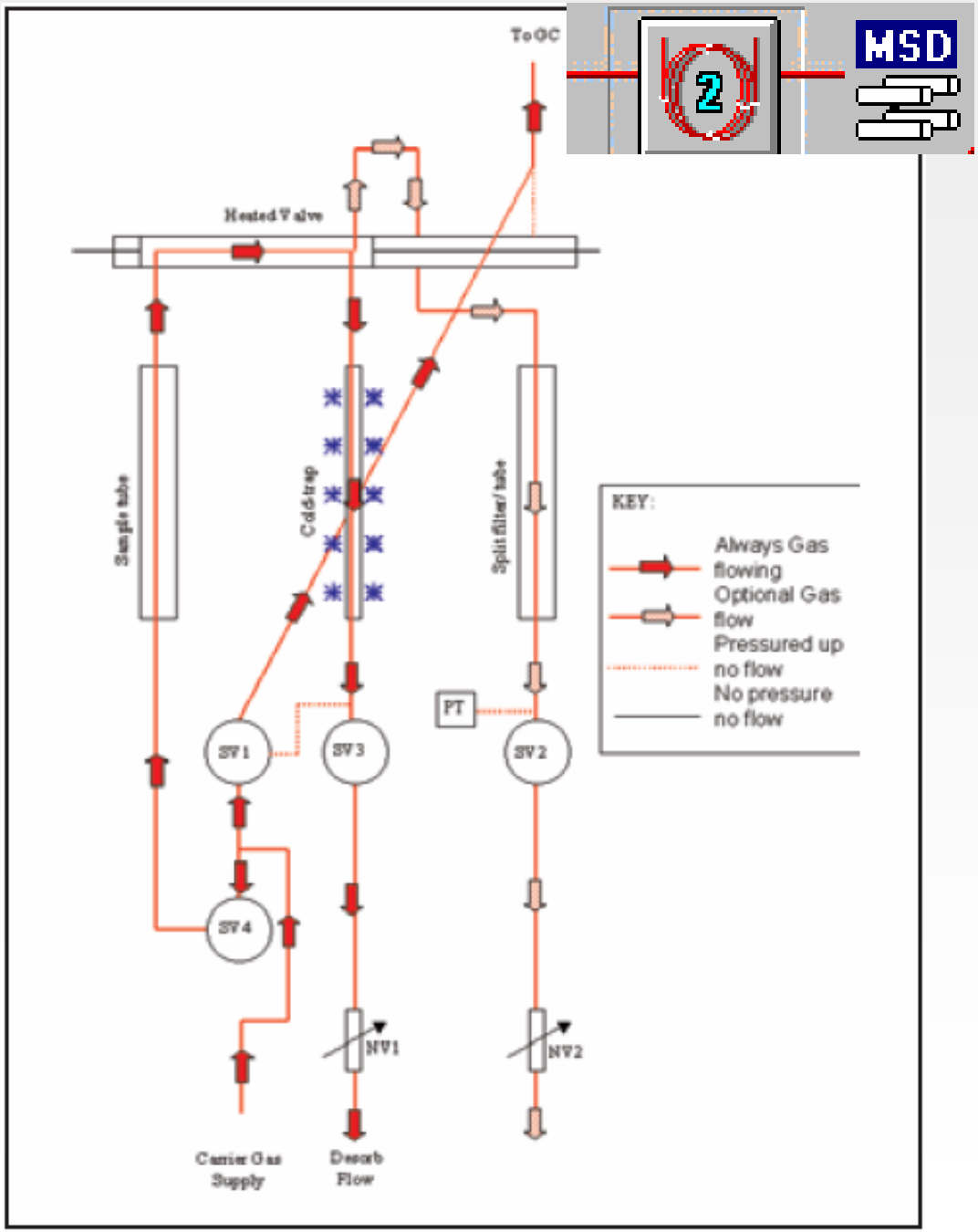
TD-GC-MS Instrumental Setup

- Sample Inlet: 2 stage thermal desorber unit

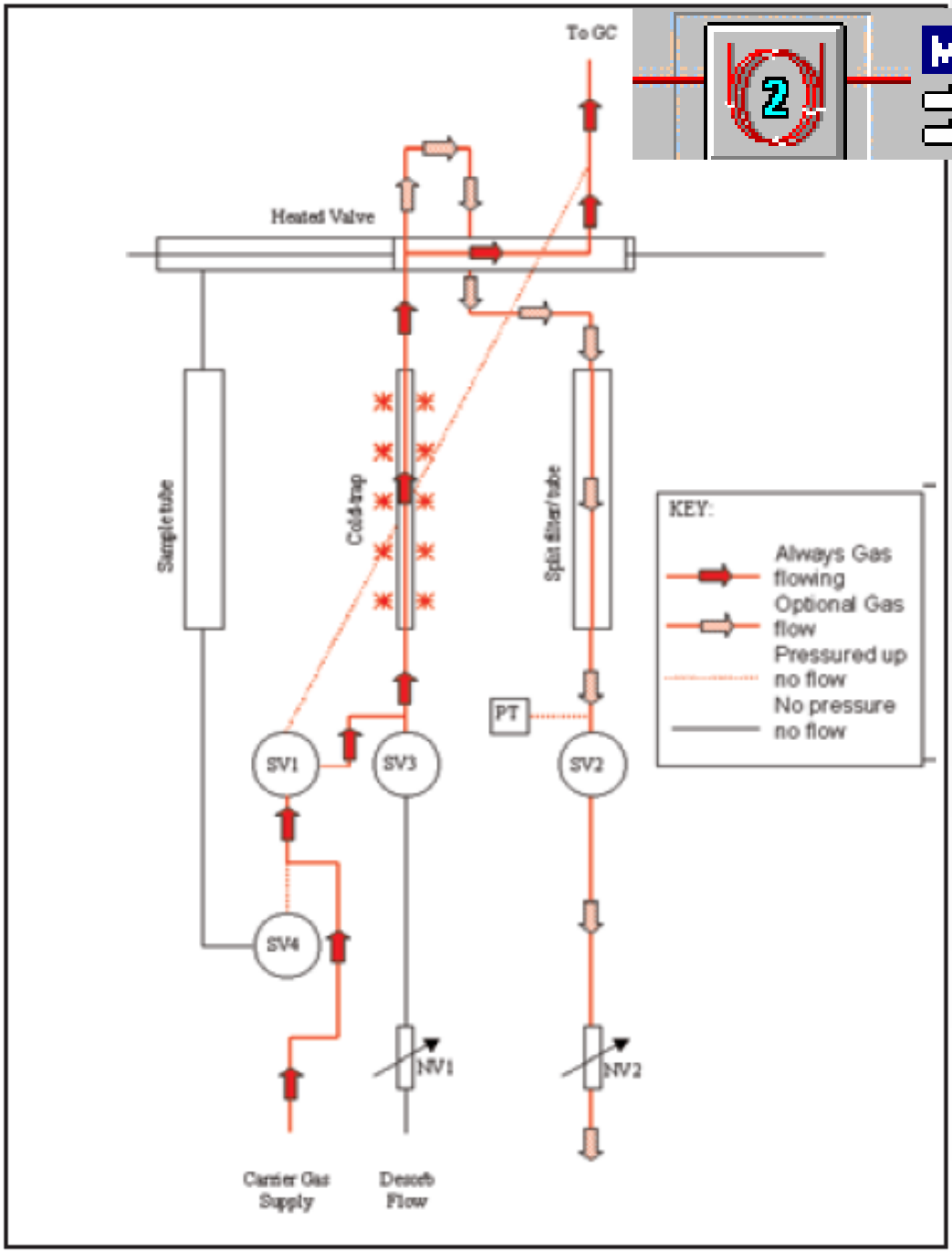
  - for solid samples an apropriate quantity (1 – 10 mg with 1 mm particle size or under 1 mm film/foil) is packed in an teflon liner with small glass wool plugs at both ends



  - the packed teflon liner is further transferred in an removable stainless steel tube that is conected into the thermal desorber flow path



• the sample tube is first purged and then desorbed at a controlled temperature and the volatile and semivolatile organic compounds (VOC / SVOC) are then cryo focused on a Peltier cooled trap (containing one or more adsorbents)



• the final desorbtion stage is made by heating the trap and releasing the VOC and SVOC through the transfer line to the GC column.

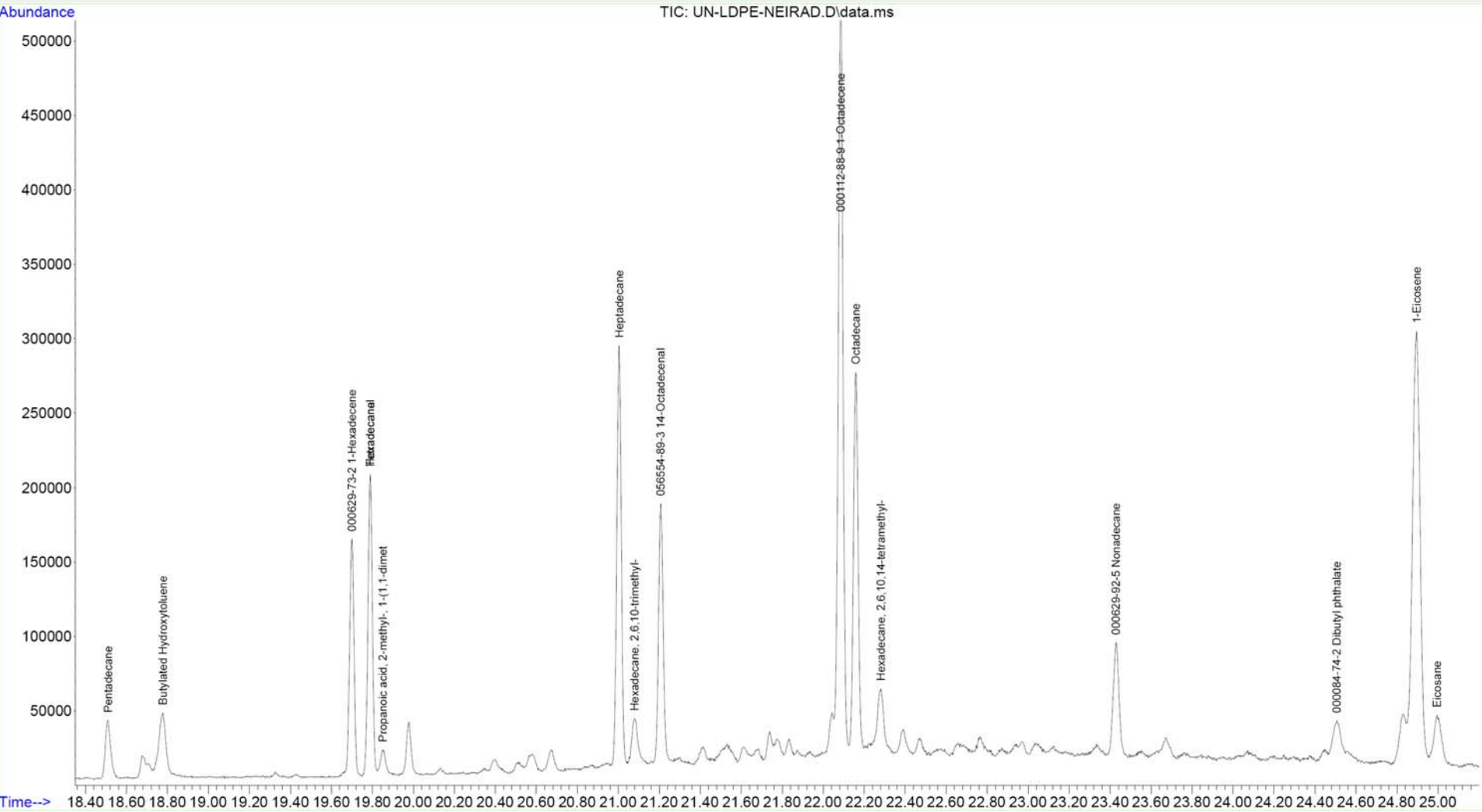
Quality Control

- External callibration with a mixture of target compounds in the sample matrix concentration range (usually ppm or trace level), usualy a five point callibration curve is aquired

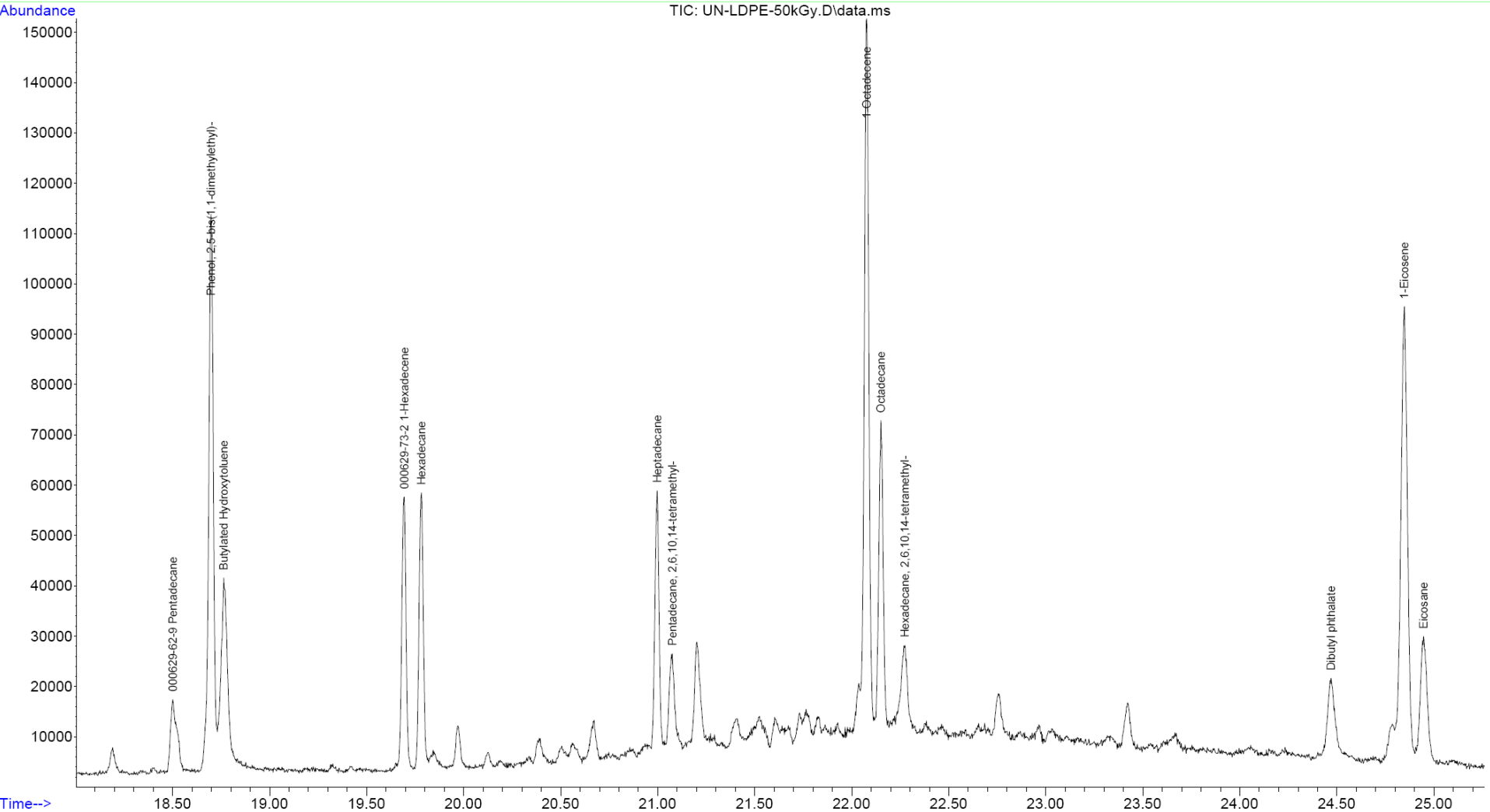
- QC-BLANK
  The chromatogram of the packed tube without the sample

- QC-Positive Control
  Pure sorts of matrix polymer irradiated at 3 different doses and nonirradiated

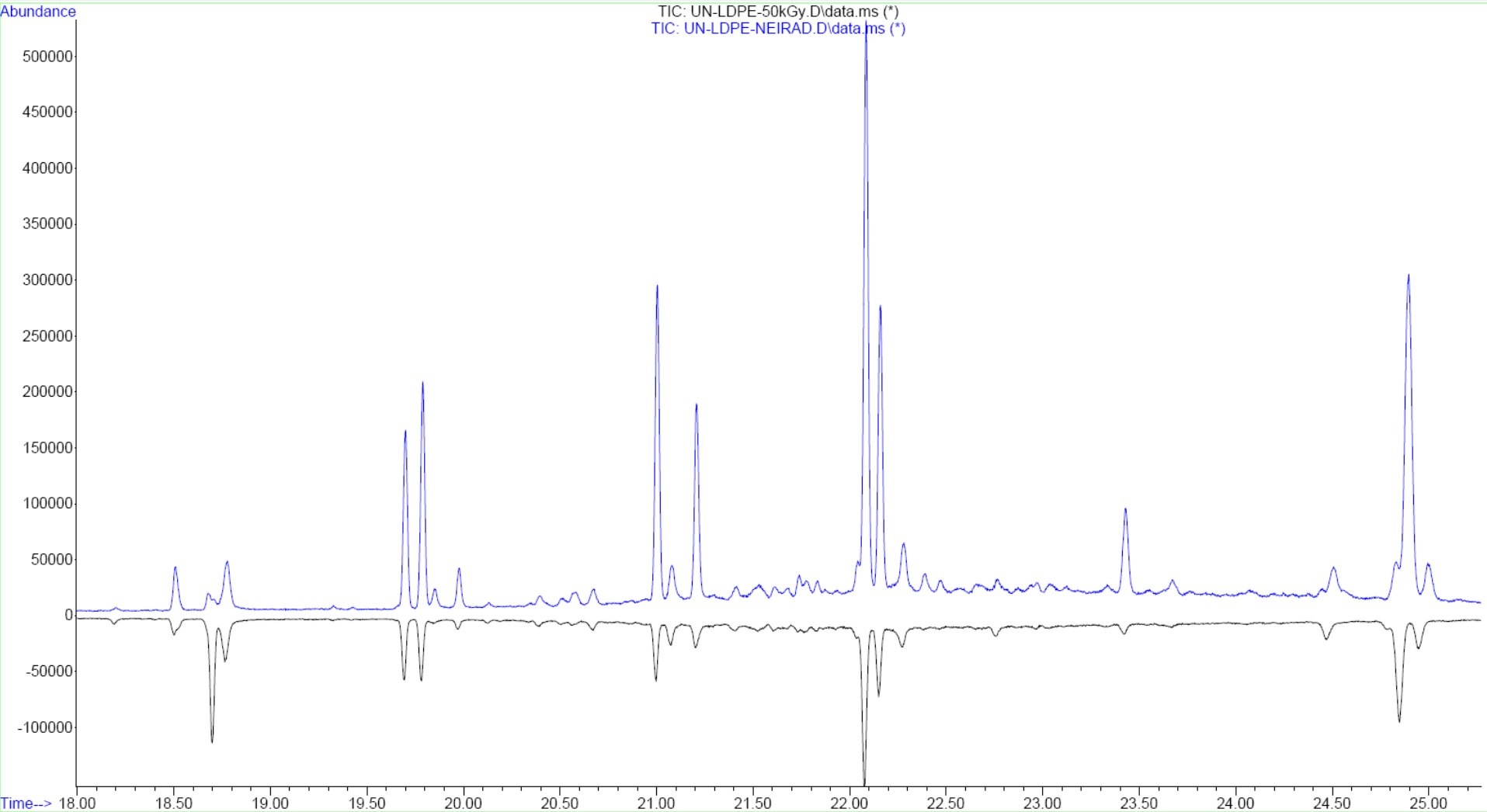
Unirradiated sort of Polyethylene - VOC Fingerprint



UN PE VOC Fingerprint 50 kGy



50kGy vs Nonirradiated PE Fingerprints



Observations

- Low molecular weight hydrocarbons C(n-1) saturated and C(n-2):1 nonsaturated, similar with fatty acids radiolysis products in irradiated food stuffs are formed.

- Also special cyclic compounds similar with 2-alchilcyclobutanones are expected to be formed in trace level concentrations as effect of radiation treatment in polymeric materials. Those compounds can be used as markers to detect radiation treatment on polymeric materials.

- Increase of VOC's concentration in packaging materials for example can have an effect on the contained product odor and flavor. VOC and SVOC monitoring can be routinely used for product qualification to radiation treatment.

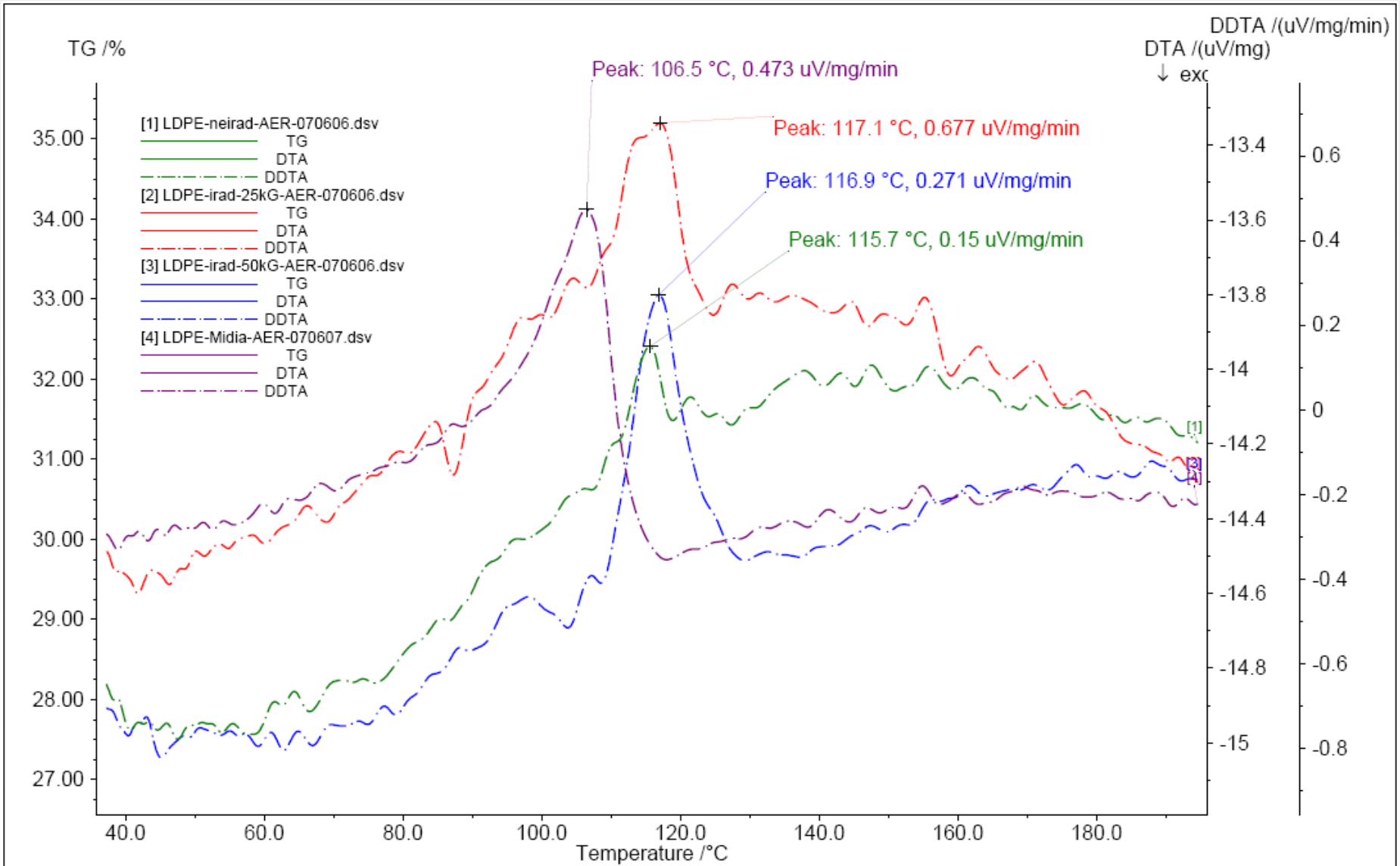
Simultaneous Thermal Analysis (STA) TG-DTA

- Thermogravimetry (TG) quantitatively measures weight change for a sample exposed to a temperature program.

- Differential Thermal Analysis is a technique in which the temperature difference between the substance and a reference material is measured as a function of temperature, while the substance and reference material are subjected to a controlled temperature program.

- STA refers to the application of two or more techniques to a (single) sample at the same time.

Experimental Melting point examination for a sort of Polyethylene

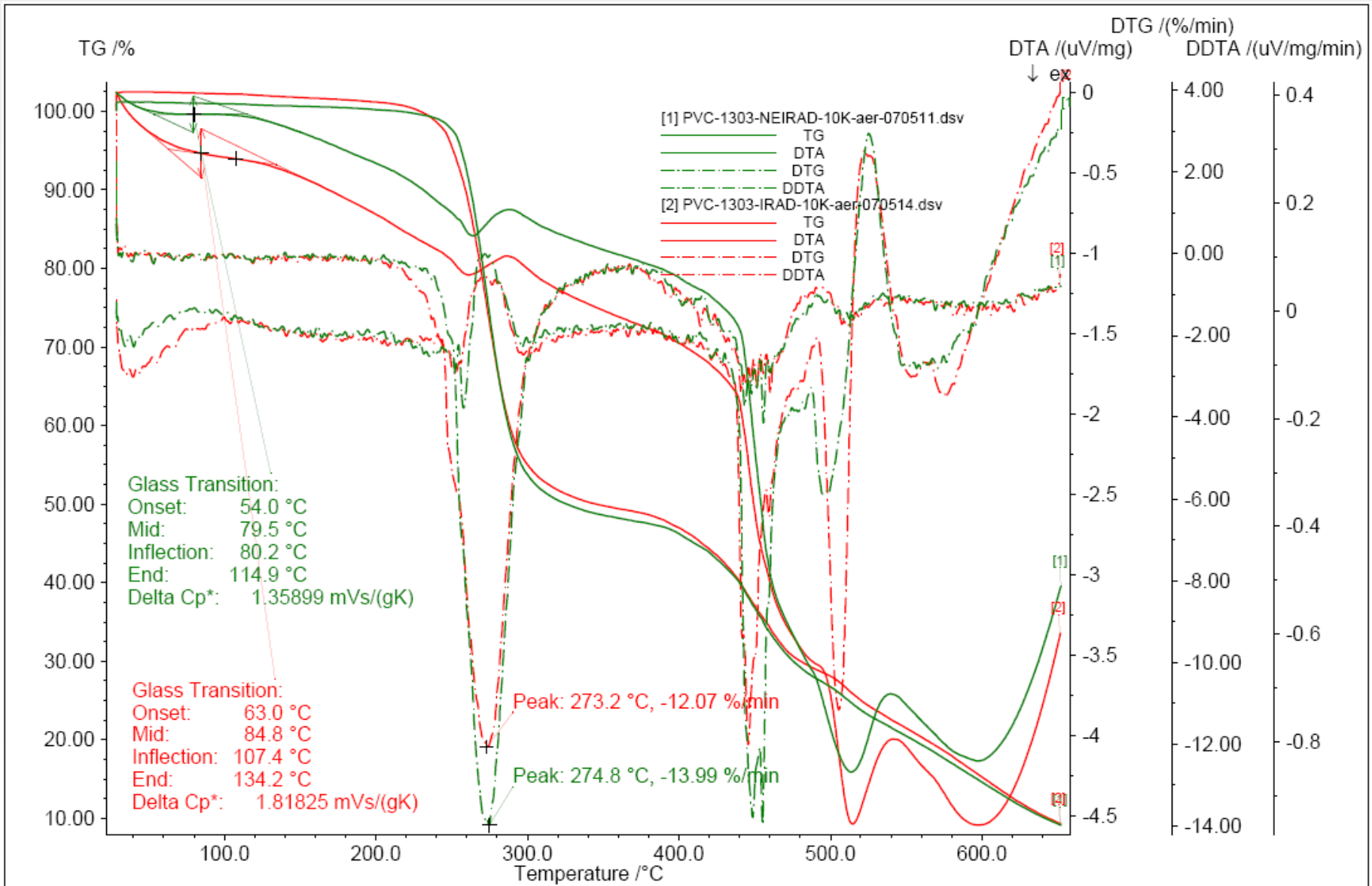


Main 2006-06-13 04:11 User: GCMSVIRTUAL

[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[1] STA 409 PC/PG	LDPE-neirad-AER-070606.dsv	2006-06-06	LDPE-neirad	LDPE-neirad	5.190	1/1	35/25.0(K/min)/600	air/20 / ---/10 / air/---	DTA:420, TG:020
[2] STA 409 PC/PG	LDPE-irad-25kG-AER-070606.dsv	2006-06-06	LDPE-irad-25kG	LDPE-irad-25kG	5.290	1/1	35/25.0(K/min)/600	air/20 / ---/10 / air/---	DTA:420, TG:020
[3] STA 409 PC/PG	LDPE-irad-50kG-AER-070606.dsv	2006-06-06	LDPE-irad-50kG	LDPE-irad-50kG	5.270	1/1	35/25.0(K/min)/600	air/20 / ---/10 / air/---	DTA:420, TG:020
[4] STA 409 PC/PG	LDPE-Midia-AER-070607.dsv	2006-06-07	LDPE-Midia	LDPE-Midia	6.200	1/1	35/25.0(K/min)/600	air/20 / ---/10 / air/---	DTA:420, TG:020

Simultaneous Thermal Analysis (STA) TG-DTA

Glass Transition – a measure of the degree of reticulation in PVC

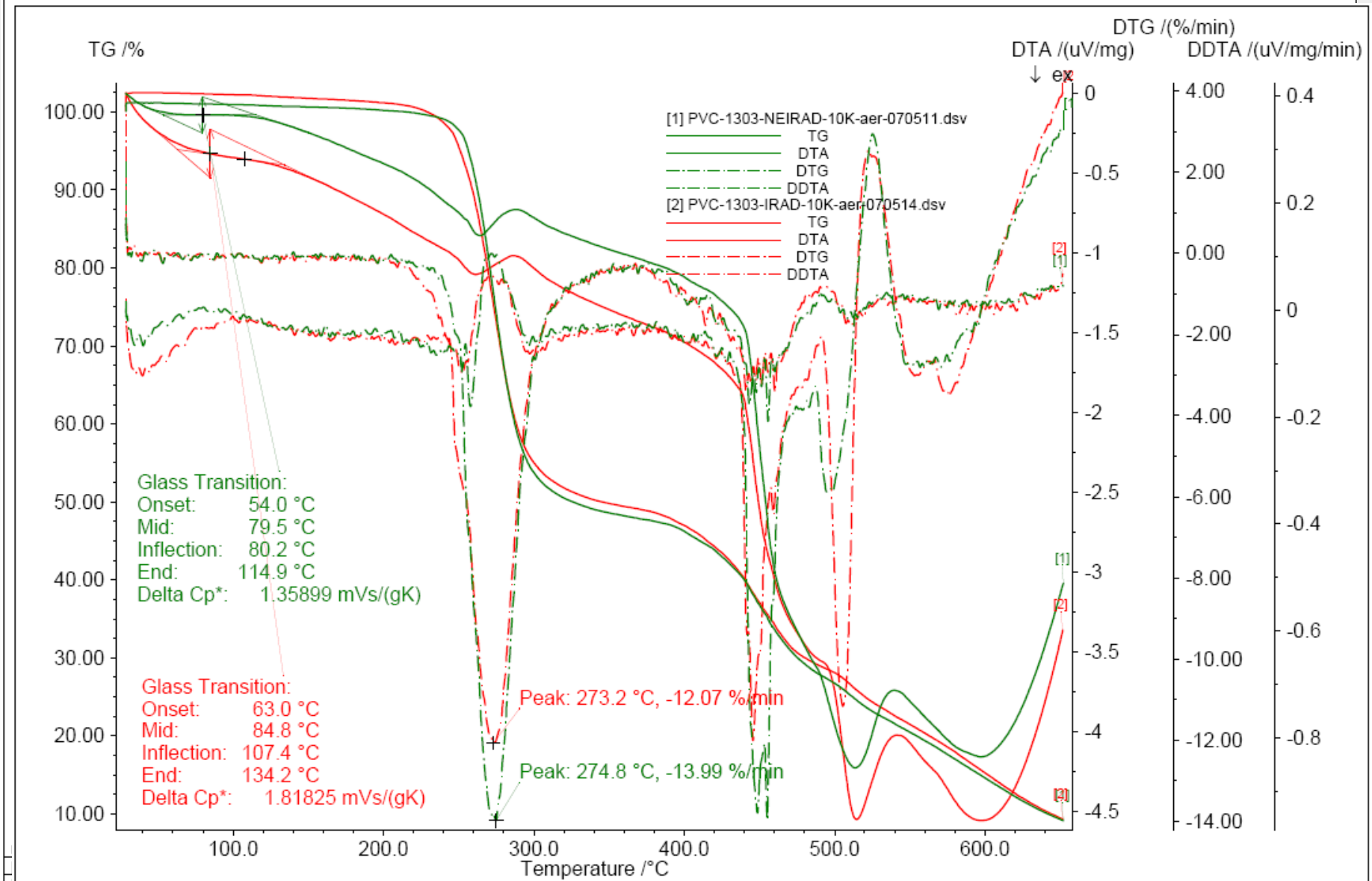


Main 2006-06-13 06:08 User: GCMSVIRTUAL

[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[1] STA 409 PC/PG	PVC-1303-NEIRAD-10K-aer-070511.dsv	2007-05-11	PVC1303ne-aer-10K-070511	PVC1303ne-aer-10K-070511	10.020	1/1	35/10.0(K/min)/650	air/20 / ---/10 / air/---	DTA:320, TG:320
[2] STA 409 PC/PG	PVC-1303-IRAD-10K-aer-070514.dsv	2007-05-14	PVC-1303-irad-10K-aer	PVC-1303-irad-10K-aer	10.270	1/1	35/10.0(K/min)/650	air/20 / ---/10 / air/---	DTA:320, TG:320

Simultaneous Thermal Analysis (STA) TG-DTA

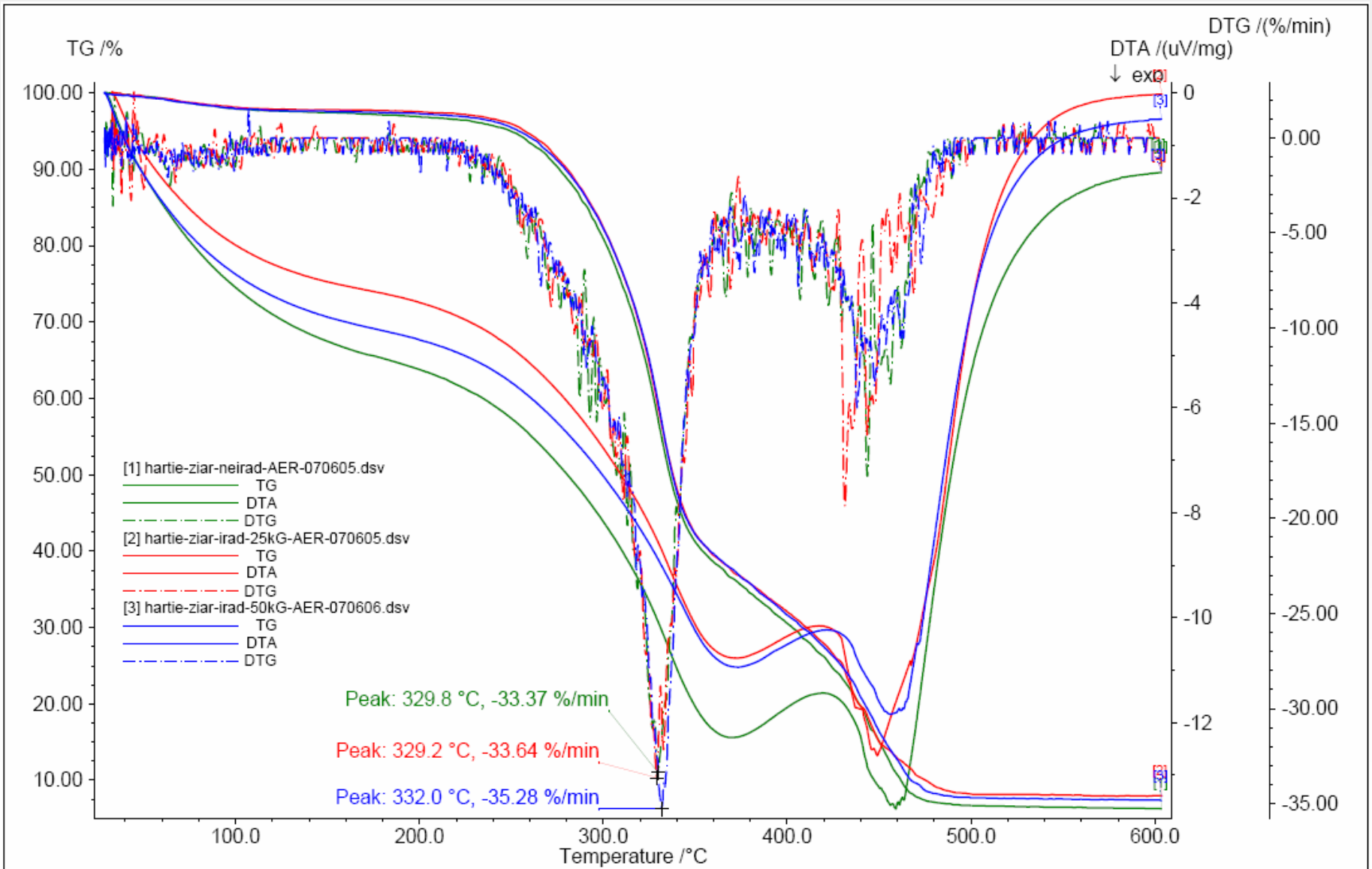
Glass Transition – a measure of the degree of reticulation in Cellulose



[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[1] STA 409 PC/PG	PVC-1303-NEIRAD-10K-aer-070511.dsv	2007-05-11	PVC1303ne-aer-10K-070511	PVC1303ne-aer-10K-070511	10.020	1/1	35/10.0(K/min)/650	air/20 / ---/10 / air/---	DTA:320, TG:320
[2] STA 409 PC/PG	PVC-1303-IRAD-10K-aer-070514.dsv	2007-05-14	PVC-1303-irad-10K-aer	PVC-1303-irad-10K-aer	10.270	1/1	35/10.0(K/min)/650	air/20 / ---/10 / air/---	DTA:320, TG:320

Simultaneous Thermal Analysis (STA) TG-DTA

Kinetics of fast endotermal degradation in cellulose

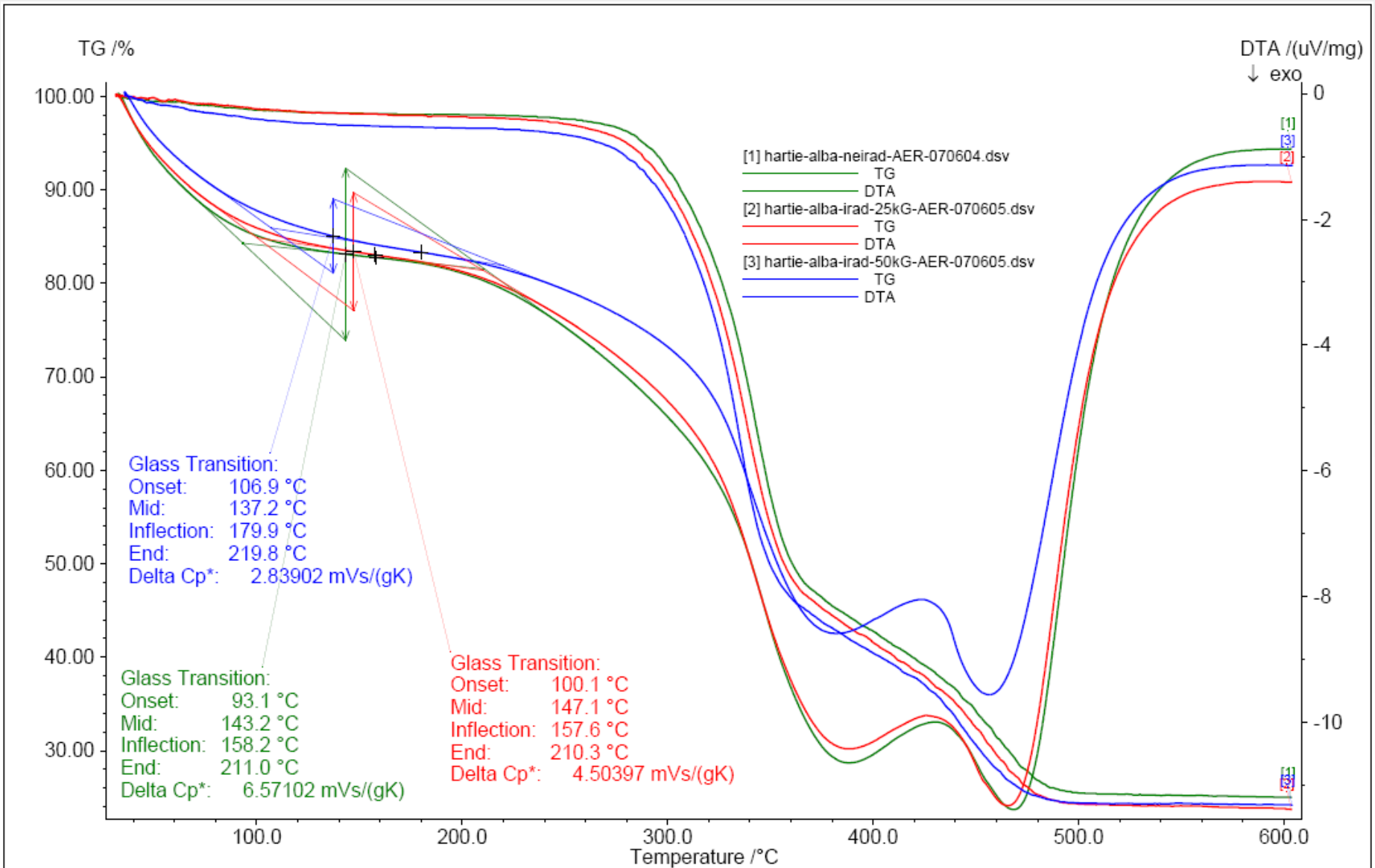


Main 2006-06-13 04:02 User: GCMSVIRTUAL

[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[1] STA 409 PC/PG	hartie-ziar-neirad-AER-070605.dsv	2006-06-05	hartie-ziar-neirad	hartie-ziar-neirad	5.500	1/1	35/25.0(K/min)/600	air/20 / ---/10 / air/---	DTA:020, TG:320
[2] STA 409 PC/PG	hartie-ziar-irad-25kG-AER-070605.dsv	2006-06-05	hartie-ziar-irad-25kG	hartie-ziar-irad-25kG	5.240	1/1	35/25.0(K/min)/600	air/20 / ---/10 / air/---	DTA:020, TG:320
[3] STA 409 PC/PG	hartie-ziar-irad-50kG-AER-070606.dsv	2006-06-06	hartie-ziar-irad-50kG	hartie-ziar-irad-50kG	6.550	1/1	35/25.0(K/min)/600	air/20 / ---/10 / air/---	DTA:020, TG:020

Simultaneous Thermal Analysis (STA) TG-DTA

Glass Transition – a measure of the degree of reticulation in Cellulose

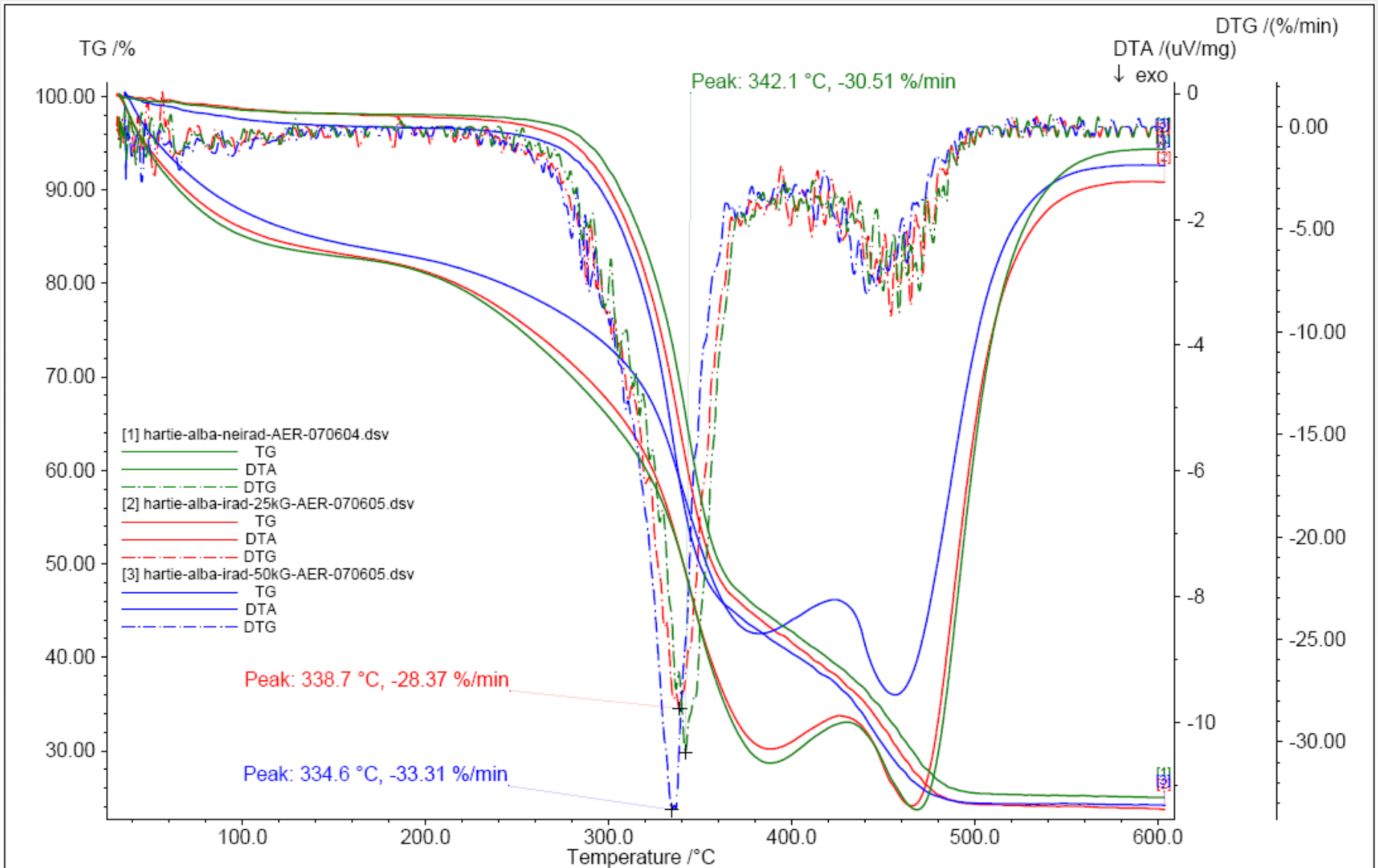


Main 2006-06-13 01:28 User: GCMSVIRTUAL

[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[1] STA 409 PC/PG	hartie-alba-neirad-AER-070604.dsv	2006-06-04	hartie-neirad	hartie-neirad	5.390	1/1	35/25.0(K/min)/600	air/20 / ---/10 / air/---	DTA:320, TG:020
[2] STA 409 PC/PG	hartie-alba-irad-25kG-AER-070605.dsv	2006-06-05	hartie-alba-irad-25kG	hartie-alba-irad-25kG	5.290	1/1	35/25.0(K/min)/600	air/20 / ---/10 / air/---	DTA:320, TG:020
[3] STA 409 PC/PG	hartie-alba-irad-50kG-AER-070605.dsv	2006-06-05	hartie-alba-irad-50kG	hartie-alba-irad-50kG	6.330	1/1	35/25.0(K/min)/600	air/20 / ---/10 / air/---	DTA:320, TG:020

Simultaneous Thermal Analysis (STA) TG-DTA

Kinetics of fast endotermal degradation in cellulose

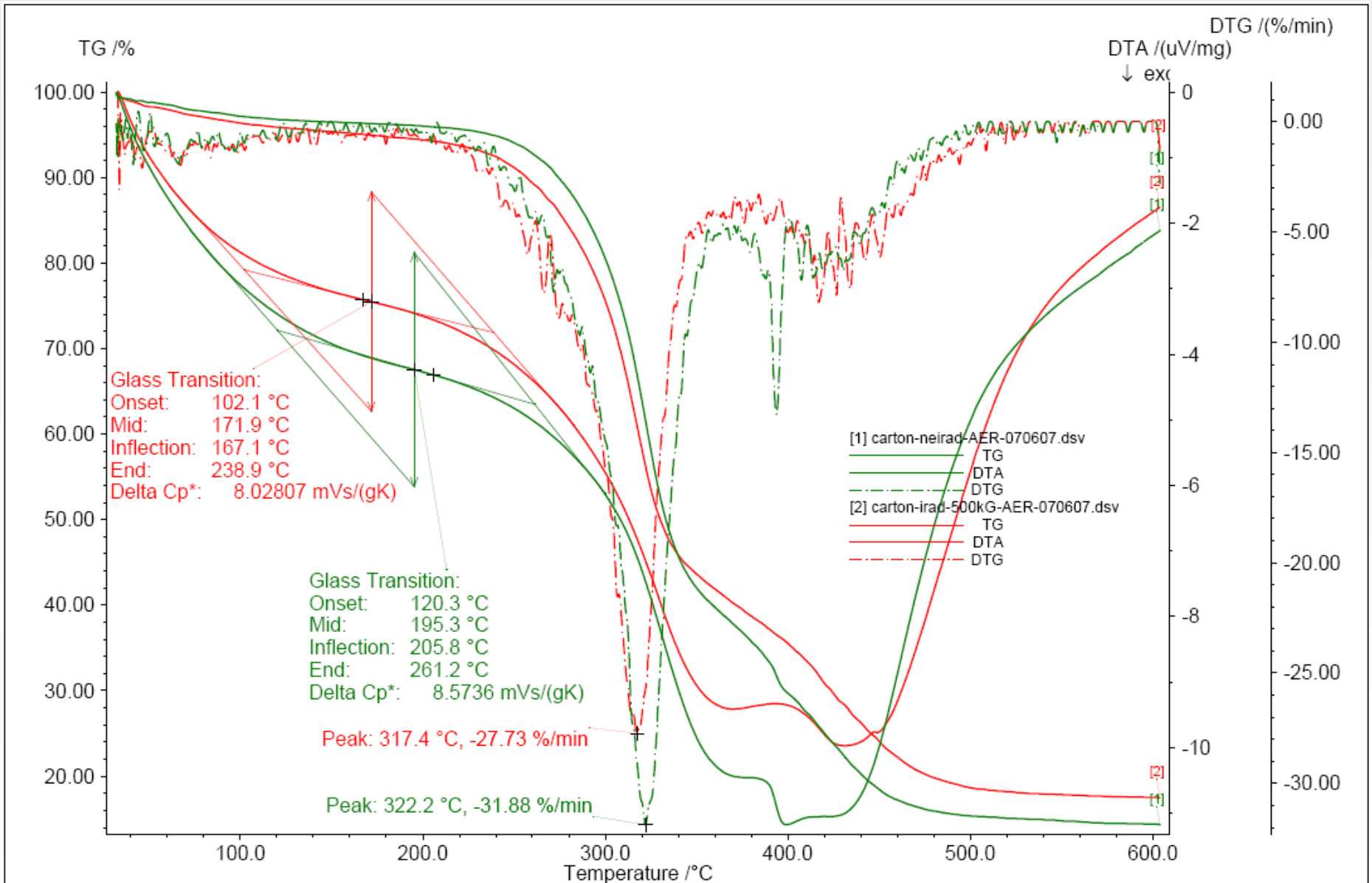


Main 2006-06-13 04:04 User: GCMSVIRTUAL

[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[1] STA 409 PC/PG	hartie-alba-neirad-AER-070604.dsv	2006-06-04	hartie-neirad	hartie-neirad	5.390	1/1	35/25.0(K/min)/600	air/20 / ---/10 / air/---	DTA:320, TG:420
[2] STA 409 PC/PG	hartie-alba-irad-25kG-AER-070605.dsv	2006-06-05	hartie-alba-irad-25kG	hartie-alba-irad-25kG	5.290	1/1	35/25.0(K/min)/600	air/20 / ---/10 / air/---	DTA:320, TG:420
[3] STA 409 PC/PG	hartie-alba-irad-50kG-AER-070605.dsv	2006-06-05	hartie-alba-irad-50kG	hartie-alba-irad-50kG	6.330	1/1	35/25.0(K/min)/600	air/20 / ---/10 / air/---	DTA:320, TG:420

Simultaneous Thermal Analysis (STA) TG-DTA

Glass Transition – a measure of the degree of reticulation in Cellulose



Main 2006-06-13 01:29 User: GCMSVIRTUAL

[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[1] STA 409 PC/PG	carton-neirad-AER-070607.dsv	2007-06-07	carton-neirad	carton-neirad	5.490	1/1	35/25.0(K/min)/600	air/20 / ---/10 / air/---	DTA:420, TG:420
[2] STA 409 PC/PG	carton-irad-500kG-AER-070607.dsv	2007-06-07	carton-irad-500kG	carton-irad-500kG	5.140	1/1	35/25.0(K/min)/600	air/20 / ---/10 / air/---	DTA:420, TG:420

Glass Transition (Defined according to DIN 51007 E)

Reversible transition of amorphous substances or of the amorphous zones of partially crystalline substances from a hard, brittle (latent) state into a fused mass or to a rubber-like state.

No	Type of test	Material	Maximal breakdown force in (%) at different doses		
			0	25k	50k
1	Tensile	HQ paper	100	97.93	92.38
2	Tensile	LQ paper	100	98.34	96.21
3	Tensile	PE foil	100	112.16	126.41
4	Tear	HQ paper	100	86.49	70.27
5	Tear	LQ paper	100	87.10	80.65
6	Tear	PE foil	100	101.68	108.72
7	Penetration	HQ paper	100	83.36	69.85
8	Penetration	LQ paper	100	96.40	85.61
9	Penetration	PE foil	100	94.60	89.65

Material	Property	Dose (kGy)			
		0	25	50	500
HQ paper	Glass transition (ºC)	158.2	157.6	179.9	-
HQ paper	Fast endothermal degradation(TG%/min)	-30.51	-28.37	-33.31	-
LQ paper	Glass transition (ºC)	172.6	174.1	179.9	-
LQ paper	Fast endothermal degradation(TG%/min)	-33.37	-33.64	-35.28	
Postal box paper	Glass transition (ºC)	205.8	-	-	167.1
Postal box paper	Fast endothermal degradation(TG%/min)	-31.88	-	-	-27.73
REF LDPE	MP(ºC)	106.5	-	-	-
UN PE	MP(ºC)	115.7	116.9	117.1	-
PVC	Glass transition (ºC)	80.2	-	107.4	-
PVC	HCl loss speed (TG%/min)	-13.99	-	-12.07	-

THANK YOU FOR YOUR ATTENTION !