WHITE PAPER

NETZSCH

Identify for DSC, TGA, DIL, TMA and c_P Data

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Overview

The *Identify* database system was introduced in autumn 2013 – simultaneously with the launch of the DSC 214 *Polyma* [1 - 3]. Initially, *Identify* could only be used for DSC measurements, and NETZSCH supplied a database with entries just from the field of polymers.

Meanwhile, *Identify* is also being opened for $\Delta L/L_0$ signals measured with DIL and TMA instruments, for c_p signals from DSC instruments and since recently, for TGA measurements from supported TG 209 instruments [4, 5].

The entire NETZSCH part of the database contains more than 1,100 entries from the fields of ceramics and inorganics (26%), metals and alloys (16%), polymers (22%), organics, food and pharma (27%) as well as chemical elements (9%), as can be seen in figure 1a.

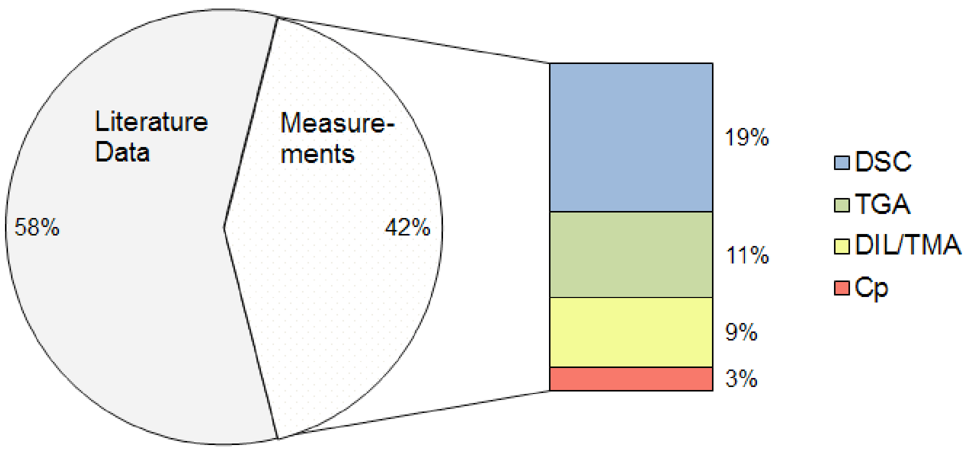
Search Libraries:

Library	Entries
Alloys Poster NETZSCH	42
Ceramics Poster NETZSCH	32
Ceramics_Inorganics NETZSCH	254
Elements Poster NETZSCH	104
Metals_Alloys NETZSCH	135
Organics_Food_Pharma NETZSCH	304
Polymers NETZSCH	176
Polymers Poster NETZSCH	70

1a Various NETZSCH libraries presented in the *Identify* database (status: 10/2016).

Identify contains not only measurements but also literature data without a measurement curve [1, 2]. Such literature data entries contain properties about endo- or exothermic effects, glass transitions and mass changes, but also the coefficient of linear thermal expansion, α, and the specific heat capacity, c_p – both at room temperature. A "literature data" database entry type is similar to items listed in the well known NETZSCH posters about thermal properties of materials. *Identify* is able to compare unknown measurements of any supported type with other such measurements – but also with literature data present in the database.

The *Identify* database shown in figure 1a is currently composed of 58% of literature data and 42% of measurements which are of type DSC (19%), TGA (11%), DIL/TMA (9%) and c_p (3%) as displayed in figure 1b.



1b Composition of the *Identify* database (status: 10/2016). Most of the literature data contain several properties (glass transition temperature T_g, melting temperature T_m, α, c_p, mass changes) – all at once.

Users can, of course, create libraries containing their own measurements and literature data that can be shared with several users in the computer network.

Identify is included in the scope of delivery for the DSC 214 *Polyma*, DSC 204 ***F1*** *Phoenix*®, TG 209 ***F1*** *Libra*®, DIL *Expedis Supreme* and TMA 402 ***F1*** *Hyperion*. For other instruments, such as the DSC 204 ***F3*** *Maia*, DSC 3500 *Sirius*, TG 209 ***F3*** *Tarsus*, DIL *Expedis Classic* or *Select* and the TMA 402 ***F3*** *Hyperion*, *Identify* is an option.

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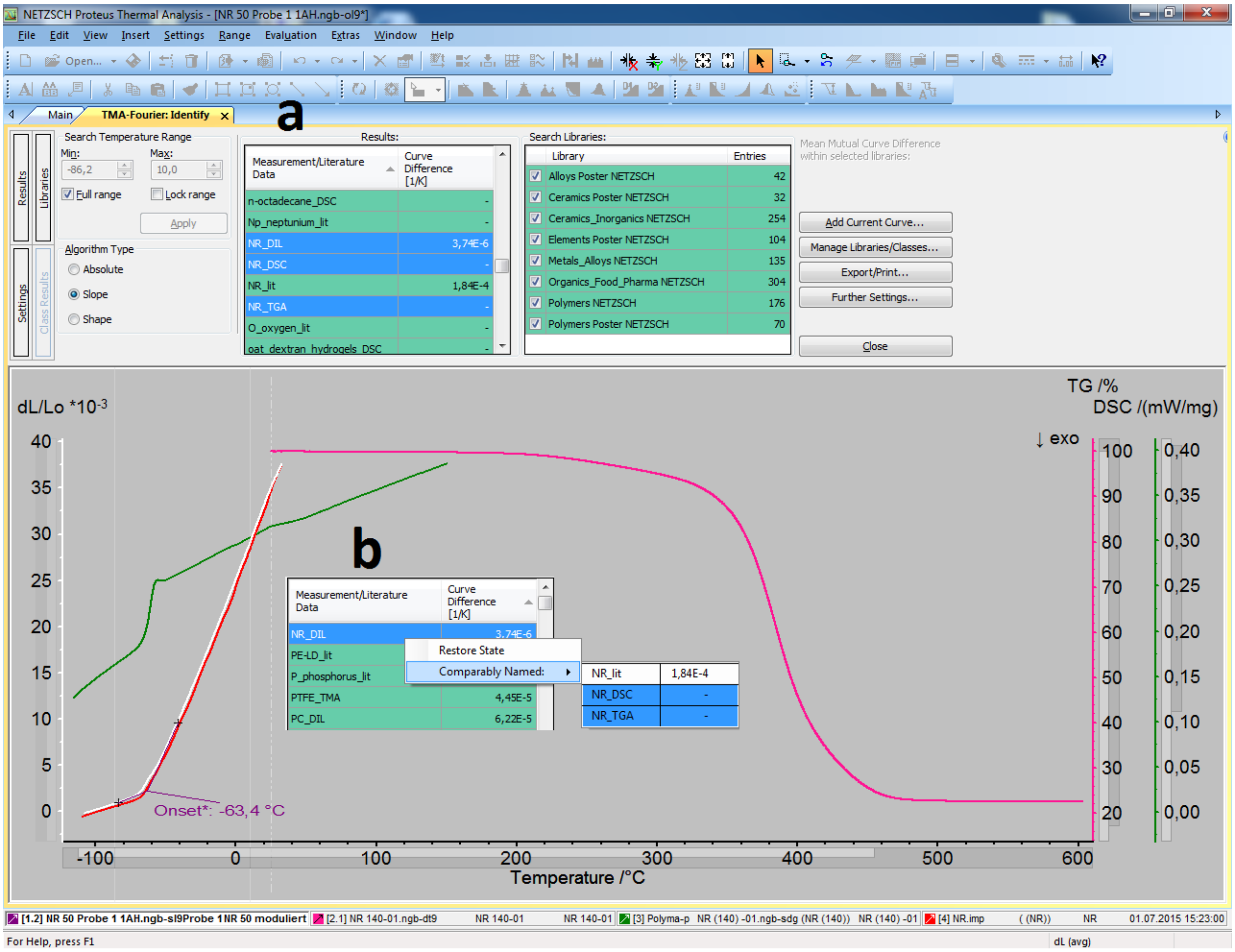
Once *Identify* is available on a computer – for example, as a result of the installation of a DSC 214 *Polyma* – signal types from all supported instruments can be used for *Identify* and it always contains the complete set of database entries. It always offers all possibilities such as overlaying of the actual measurement curve with any database curve – even those of other signal types (see figure 2).

Algorithms Used by *Identify*

For DSC and TGA signals, *Identify* uses an effect-based approach and effect-based algorithms for identification of a measurement curve [4]. This means that energetic effects and mass changes are first evaluated – even automatically applying *AutoEvaluation* if desired – and then all properties of the effects are taken into consideration in a calculation of the "similarity value" between two measurements or between a measurement and literature data. This effect-based approach has several advantages: it provides results extremely fast (in-situ), it is intelligent and it can be adapted to the application even by users. Last but not least, the effect-based approach performs very well and yields satisfying results [3].



2 *Identify* applied to a DIL measurement on a natural rubber (NR) displayed in white. Overlaid are the database curves "NR_DIL" (red), "NR_DSC" (green) and NR_TGA (pink). The DIL measurements as well as the DSC curve exhibit a glass transition in the temperature range around -65…-60°C. In order to find database entries, the hit list can either be sorted alphabetically (a) or comparably named hits can be shown via the right mouse button (b). Left mouse button and Ctr-key are used to display one or several curves.

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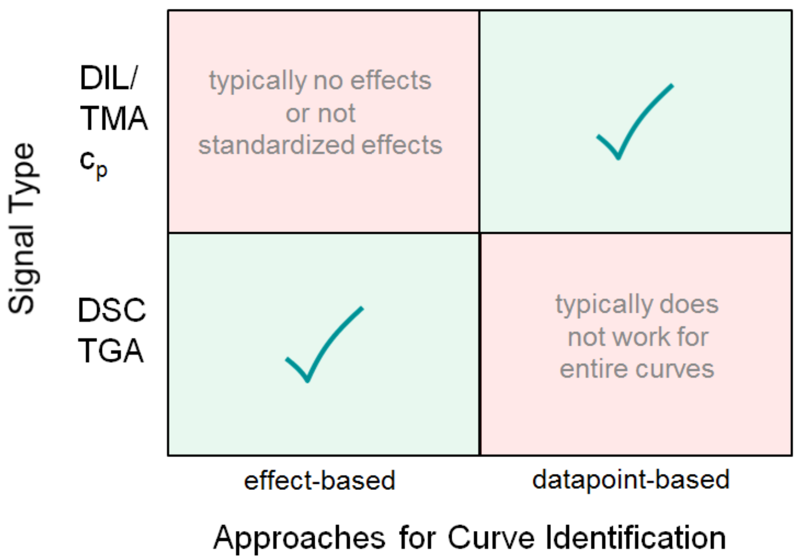
In contrast to typical DSC and TGA measurements, neither $\Delta L/L_0$ signals from DIL and TMA nor c_p measurement curves exhibit any effects in most cases, but they do show, for example, an increase in the signal as a function of temperature. Effects occuring in DIL, TMA and c_p curves sometimes do not have a standardized shape and the evaluation of such effects may be difficult. In contrast to DSC signals, the absolute values of $\Delta L/L_0$ and c_p signals are clearly in the scope of interest. Absolute values of, for example, $\Delta L/L_0$ curves can differ by more than four orders of magnitude for different materials. Because of these fundamental differences between DSC and TGA curves on the one hand and DIL, TMA and c_p curves on the other, *Identify* always successfully uses datapoint-based algorithms for the recognition of DIL, TMA and c_p curves, while effect-based algorithms are always used for DSC and TGA curves (see figure 3). The datapoint-based approach uses the signal data as a function of temperature to calculate the mean difference between two curves within a selectable, overlapping temperature range. Depending on the type of datapoint-based algorithm (see below), the "curve difference" can be in dimensionless units between 0 and 100% as is the case for effect-based algorithms, or it can be in absolute units, such as in J/(g·K) for c_p curves.

All cases yield a hit list as the search result, where the database entries are sorted according to the similarity or curve difference as compared to the unknown measurement.

Use of *Identify*

In general, *Identify* is useful for the recognition of unknown measurements and thus for material identification and quality control applications; furthermore, it serves as an archiving system. Since the application of *Identify* on DSC curves was already highlighted in references [1-3], investigation of TGA, $\Delta L/L_0$ and c_p data is focused in this work.



3 Approaches for curve identification used by *Identify* for different signal types. Datapoint-based algorithms are always used for DIL, TMA and c_p data, while effect-based algorithms are always used for DSC and TGA curves.

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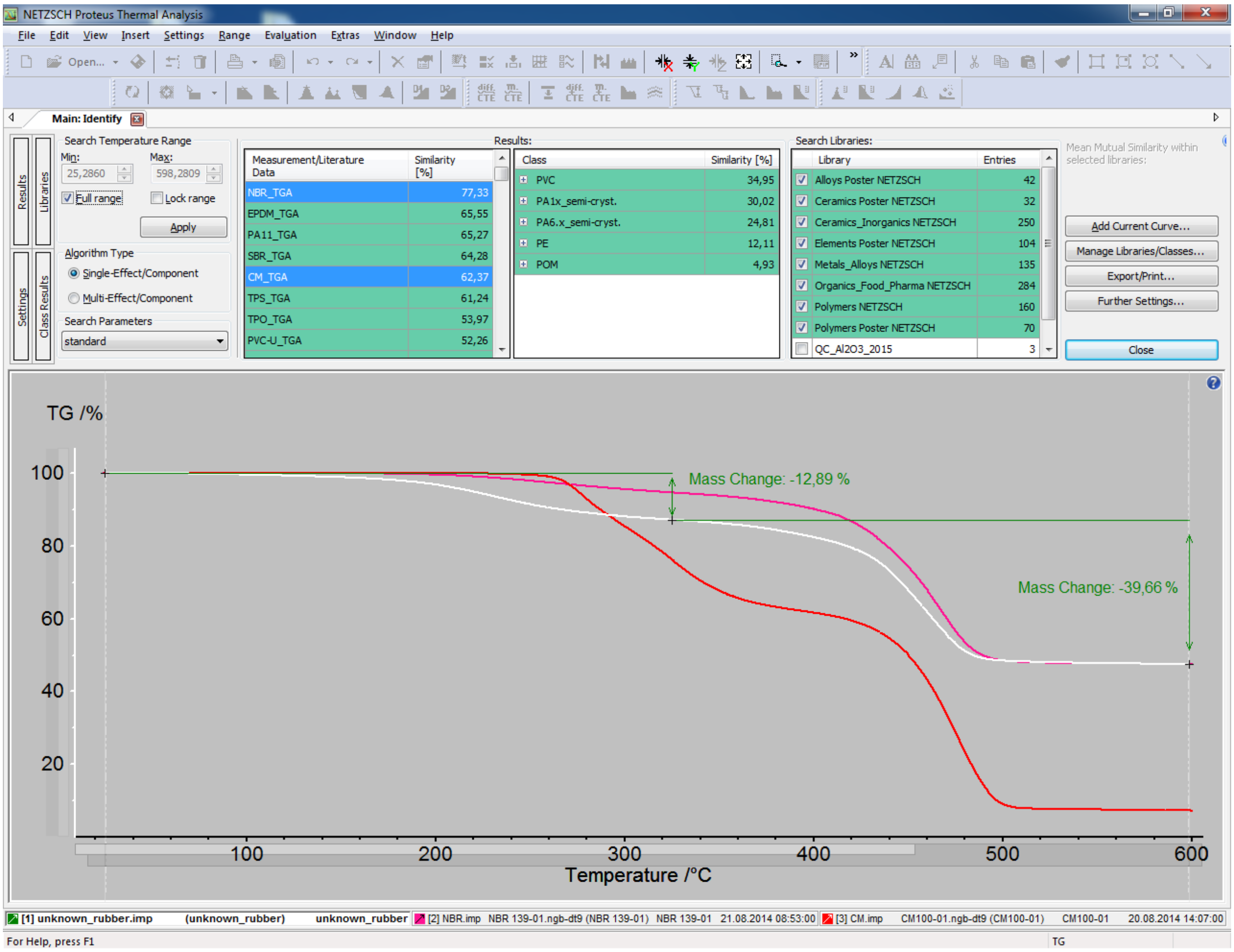
Curve and Material Identification

Figure 4 shows how *Identify* was applied to a TGA measurement performed on an unknown rubber sample. After only one click, the measurement was automatically evaluated applying *AutoEvaluation* and the main view of *Identify* appeared with its hit lists showing database entries similar to the unknown curve. *AutoEvaluation* revealed two mass-loss steps of 12.9% and 39.7% occurring in the temperature regions below about 320°C and between this temperature and about 600°C. Based on these evaluation results, *Identify* found the database entry "NBR_TGA", a measurement on acrylonitrile-butadiene rubber, as best hit displayed in pink (see figure 4). Another exemplary database curve, hit no. 5, is displayed as well which is a measurement on CM (chlorinated polyethylene rubber). This measurement has obviously a lower similarity compared to the NBR measurement – mostly due to the fact that the first mass-loss step is significantly larger and occurs at higher temperatures. It should be mentioned that all libraries available were included in the search; the TGA measurements on the unknown rubber sample as well as the database measurements on polymers were performed at 10 K/min under a dynamic nitrogen atmosphere on samples with an initial mass of about 10 mg.



4 *Identify* applied to an unknown TGA measurement (white). Hits no. 1 and 5 are displayed in pink and red. The unknown measurement was evaluated automatically by *AutoEvaluation*.

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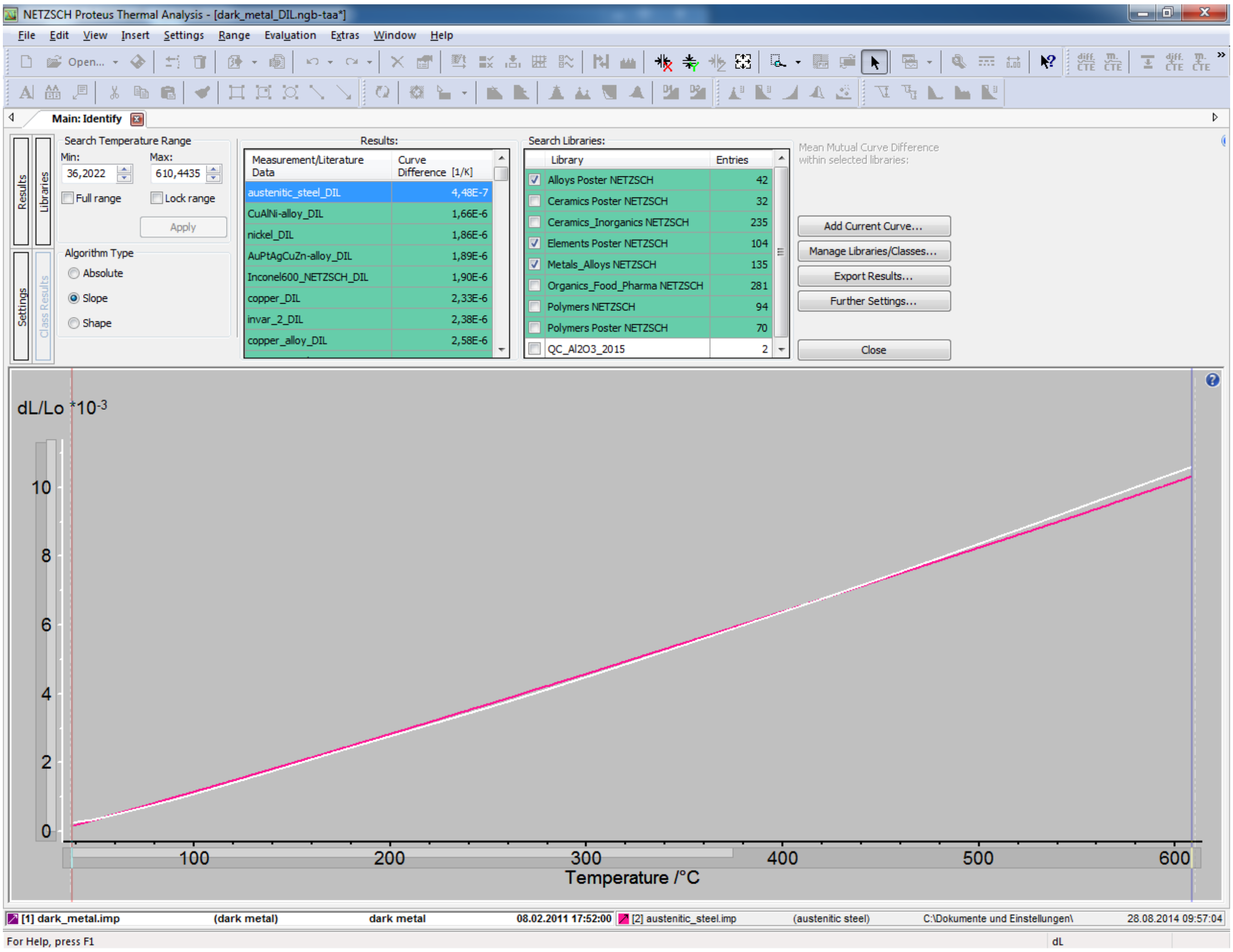
Figure 5 depicts how a DIL measurement on an unknown sample ("dark metal") is analyzed by means of *Identify*. The best hit in this case is the measurement "austenitic_steel_DIL" displayed in pink which shows a very similar increase in $\Delta L/L_0$ reflecting the linear thermal expansion of the material. Only the libraries "Alloys Poster NETZSCH", "Elements Poster NETZSCH" and "Metals_Alloys NETZSCH" were included in the search. The standard algorithm type for $\Delta L/L_0$ data – "Slope" – was used, which takes just the slope of the curves into consideration for its calculations and reveals [1/K] as unit for the curve difference.



5 *Identify* applied to an unknown DIl measurement (white). The best hit curve is displayed in pink.

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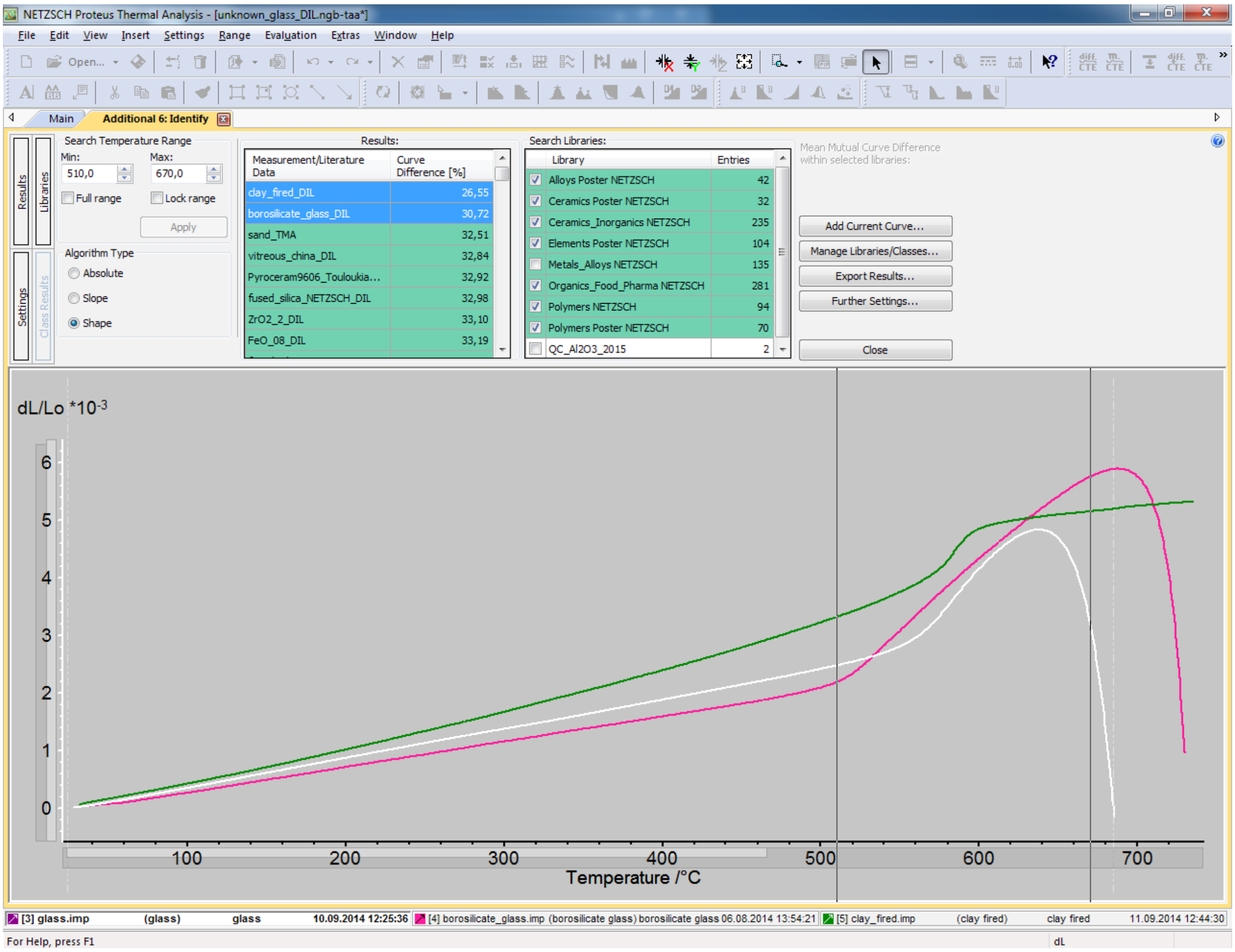
The algorithm type "Shape" allows for the finding of data-base curves with a similar characteristic shape compared to the unknown curve, as illustrated in figure 6. The unknown DIL measurement on a glass sample exhibits a glass transition and softening between about 550°C and 600°C. In the limited search temperature range between 510°C and 670°C set by the user, the database entries "clay_fired_DIL" and "borosilicate_glass_DIL" have the most similarly shaped curves. The step occurring in the "clay_fired_DIL" curve is due to the α→β transformation of quartz, while the "borosilicate_glass_DIL" curve also exhibits a glass transition and softening; however, these occur at slightly different temperatures than in the unknown glass sample.



6 *Identify* applied to an unknown DIL measurement (white). Hits no. 1 and 2 are displayed in green and pink.

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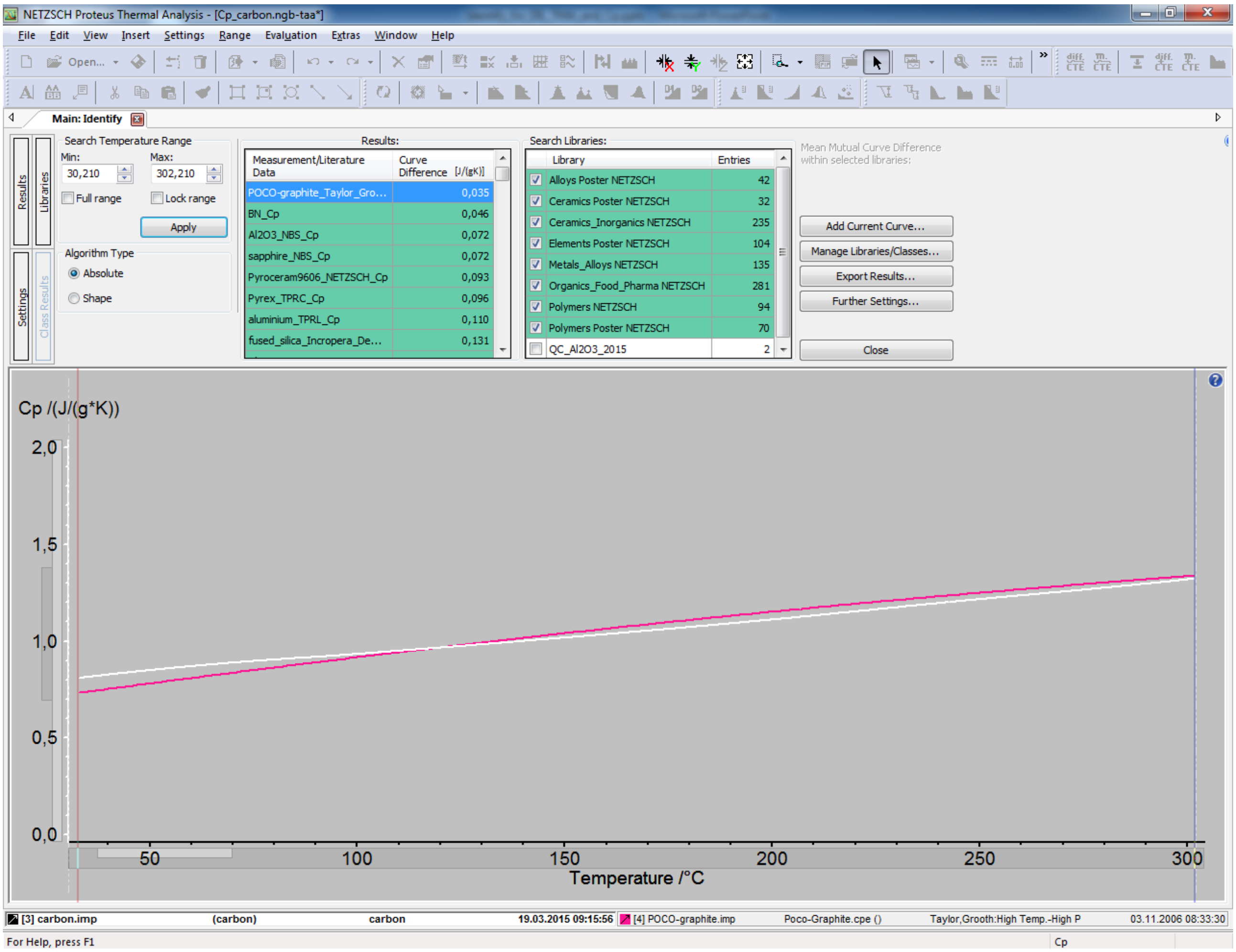
For c_p curves, the algorithm type "Absolute" – which takes the absolute curve differences into consideration – is used by default. The example displayed in figure 7 shows how the c_p curve measured on a carbon sample is analyzed by means of *Identify*. The best hit is the c_p curve "POCO graphite" published by Taylor and Grooth; it shows a mean curve difference of 0.035 J/(g·K) compared to the curve of the carbon sample.



7 *Identify* applied to a c_p curve of carbon (white). The best hit, "POCO graphite", is displayed in pink.

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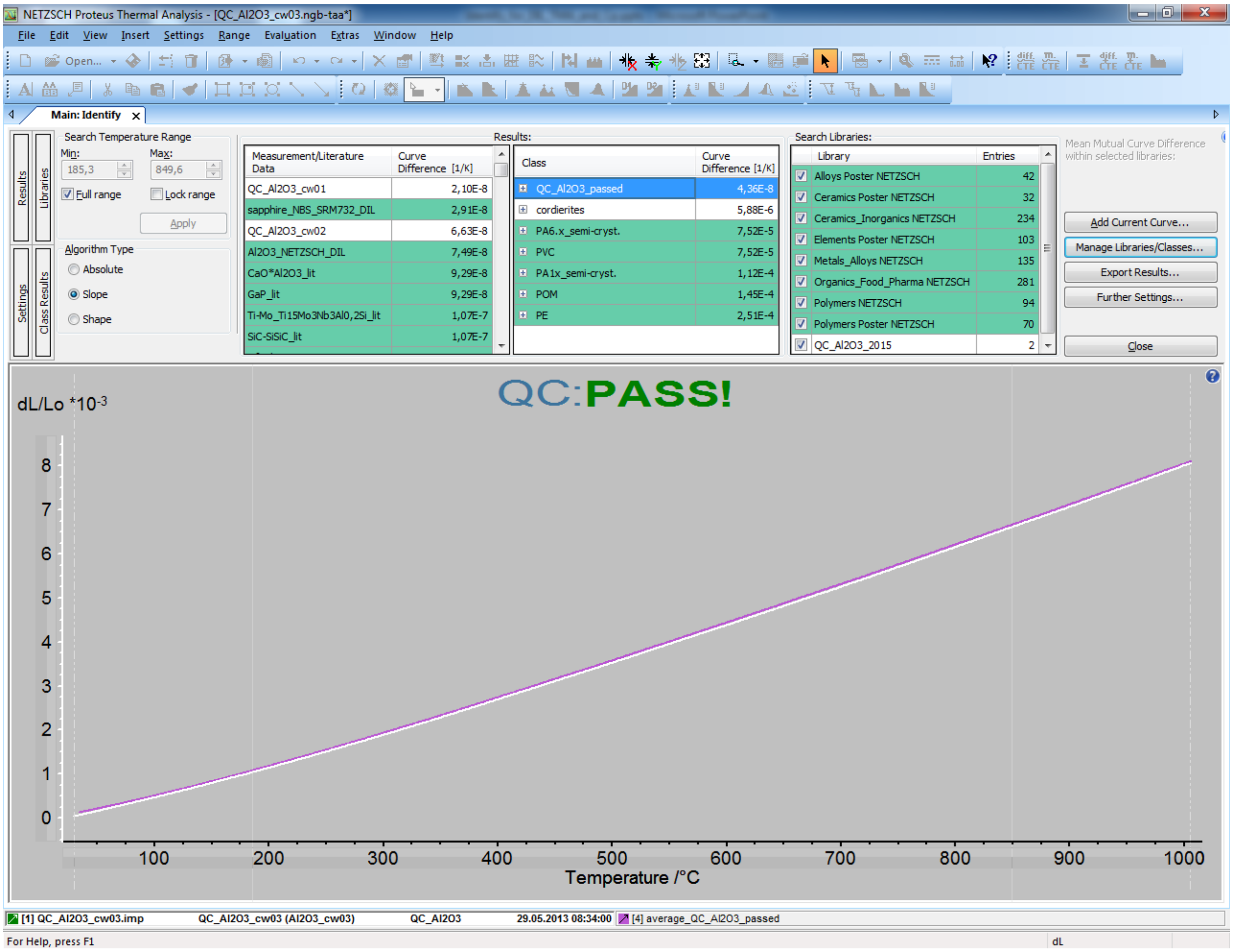
Quality Control

Another main use of *Identify* is quality control (QC) as displayed in figures 8a and 8b. In this example, a user has created a class called "QC_Al2O3_passed" which contains the DIL measurements on Al_2O_3 (alumina) of "QC_Al2O3_cw01" and "QC_Al2O3_cw02"; these were considered to fulfill the quality criteria. Figure 8a shows how an additional measurement, "QC_Al2O3_cw03", compares to class "QC_Al2O3_passed": Measurement "QC_Al2O3_cw03" is in accordance with class "QC_Al2O3_passed" represented by the average curve (purple) leading automatically to the message "QC: PASS!".



8a DIL measurement "QC_Al2O3_cw03" (white) analyzed by means of *Identify*. Measurement "QC_Al2O3_cw03" is in accordance with class "QC_Al2O3_passed", which is represented by the average curve (purple); this automatically yields the message "QC: PASS!".

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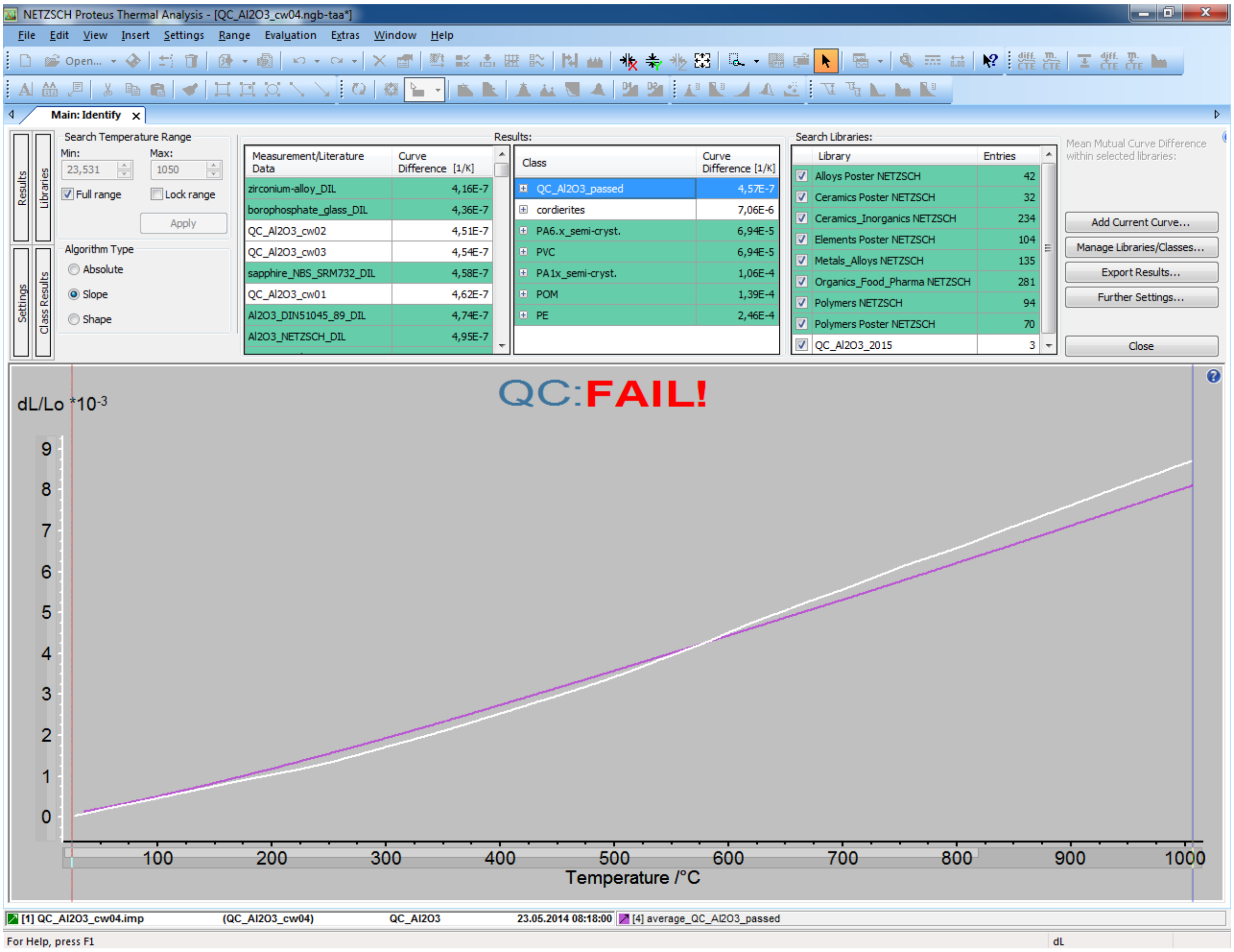
The accepted measurement "QC_Al2O3_cw03" was then added to the database and to the class "QC_Al2O3_passed" before *Identify* was applied to the next measurement, "QC_Al2O3_cw04" (figure 8b): Here, an excessive difference in the curves between the measurement "QC_Al2O3_cw04" and the class "QC_Al2O3_passed" automatically triggered the message "QC: FAIL!".

By applying "Export Results", a customizable report for any case is generated showing all aspects of the actual *Identify* results.

It is important to emphasize that the user defines the threshold for quality control, which is a maximum allowed curve difference for $\Delta L/L_0$ and c_p signals; this may be the maximum difference with regard to the algorithm types "Absolute", "Slope" or "Shape". In the case of DSC and TGA data, a user-defined similarity value marks the threshold for quality control.



8b DIL measurement "QC_Al2O3_cw04" (white) analyzed by means of *Identify*. The difference between the curve for the "QC_Al2O3_cw04" measurement and the curves of the class "QC_Al2O3_passed", represented by the average curve (purple) automatically triggers the message "QC: FAIL!".

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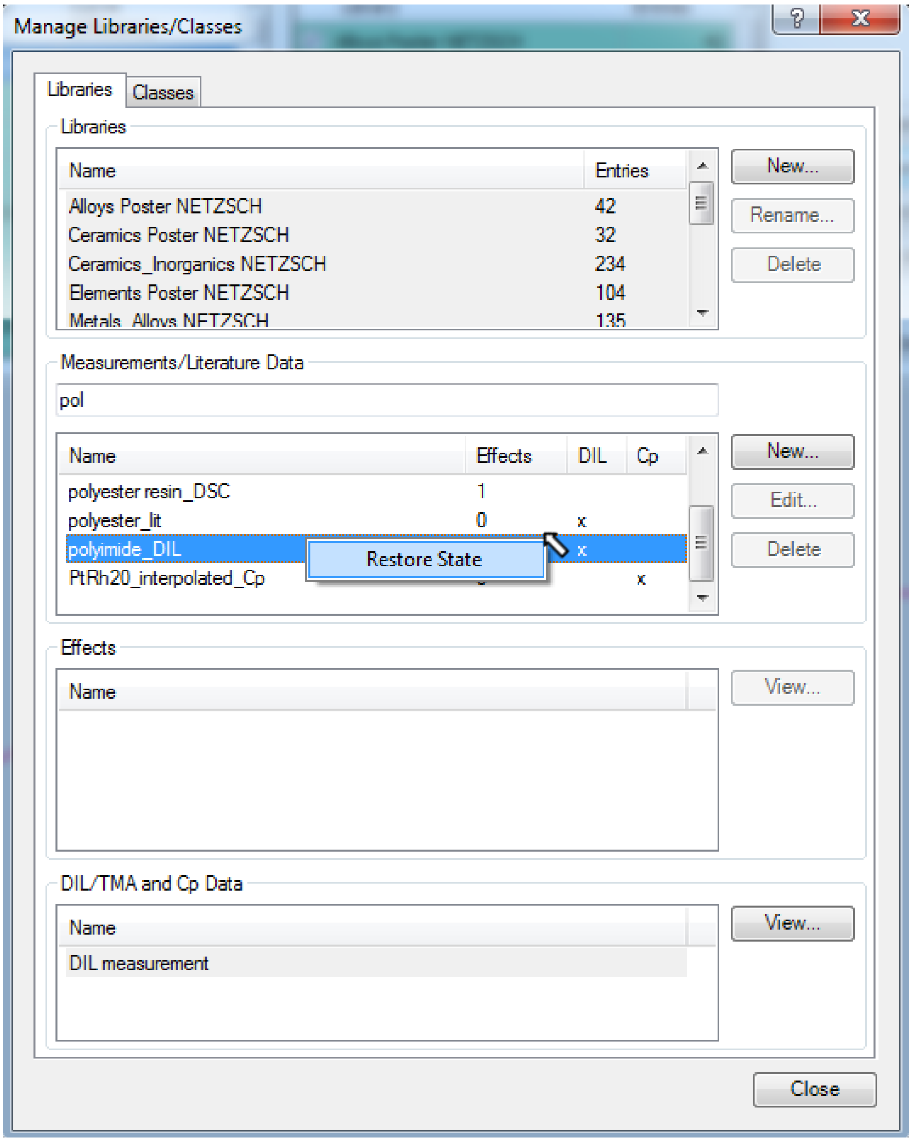
Archiving/Searching

Another strenght of *Identify* is that it can be used as an archiving system for NETZSCH and user data [3]. On the one hand, a measurement can easily be added to one or several libraries [1], and on the other hand, particular measurements and literature data can also be easily searched and found within the database. This is particularly useful for gathering information about what measurement results can be expected from a sample that has not yet been measured by the user. It is also helpful prior to a measurement because suitable measurement conditions can be seen in the database entry.

Some possibilities regarding the search for a database entry are illustrated in figure 2. Further options are diplayed in figure 9, where certain libraries were selected and "pol" was typed in for alphabetical filtering. The analysis state of the "polyimide_DIL" measurement which was found, for example, could then be restored with a single click. In the case of user measurements, evaluations could be edited and any modifications applied to the database or discarded. Analysis states can also be restored directly from the hit lists.

Further filter criteria for database entries are shown in figure 10.



9 Database entries can be searched via selection of libraries and alphabetical filtering (here: "pol" was used) and their analysis states can easily be restored.

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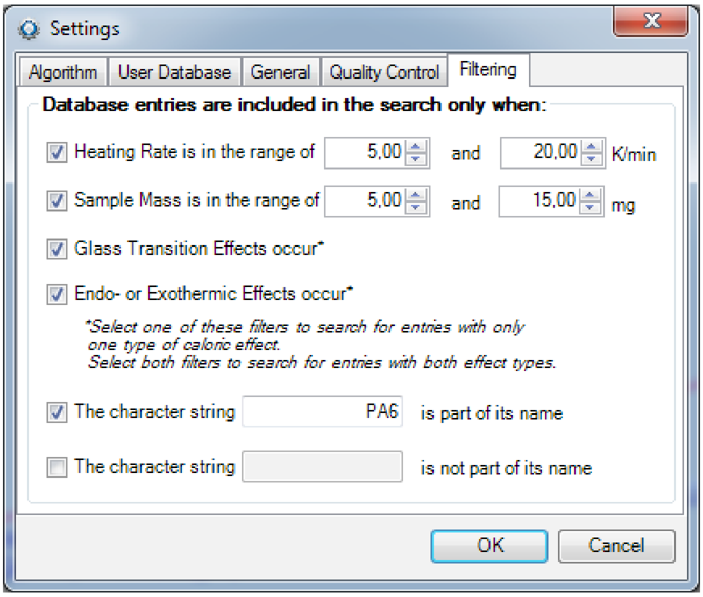

10 Possibilities for filtering of the database entries according to the measurement conditions heating rate and sample mass, to the occurrence of caloric effects and according to their names

Summary

Identify …

- … is a unique database system for Thermal Analysis (status 10/2016: for DSC, TGA, DIL/TMA and c_p data).
- … includes NETZSCH libraries with more than 1,100 entries from the fields of ceramics and inorganics, metals and alloys, polymers, organics, food and pharmaceuticals, as well as chemical elements (status 10/2016).
- … can be expanded by users' own libraries that can be shared with several users in the computer network.
- … can with a single click:
  – recognize measurement curves
  – be used for quality control with user-defined thresholds.
- … serves as an archiving system.

The Author

Dr. Alexander Schindler has worked in the fields of experimental physics, thermal analysis and thermophysical properties for over 18 years. He is a known expert in thermal characterization methods and their applications.

Literature

[1] A. Schindler, *Identify* – How this New DSC Curve Recognition System Simplifies Polymer Characterization, White Paper, www.netzsch-thermal.analysis.com/en
[2] A. Schindler, Automatic Evaluation and Identification of DSC Curves, Plastics Engineering 2014, www.plasticsengineering.org/ProductFocus/productfocus.aspx?ItemNumber=20498
[3] See Application Notes and Application Sheets at www.netzsch-thermal.analysis.com/en
[4] A. Schindler, C. Strasser, S. Schmölzer, M. Bodek, R. Seniuta and X. Wang, Database-supported thermal analysis involving automatic evaluation, identification and classification of measurement curves, Journal of Thermal Analysis and Calorimetry, DOI 10.1007/s/10973-015-5026-x, http://link.springer.com/article/10.1007/s10973-015-5026-x
[5] See video at https://vimeo.com/143356782

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