Electronic Supplementary Material (ESI) for Analytical Methods.

Electronic Supplementary Information for

Library based identification and characterisation of polymers with nano-FTIR and IR-sSNOM imaging

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Content: Dendrogram of cluster analysis for the range 1700-1300 cm^{-1}

Polymer spectra with library search results

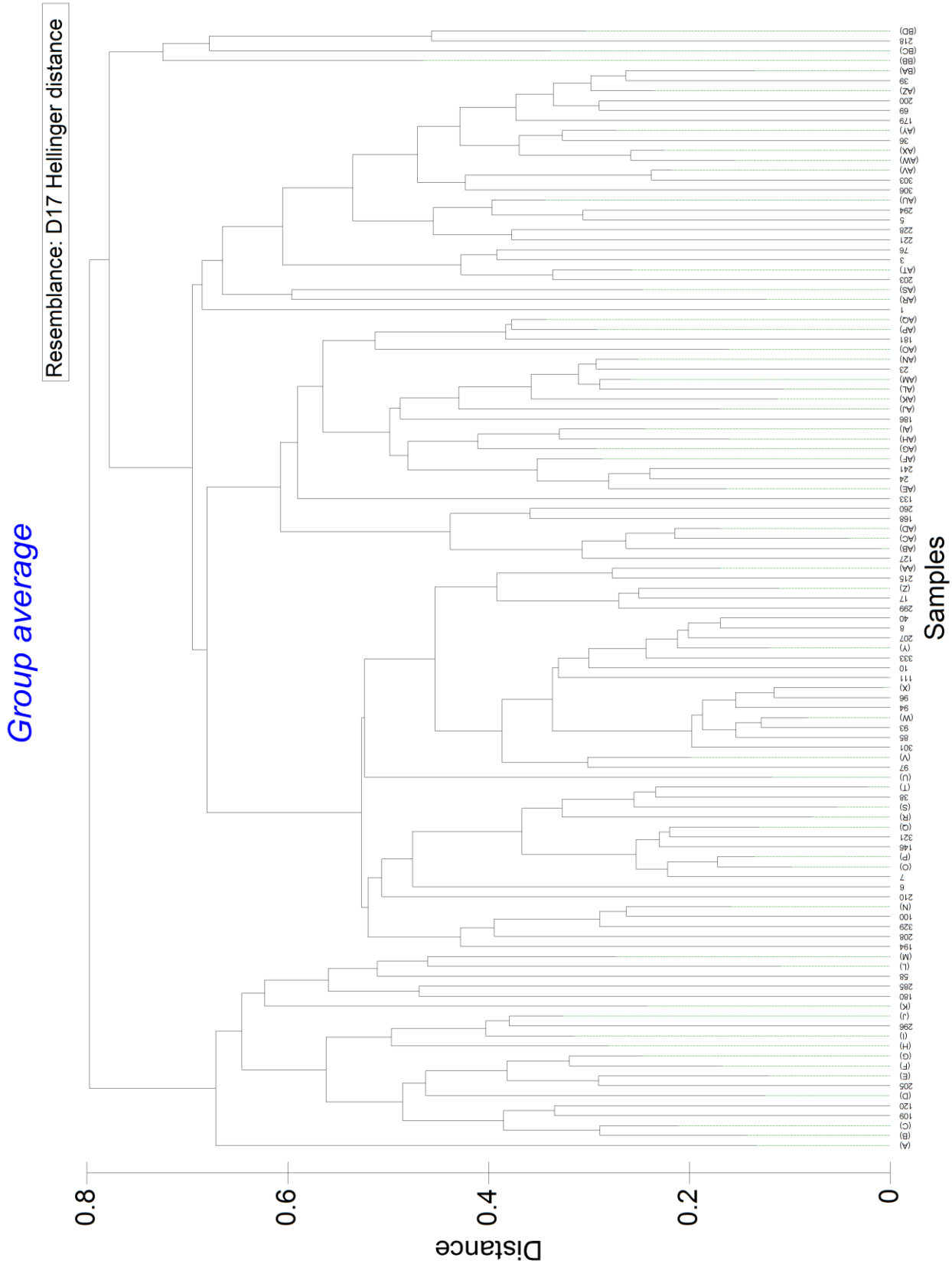


Figure S1. Dendrogram for cluster analysis of reference spectra in the range of 1700-1300 cm^{-1}. The numbers are representing the ID of the spectrum of the database available in reference 1. A:187+188 (PEG), B:117+272+273 (LDPE), C: 53+12+13+52+54+88+80+319+124+224+86+87+276+277+278+219+118+119+116+320+300+225+123+270 (PE), D:78+79 (EVA), E:154+131+63+83+84 (Bee wax), F:74+75 (EVAc), G:71+14+226 (PE wax), H:209+176+177 (PLA), I:178+183 (P1B,P4M1P), J:231+108+325+143+248+247+252+249+229+230+232+250

(PP), K:56+73 (PE-PP copolymer), L:206+244 (POM), M:220+222 (PE-chlorinated), N:55+60 (EPDM), O:330+332+331+334 (Coal), P:302+144+289 (Silk), Q:266+50+11+115+30+313+132+27+28+15+126+267+287+26+29+312+311+315+62+268+314+316+310+317 (Fur), R:149+281+151+152+279+148+147+156+155+160+150+41+42+280+137+105+161+159+157+158, S:196+235 (PA), T:37+51 (Chitin), U:134+135 (Aramid), V:264+265 (Quartz), W:16+286 (Bee wax aged), X:104+106 (fiber natural jute/kapok), Y:245+246 (fiber poplar), Z:121+9+81 (fiber linen/algae), AA:130+129+184 (PAA,MVEMA), AB:153+243 (PVP), AC:238+239 (PUR 1), AD:258+259 (PEUR 1), AE:284+282+283+256+257 (PEUR 2), AF:91+92 (alkyd varnish 1), AG:211+212+236+237 (PCL/PUR), AH:2+182 (ABS/PDDPF), AI:141+142 (PEST 1), AJ:18+20+21 (PEST resin), AK:139+216+217+227+171+172+136+323+174+98+99 (PEST/PET 1), AL:274+275+44+45 (PEST 2), AM:173+189 (PET), AN:43+170+164+163+185 (PBT), AO:261+65+66 (PEST 3), AP:70+72 (EAA/EMA), AQ:192+324+190+191+25+193 (P(R)MA), AR:295+125+112+114 (alkyd varnish 2), AS:204+242 (PVF), AT:67+288 (Silicone rubber), AU:4+95+197+33+35+32+318 (CA), AV:145+328+223+297 (nitrile and natural rubber), AW:307+201+327+202+107+263 (PVC), AX:101+102+128 (hydroxypropyl-Ce), AY:309+89+90+47+48+49+103+308+113+31+269+34+82+122 (Ce), AZ:140+304+305 (Carboxylated PVC), BA:198+199+77+240 (PVA), BB:59+57+61 (rubber), BC:298+291+290+293+271+292+255+233+254+253+326+64+68 (PS), BD:175+138+165+166+214+ 213+322 (PC), BE:234+195+251 (P(P)SU).

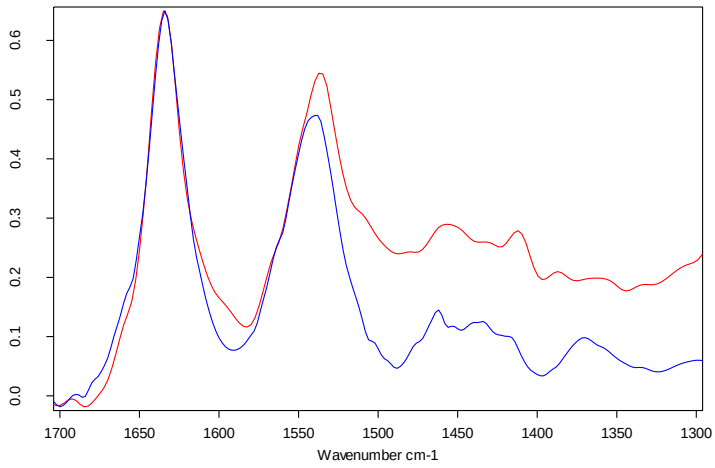
Library search results

The two examples of polyamide, a compound with strong signals in the analysed regions, and polyethylene, a compound with few and weak signals, illustrate the influence of search settings and data treatment for library search results.

1. Library search with *OPUS 7.5* (© Bruker)

The following graphs show nano-FTIR spectra and library search reference spectra after different data treatment steps with *OPUS 7.5* (© Bruker) in red and blue, respectively. All spectra are maximized in absorbance units here for better visibility. The number in the field of compound name (*Substanzname*) is an indicator for the cluster of spectroscopically indistinguishable compounds that the reference spectrum is assigned to in automatic analyis.[1]

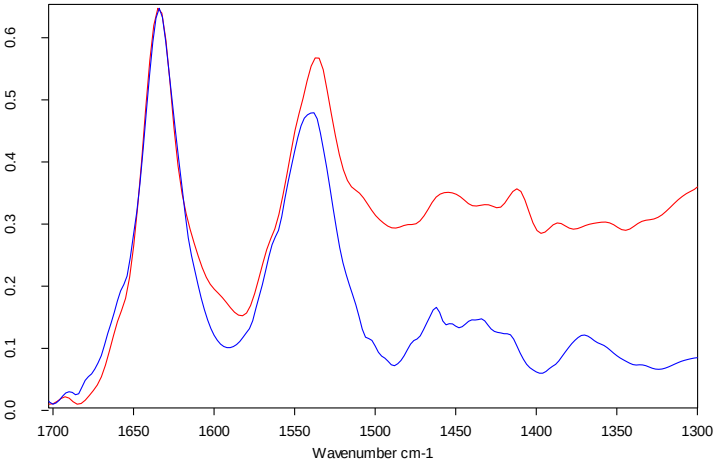
a. Polyamide (PA)



Substanz	7
Kurzzeichen	PA 6
Hersteller	BASF
Nummer	Ultramid B3K
Form (Pulver, Pellet, Folie, Stü	Platte
Messmethode	ATR
Eintrag Nr.	115
Bibliotheksname	BASEMAN_AUTOMATED.S01
Bibliotheksbeschreibung	Finale Bibliothekt für die automatische Auswe
Copyright	Sebastian Primpke

Color	Hit Quality	Compound name	CAS Number	Molecular formula	Molecular weight
	797	7			

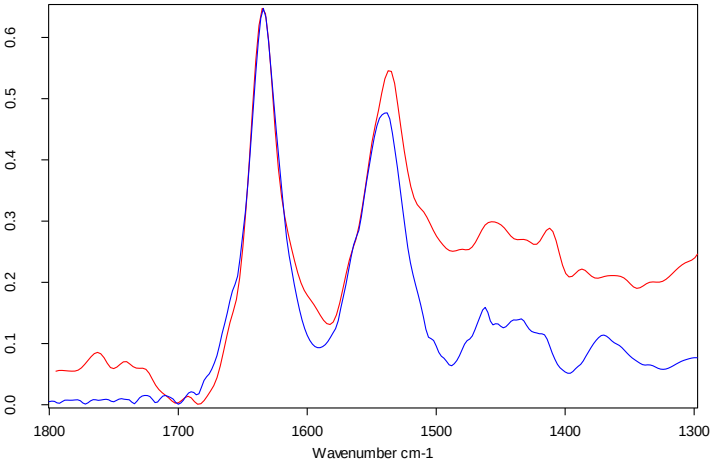
Figure S2. Polyamide, 1700-1300 cm^{-1}, uncorrected.



Substanz	7
Kurzzeichen	PA 6
Hersteller	BASF
Nummer	Ultramid B3K
Form (Pulver, Pellet, Folie, Stü	Platte
Messmethode	ATR
Eintrag Nr.	115
Bibliotheksname	BASEMAN_AUTOMATED.S01
Bibliotheksbeschreibung	Finale Bibliothekt für die automatische Auswe
Copyright	Sebastian Primpke

Color	Hit Quality	Compound name	CAS Number	Molecular formula	Molecular weight
	797	7			

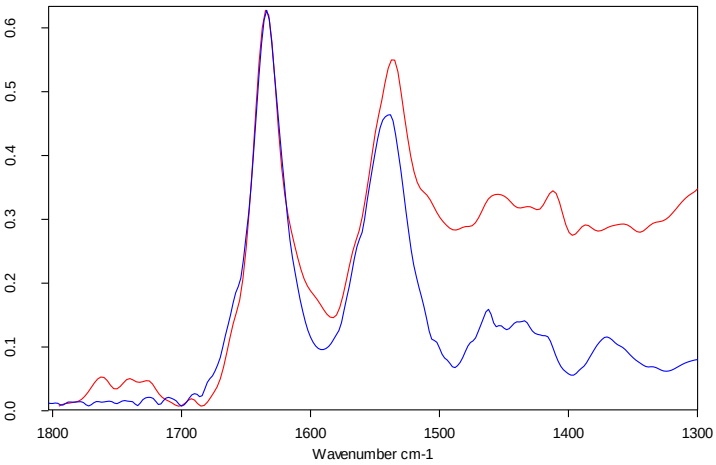
Figure S3. Polyamide, 1700-1300 cm^{-1}, with rubberband correction.



Substanz	7
Kurzzeichen	PA 6
Hersteller	BASF
Nummer	Ultramid B3K
Form (Pulver, Pellet, Folie, Stü	Platte
Messmethode	ATR
Eintrag Nr.	115
Bibliotheksname	BASEMAN_AUTOMATED.S01
Bibliotheksbeschreibung	Finale Bibliothekt für die automatische Auswe
Copyright	Sebastian Primpke

Color	Hit Quality	Compound name	CAS Number	Molecular formula	Molecular weight
	787	7			

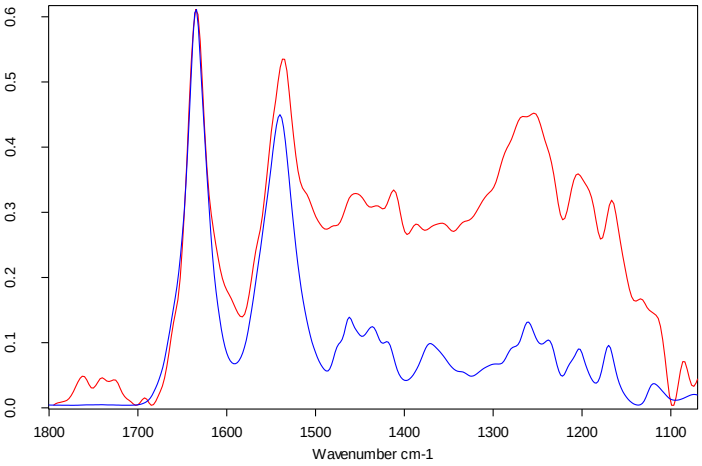
Figure S4. Polyamide, 1800-1300 cm^{-1}, uncorrected.



Substanz	7
Kurzzeichen	PA 6
Hersteller	BASF
Nummer	Ultramid B3K
Form (Pulver, Pellet, Folie, Stü	Platte
Messmethode	ATR
Eintrag Nr.	115
Bibliotheksname	BASEMAN_AUTOMATED.S01
Bibliotheksbeschreibung	Finale Bibliothekt für die automatische Auswe
Copyright	Sebastian Primpke

Color	Hit Quality	Compound name	CAS Number	Molecular formula	Molecular weight
	788	7			

Figure S5. Polyamide, 1800-1300 cm^{-1} with rubberband correction.

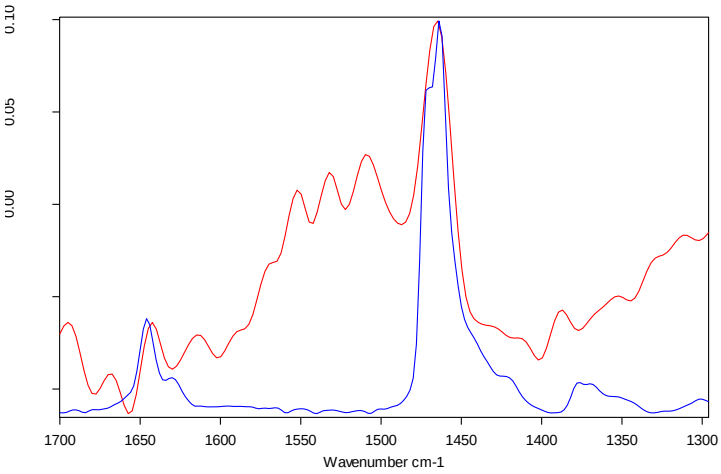


Substanz	7
Kurzzeichen	PA6
Hersteller	mf-folien GmbH
Nummer	cast polyamid-folie PA 6 60µm
Form (Pulver, Pellet, Folie, Stü	Folie
Farbe	transparent
Messmethode	ATR
Eintrag Nr.	114
Bibliotheksname	BASEMAN_AUTOMATED.S01
Bibliotheksbeschreibung	Finale Bibliothekt für die automatische Auswe

Color	Hit Quality	Compound name	CAS Number	Molecular formula	Molecular weight
	697	7			

Figure S6. Polyamide, 1800-1070 cm^{-1} with rubberband correction.

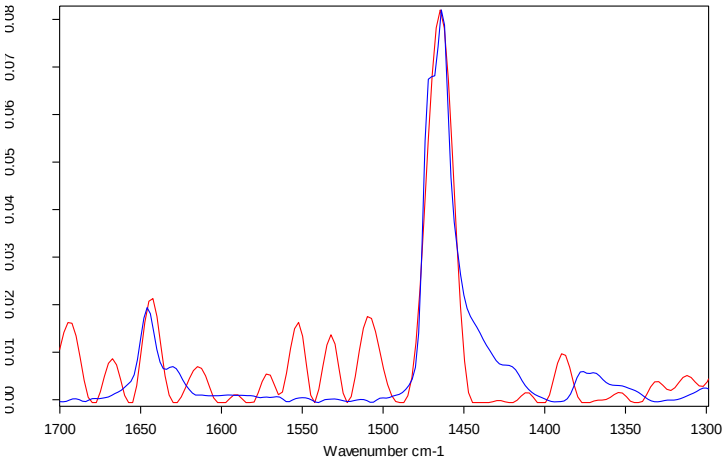
b. Polyethylene (PE)



Substanz	1
Kurzzeichen	LDPE
Hersteller	RSH Polymere
Form (Pulver, Pellet, Folie, Stü	Granulat
Messmethode	ATR
Eintrag Nr.	85
Bibliotheksname	BASEMAN_AUTOMATED.S01
Bibliotheksbeschreibung	Finale Bibliothekt für die automatische Auswe
Copyright	Sebastian Primpke

Color	Hit Quality	Compound name	CAS Number	Molecular formula	Molecular weight
	530	1			

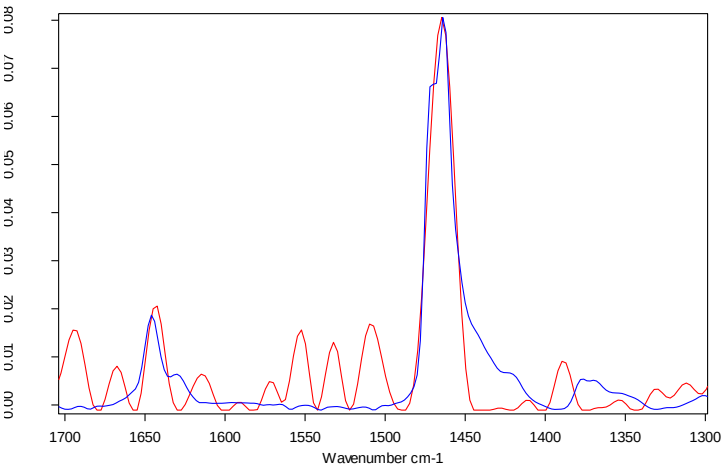
Figure S7. Polyethylene, 1700-1300 cm^{-1}, uncorrected.



Substanz	1
Kurzzeichen	LDPE
Hersteller	RSH Polymere
Form (Pulver, Pellet, Folie, Stü	Granulat
Messmethode	ATR
Eintrag Nr.	85
Bibliotheksname	BASEMAN_AUTOMATED.S01
Bibliotheksbeschreibung	Finale Bibliothekt für die automatische Auswe
Copyright	Sebastian Primpke

Color	Hit Quality	Compound name	CAS Number	Molecular formula	Molecular weight
	591	1			

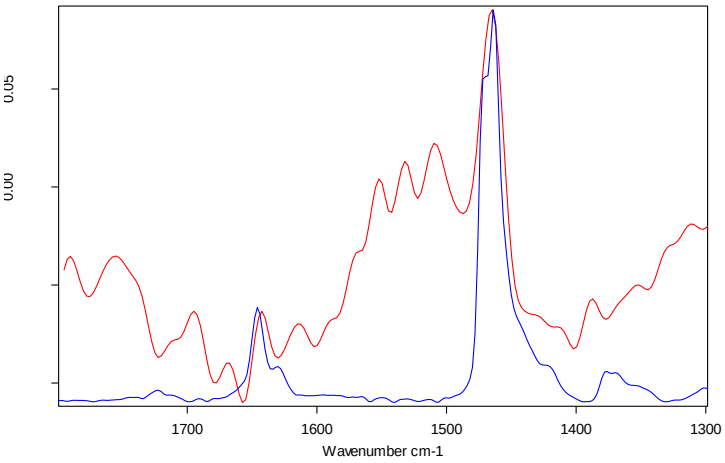
Figure S8. Polyethylene, 1700-1300 cm^{-1}, with rubberband correction.



Substanz	1
Kurzzeichen	LDPE
Hersteller	RSH Polymere
Form (Pulver, Pellet, Folie, Stü	Granulat
Messmethode	ATR
Eintrag Nr.	85
Bibliotheksname	BASEMAN_AUTOMATED.S01
Bibliotheksbeschreibung	Finale Bibliothekt für die automatische Auswe
Copyright	Sebastian Primpke

Color	Hit Quality	Compound name	CAS Number	Molecular formula	Molecular weight
	648	1			

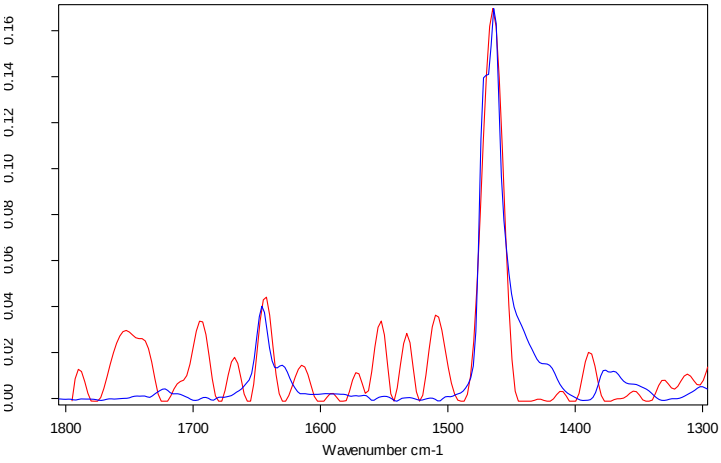
Figure S9. Polyethylene, 1700-1300 cm^{-1} with rubberband correction and exclusion of water (1600-1500 cm^{-1}).



Substanz	1
Kurzzeichen	LDPE
Hersteller	RSH Polymere
Form (Pulver, Pellet, Folie, Stü	Granulat
Messmethode	ATR
Eintrag Nr.	85
Bibliotheksname	BASEMAN_AUTOMATED.S01
Bibliotheksbeschreibung	Finale Bibliothekt für die automatische Auswe
Copyright	Sebastian Primpke

Color	Hit Quality	Compound name	CAS Number	Molecular formula	Molecular weight
	505	1			

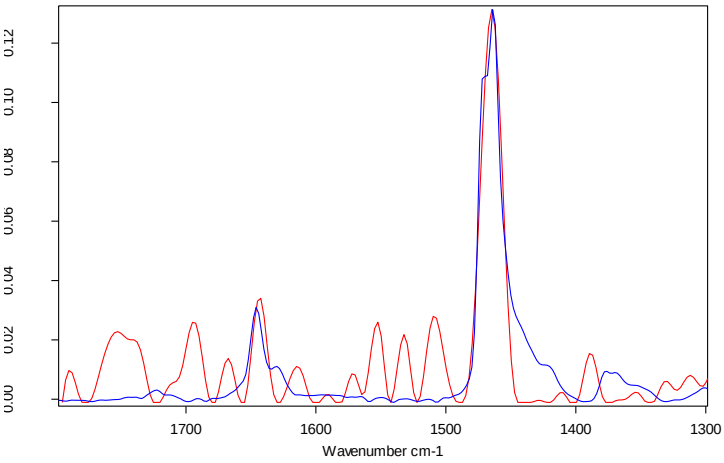
Figure S10. Polyethylene, 1800-1300 cm^{-1}, uncorrected.



Substanz	1
Kurzzeichen	LDPE
Hersteller	RSH Polymere
Form (Pulver, Pellet, Folie, Stü	Granulat
Messmethode	ATR
Eintrag Nr.	85
Bibliotheksname	BASEMAN_AUTOMATED.S01
Bibliotheksbeschreibung	Finale Bibliothekt für die automatische Auswe
Copyright	Sebastian Primpke

Color	Hit Quality	Compound name	CAS Number	Molecular formula	Molecular weight
	572	1			

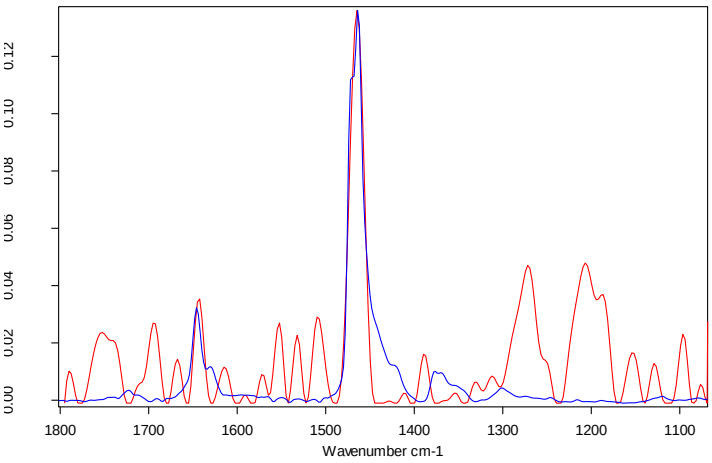
Figure S11. Polyethylene, 1800-1300 cm^{-1} with rubberband correction.



Substanz	1
Kurzzeichen	LDPE
Hersteller	RSH Polymere
Form (Pulver, Pellet, Folie, Stü	Granulat
Messmethode	ATR
Eintrag Nr.	85
Bibliotheksname	BASEMAN_AUTOMATED.S01
Bibliotheksbeschreibung	Finale Bibliothekt für die automatische Auswe
Copyright	Sebastian Primpke

Color	Hit Quality	Compound name	CAS Number	Molecular formula	Molecular weight
	623	1			

Figure S12. Polyethylene, 1800-1300 cm^{-1} with rubberband correction and exclusion of water (1600-1500 cm^{-1}).



Substanz	1
Kurzzeichen	LDPE
Hersteller	RSH Polymere
Form (Pulver, Pellet, Folie, Stü	Granulat
Messmethode	ATR
Eintrag Nr.	85
Bibliotheksname	BASEMAN_AUTOMATED.S01
Bibliotheksbeschreibung	Finale Bibliothekt für die automatische Auswe
Copyright	Sebastian Primpke

Color	Hit Quality	Compound name	CAS Number	Molecular formula	Molecular weight
	514	1			

Figure S13. Polyethylene, 1800-1070 cm^{-1} with rubberband correction.

2. Library search with freeware *siMPle (Aalborg University and Alfred-Wegener-Institute)*
   a. PA

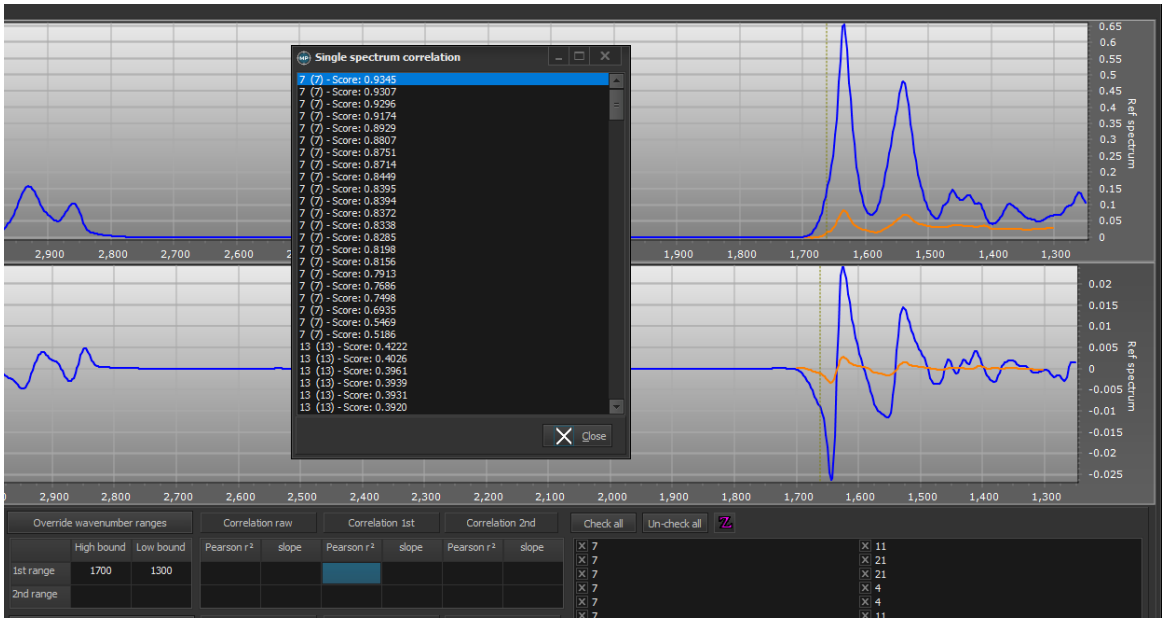


Figure S14. Polyamide, library search in the range 1700-1300 cm^{-1} with clustered database from ref. 1, returning cluster 7, polyamide.

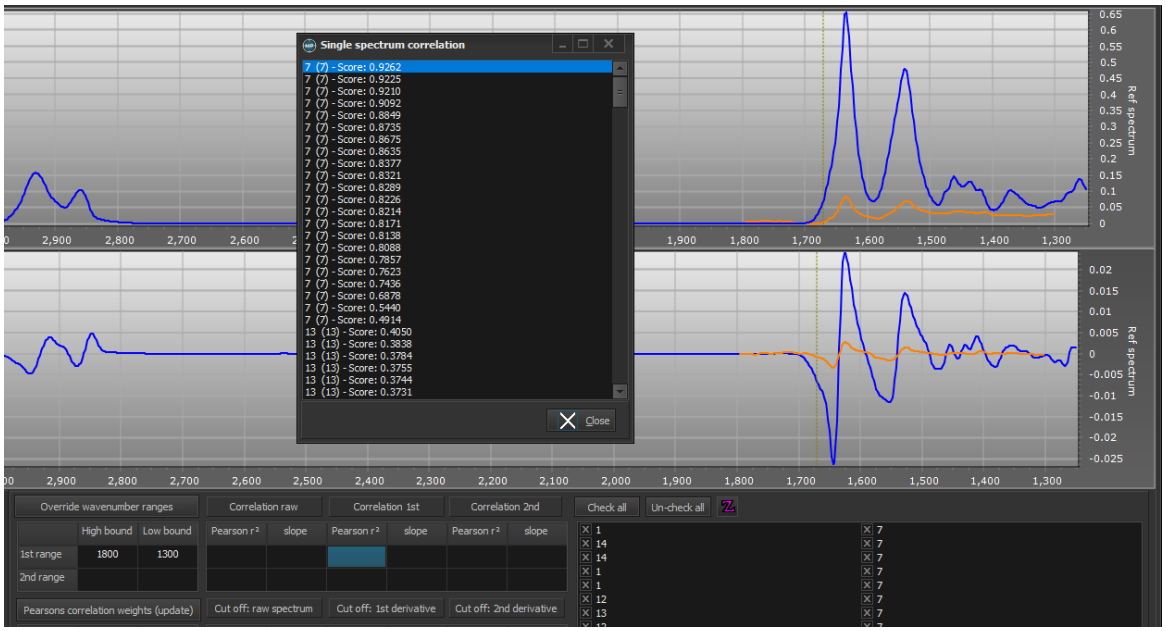


Figure S15. Polyamide, library search in the range 1700-1300 cm^{-1} with clustered database from ref. 1, returning cluster 7, polyamide.

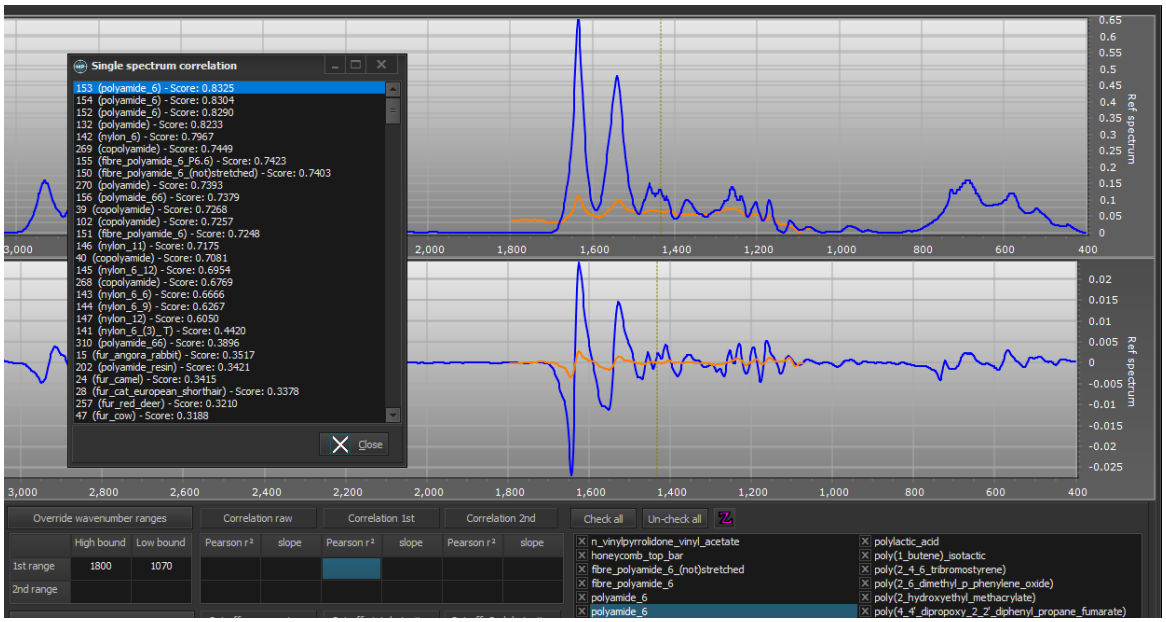


Figure S16. Polyamide, library search with in-house ATR-IR database in the range 1800-1070 cm^{-1} returning polyamide.

b. PE

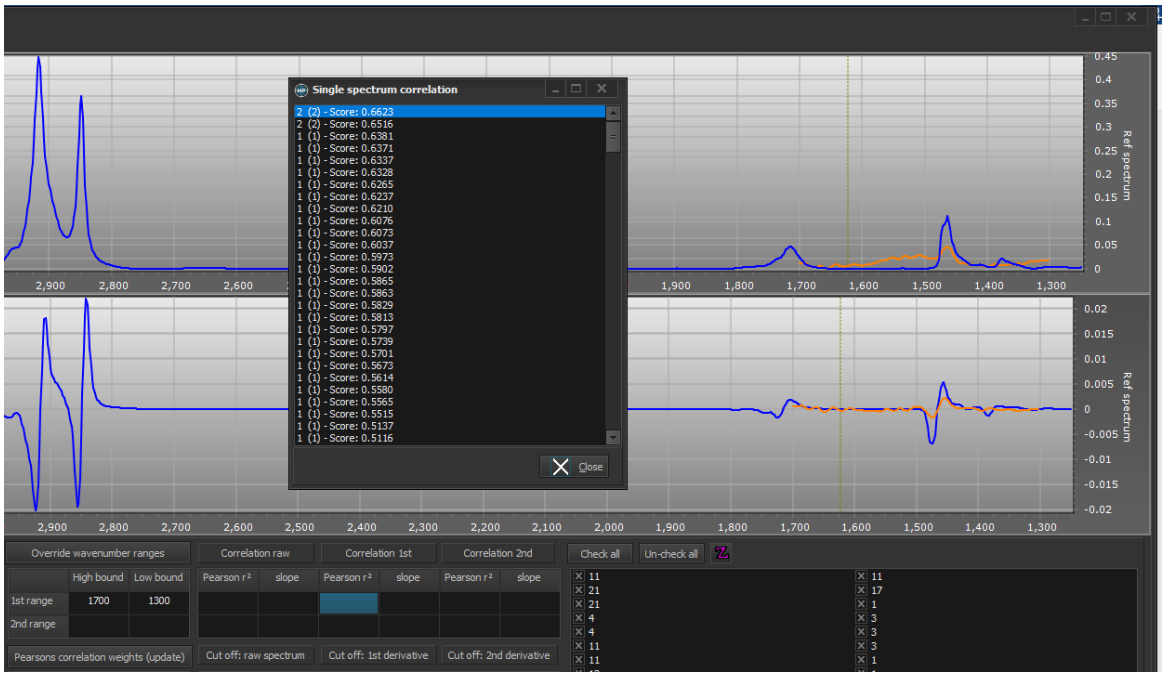


Figure S17. Polyethylene, library search in the range 1700-1300 cm^{-1} and clustered database from ref. 1, returning cluster 2, polyethylene oxidized.

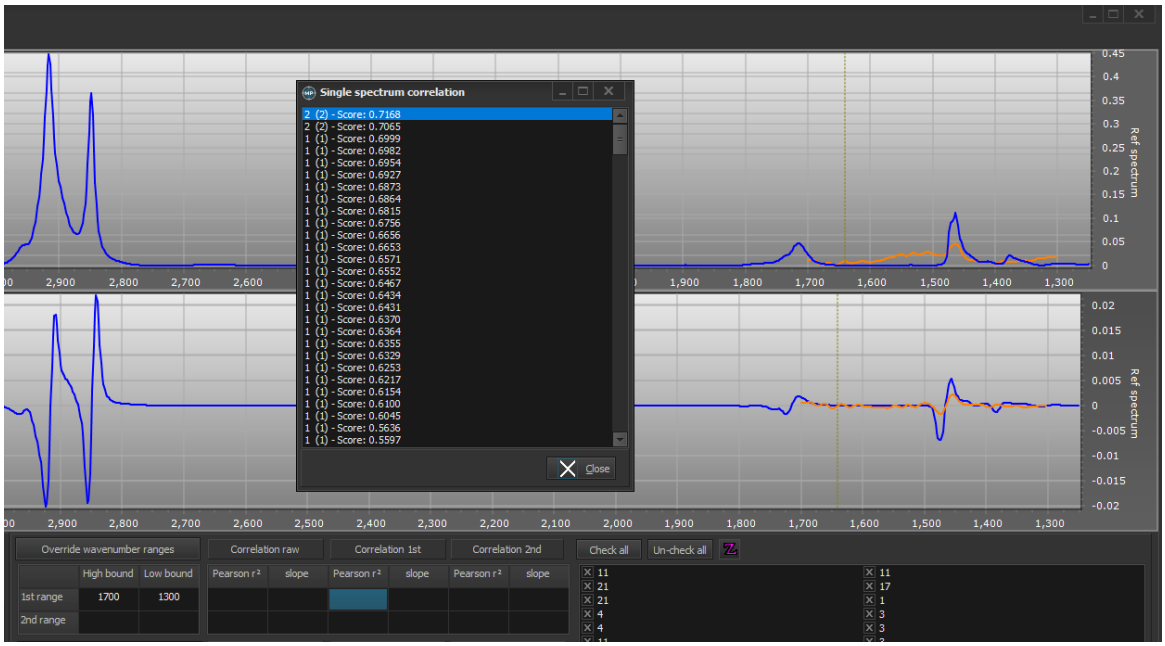


Figure S18. Polyethylene, library search in the range 1700-1300 cm^{-1} with exclusion of water (1600-1500 cm^{-1}) and clustered database from ref. 1, returning cluster 2, polyethylene oxidized.

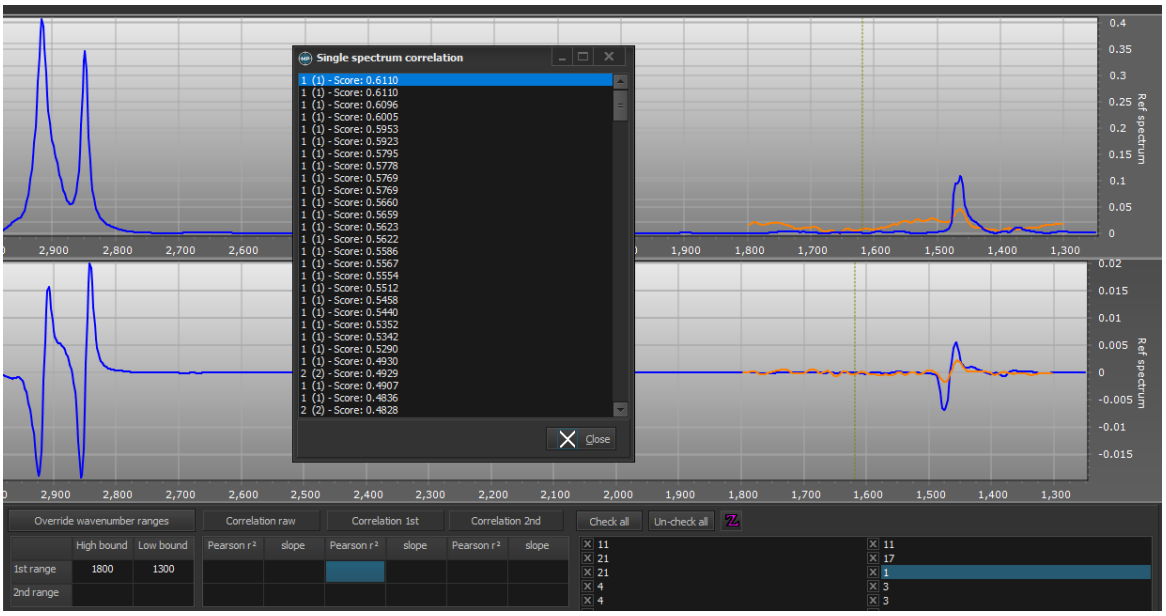


Figure S19. Polyethylene, library search in the range 1800-1300 cm^{-1} and clustered database from ref. 1, returning cluster 1, polyethylene.

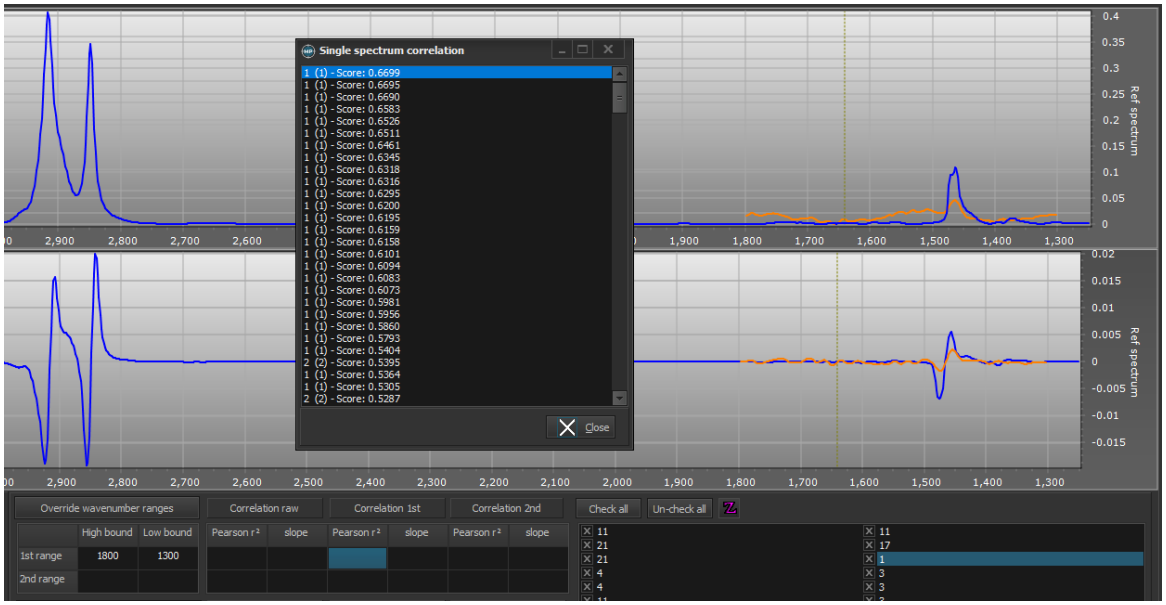


Figure S20. Polyethylene, library search in the range 1800-1300 cm^{-1} with exclusion of water (1600-1500 cm^{-1}) and clustered database from ref. 1, returning cluster 1, polyethylene.

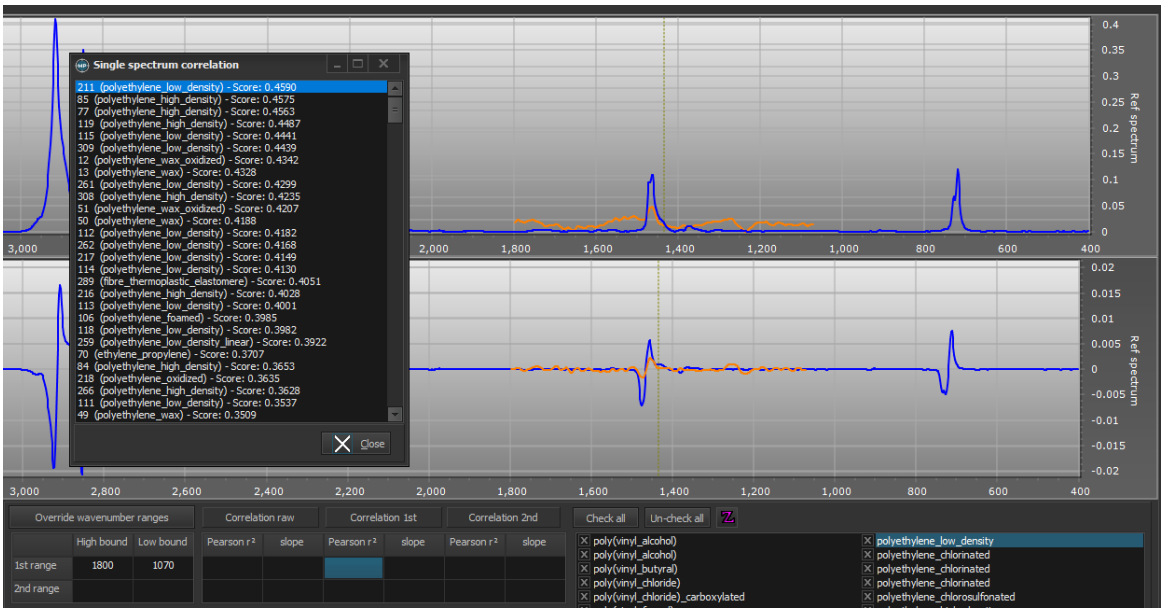
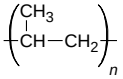
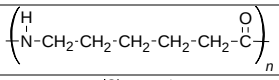
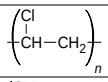
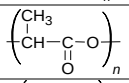
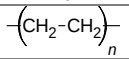
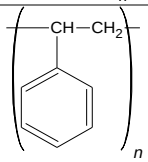
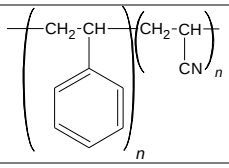
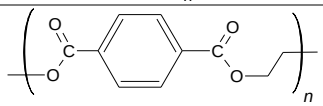
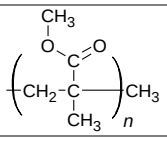
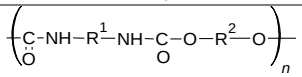


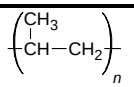
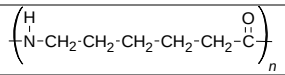
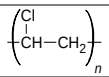
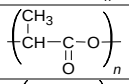
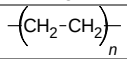
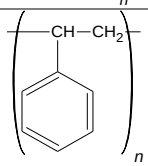
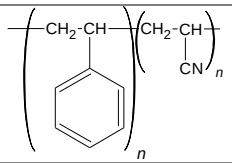
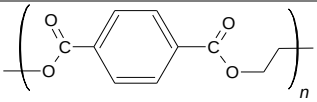
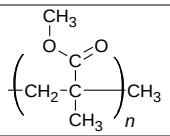
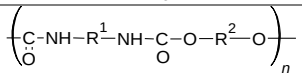
Figure S21. Polyethylene, library search with in-house ATR-IR database in the range 1800-1070 cm^{-1}. Low and high density polyethylene are hardly separable, in the clustered database they belong to the same cluster, "polyethylene".[1]

Table S1. Polymer types, formula unit and OPUS hit qualities (*HQ*) for database comparison in the ranges of 1700-1300 cm^{-1}, 1800-1300 cm^{-1} and over the complete accessible range 1800-1070 cm^{-1}. RB: additional concave rubberband background correction; H_2O excl.: exclusion of water bands between 1600 and 1500 cm^{-1}.

		1700-1300 cm^{-1}			1800-1300 cm^{-1}			1800-1070 cm^{-1}
Polymer	**Formula unit**	***HQ***	***HQ* RB**	***HQ* H_2O excl.**	***HQ***	***HQ* RB**	***HQ* H_2O excl.**	***HQ* RB**
PP		661	693	717	641	655	675	601
PA		797	797	*	787	788	*	697
PVC		572	705*	*	529	579	*	492
PLA		754	768	791	709	710	711	614
PE		530	591	648	505	572	623	514
PS		427	441	469**	406	423	446**	333
SAN		606	615	632	592	610	626	544
PET		501	542	551	770	772	776	716
PMMA		524	592	621	779***	801***	803***	739
PEUR		465	463	*	492	494	*	447

*Water bands were not excluded due to the presence of sample signals in the region. **The boundaries for water exclusion were set to 1584-1519 cm^{-1}.*** assigned to PB(utyl)MA within the same cluster of spectra.

Table S2. Polymer types, formula unit, Pearson coefficient *r* from siMPle for database comparison in the ranges of 1700-1300 cm^{-1}, 1800-1300 cm^{-1} and over the complete accessible range 1800-1070 cm^{-1}. H_2O excl.: exclusion of water bands between 1600 and 1500 cm^{-1}.

		1700-1300 cm^{-1}		1800-1300 cm^{-1}		1800-1070 cm^{-1}
Polymer	**Formula unit**	***r***	***r* H_2O excl.**	***r***	***r* H_2O excl.**	***r***
PP		0.8005	0.8301	0.7487	0.7757	0.6087
PA		0.9345	*	0.9262	*	0.8325
PVC		0.6415	*	0.5730	*	0.4423
PLA		0.8850	0.9063	0.8458	0.8476	0.7182
PE		0.6623	0.7168	0.6110	0.6699	0.4590
PS		0.4724	0.5063**	0.4450	0.4794**	0.3640
SAN		0.7393	0.7494	0.7101	0.7130	0.4639
PET		0.6880	0.7025	0.9420	0.9448	0.8700
PMMA		0.4917	0.5437	0.8321	0.8423	0.7821
PEUR		0.5760	*	0.5643	*	0.5564

*Water bands were not excluded due to the presence of sample signals in the region. **The boundaries for water exclusion were set to 1584-1519 cm^{-1}.

1. Primpke, S.; Wirth, M.; Lorenz, C.; Gerdts, G., Reference database design for the automated analysis of microplastic samples based on Fourier transform infrared (FTIR) spectroscopy. *Anal Bioanal Chem* **2018,** *410* (21), 5131-5141.