Addendum to PT report on SCCP & MCCP in Polymer April 2016

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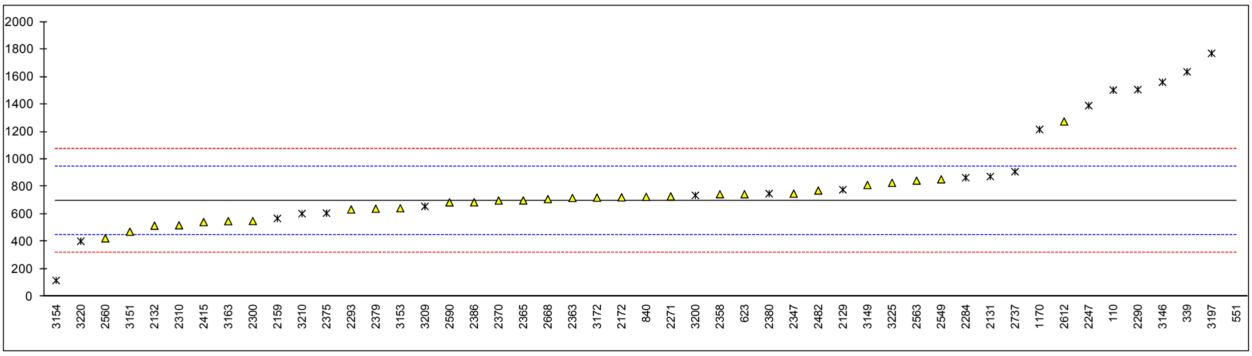
CONTENTS

1 INTRODUCTION

After the publication of the PT report iis16P06 a participant questioned the evaluation of SCCP in sample #16571, as visualized in below graph:



A relatively large group of nine laboratories reported significantly higher SCCP concentrations in sample #16571 than the other laboratories. From the nine high test results, no less than eight were excluded from the statistical evaluation, see the PT report iis16P06. In this addendum it is tried to find an explanation for the deviating test results.

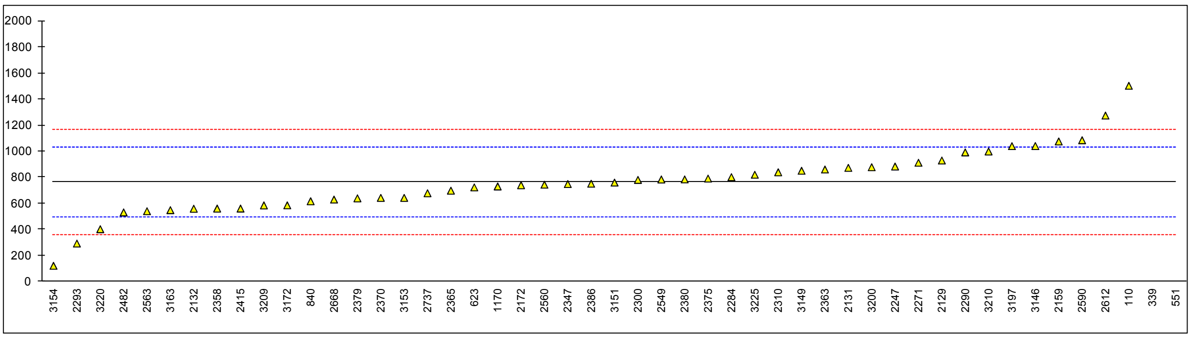
2 EVALUATION

During the evaluation of the reported test results in the report iis16P06, the different procedures as used by the participants for detection, identification and quantification, were not taken into account. Therefore the participants were requested to report some details about this after publication of the PT report. The received details are listed in appendix 2.

The method used by the majority of the laboratories, ISO/DIS18219 (and ISO18219:2015), mentions (requires) to use electron capture negative ionization mass spectrometry (GC-ECNI-MS). This technique is also used in the test method published by CADS (Cooperation at DSI, the German Shoe Institute). Other laboratories did use GC/MSD, GC/MS/MS, GC/ECD and GC/MS after catalytic hydrogenation.
A problem associated with this GC-ECNI-MS is lack of selectivity, which is also a problem with GC-EI-MS and GC/MSD. Especially problems might occur when mixtures of SCCPs and MCCPs are present. Reth and Oehme (literature 3) studied the limitations of GC-ECNI-MS for the analysis of SCCP and MCCP. The analysis can be disturbed by mass overlap caused by congeners with the same nominal mass, but with five carbon atoms more and two chlorine atoms less (e.g., C11H1737Cl35Cl6 (m/z 395.9), a SCCP component and C16H2935Cl5 (m/z 396.1), a MCCP component). Similar is valid for m/z 347 and m/z 349, both abundant ions for C10H15Cl7 (=SCCP) and C15H27Cl5 (= MCCP), see literature 4. This can lead to over- and under-estimations of the concentrations of the congener-groups. The authors of the study concluded that quantification of the most abundant congeners (C11–C14) may not be affected by this interference, if isotopic ratios, retention time changes and shapes of the signals are investigated. The impact of the problem with ECNI-MS may further be reduced when a good choice of ions, e.g. the [HCl2]- and [Cl2]- ions are selected for quantification instead of the [M–Cl]- and [M–HCl]- cluster ions that are subject to interference from other CP homologues. Moreover, [M–Cl]- ions always show lower responses than the [HCl2]- and [Cl2]- ions, see literature 2. Another solution for the above problems is to use HRMS, but this technique is quite expensive and is therefore rarely used in routine analyses.

ISO18219:2015 mentions that ions m/z 347, 361, 375 and 389 should be used for SCCP. The CADS method mentions the same ion masses, but also it mentions that ions m/z 403, 417, 431 and 445 should be used for MCCP. The draft ISO/DIS18219:2013 did mention 4 other ions m/z 327, 375, 409 and 423, which are the preferred ions in the above mentioned literature studies. Unfortunately, the reason for the choice of the ion masses is not mentioned in the test methods.
As the wrong choice of ions may lead to over-or under-estimation of SCCP, this may be visible in the ratio of reported SCCP:MCCP concentrations. Overestimation of SCCP will lead to a high ratio and underestimation will lead to a low ratio. In the table 1, the ratios for all reported test results are given. The majority of the laboratories agrees about a low ratio SCCP:MCCP of 0.28:0.72 (see page 6), meaning that 28% of the mixture will consist of SCCP. Only few laboratories reported that the mixture contained more than 50% SCCP.
It is remarkable to observe that most of the laboratories that reported a high ratio, are in the group of relatively high test results on sample #16571: lab 1170 (ratio 0.47:0.53), lab 2247 (ratio 0.44:0.56), lab 2290 (ratio 0.42:0.58), lab 3146 (ratio 0.42:0.58), lab 3197 (ratio 0.48:0.52). Exceptions are labs 339 and 551, both have low ratios, but also high test results.

The above observed phenomenon may give a solution for the evaluation of the reported test results without having detailed knowledge of the identification and quantification method of each of the participating laboratories. All laboratories did receive identical samples that all contained the same SCCP/MCCP mixture and therefore all laboratories should have found the same ratio SCCP/MCCP in both PT samples.
Therefore it was decided to use the sum of the reported SCCP and MCCP test results together with the average ratio SCCP/MCCP to recalculate all individual SCCP and MCCP test result by first summation of the SCCP and MCCP test results per sample and then re-dividing the sum by means of the average ratio 0.28:0.72.
When all test results are thus recalculated by application of one ratio for all laboratories, the largest part of the group of high test results for sample #16571 has disappeared, see below graph.



recalculated SCCP test results of sample #16571 using a fixed ratio 0:28:0.72 for all laboratories

3 CONCLUSION

The conclusion is that the influence of the identification and quantification procedures is significant. During next year's PT the participants will be requested to report details about the identification and quantification of SCCP in the extract solution. The answers will enable investigation of the influence of this part of the analysis on the test results during the writing of the final report.

APPENDIX 1

table 1 – reported test results and ratios SCCP:MCCP per laboratory

lab	method	sample #16570			sample #16571		
		SCCP	MCCP	ratio	SCCP	MCCP	ratio
110	In house	2803.0431	-----	-----	1503.6404	-----	-----
339	In house	2936	11920	0.20 : 0.80	1637	7140	0.19 : 0.81
551	In house	5458.70	31117.64	0.15 : 0.85	4062.74	31805.80	0.11 : 0.89
623	ISO18219	1653.44	4052.77	0.29 : 0.71	746.21	1841.58	0.29 : 0.71
840	In house	1361	3349	0.29 : 0.71	727	1481	0.33 : 0.67
1170	In house	1813	2015	0.47 : 0.53	1217	1396	0.47 : 0.53
2115		-----	-----	-----	-----	-----	-----
2129	ISO/DIS18219	1963	4935	0.28 : 0.72	779	2545	0.23 : 0.77
2131	In house	1765	-----	-----	874.5	-----	-----
2132	ISO/DIS18219	1030	2954	0.26 : 0.74	517	1486	0.26 : 0.74
2159	In house	1307.66	4744.4	0.22 : 0.78	569.56	3275.85	0.15 : 0.85
2172	In house	1231.40	4156.67	0.23 : 0.77	723.55	1923.01	0.27 : 0.73
2247	In house	2266.43	4237.72	0.35 : 0.65	1390.66	1768.12	0.44 : 0.56
2255		-----	-----	-----	-----	-----	-----
2271	ISO/DIS18219	1933	5047	0.28 : 0.72	730	2532	0.22 : 0.78
2284	ISO/DIS18219	2229.58	4737.03	0.32 : 0.68	866.37	2001.96	0.30 : 0.70
2290	ISO/DIS18219	2909	3705	0.44 : 0.56	1507	2039	0.42 : 0.58
2293	ISO/DIS18219	1166.72	952.00	**0.55 : 0.45**	634.920	414.40	**0.61 : 0.39**
2300	In house	1242.08	4355.74	0.22 : 0.78	551.15	2241.38	0.20 : 0.80
2310	ISO/DIS18219	1181	3861	0.23 : 0.77	520	2481	0.17 : 0.83
2347	ISO/DIS18219	1503.50	-----	-----	750.25	-----	-----
2350		-----	-----	-----	-----	-----	-----
2358	ISO/DIS18219	1537.1	2854.7	0.35 : 0.65	745.9	1261.6	0.37 : 0.63
2363	ISO/DIS18219	1515.5	4244.7	0.26 : 0.74	718.9	2359.5	0.23 : 0.77
2365	ISO/DIS18219	1513.5	3806.0	0.28 : 0.72	700.5	1797.5	0.28 : 0.72
2369		-----	-----	-----	-----	-----	-----
2370	EPA8082A	1300	3500	0.27 : 0.73	700	1600	0.30 : 0.70
2375	ISO/DIS18219	1190.51	4226.32	0.22 : 0.78	607.93	2221.62	0.21 : 0.79
2379	ISO/DIS18219	1719.8	-----	-----	640.6	-----	-----
2380	CADS v4:112015	1230.15	3292.34	0.27 : 0.73	750.16	2056.25	0.27 : 0.73
2386	ISO/DIS18219	1586	4014	0.28 : 0.72	687	2001	0.26 : 0.74
2390		-----	-----	-----	-----	-----	-----
2415	In house	1147	2861	0.29 : 0.71	543	1465	0.27 : 0.73
2482	CADS v1:072015	1641	2232	0.42 : 0.58	772.7	1130	0.41 : 0.59
2549	ISO/DIS18219	2201.0	3958.7	0.36 : 0.64	854.5	1950.6	0.30 : 0.70
2560	In house	173	890	0.16 : 0.84	425	2237	0.16 : 0.84
2563	ISO/DIS18219	1804	2103	0.46 : 0.54	845	1090	0.44 : 0.56
2590	ISO/DIS18219	1936.56	6420.77	0.23 : 0.77	686.44	3192.44	0.18 : 0.82
2612	In house	2233.95	-----	-----	1275.45	-----	-----
2661		639	772	0.45 : 0.55	-----	-----	-----
2668	ISO/DIS18219	2138.57	3946.52	0.35 : 0.65	710.37	1544.22	0.32 : 0.68
2737	In house	1425.0	3736.0	0.28 : 0.72	910.0	1517.0	0.37 : 0.63
3124	In house	1887	1523	**0.55 : 0.45**	-----	-----	-----
3146	In house	3070.08	4166.82	0.42 : 0.58	1561.2	2158.7	0.42 : 0.58
3149	In house	1370	3300	0.29 : 0.71	813	2230	0.27 : 0.73
3151	In house	1121.9	3780.63	0.23 : 0.77	473.3	2245.65	0.17 : 0.83
3153	In house	1447	-----	-----	644	-----	-----
3154	In house	232.49	504.28	0.32 : 0.68	118.87	321.10	0.27 : 0.73
3163	In house	210	-----	-----	550	-----	-----
3172	ISO/DIS18219	1319	2592	0.34 : 0.66	721	1375	0.34 : 0.66
3197	In house	2547	2912	0.47 : 0.53	1771	1947	0.48 : 0.52
3200	In house	1258.3	2294.3	0.35 : 0.65	737.4	2403.2	0.23 : 0.77
3209	ISO18219	1077.3	3232.1	0.25 : 0.75	657.3	1437.8	0.31 : 0.69
3210	In house	1067.41	4823.07	0.18 : 0.82	604.47	2966.53	0.17 : 0.83
3220	In house	839.1	-----	-----	403.9	-----	-----
3225	ISO/DIS18219	2545.83	4426.50	0.37 : 0.63	829.04	2103.96	0.28 : 0.72
3237		-----	-----	-----	-----	-----	-----
	min SCCP			0.15 : 0.85			0.11 : 0.89
	max MCCP			0.55 : 0.45			0.61 : 0.39
	average ratio			0.29 : 0.71			0.27 : 0.73
	st.dev (ratio)			0.10			0.11
	RSD%	33%	39%		23%	31%	

When the reported test results are recalculated using the average ratio SCCP : MCCP = 0.28 : 0.72, a better agreement between the test results is observed, see below table.

lab	method	sample #16570			sample #16571		
		SCCP	MCCP	ratio	SCCP	MCCP	ratio
110	In house	-----	-----	-----	-----	-----	-----
339	In house	4160	10696	0.28 : 0.72	2458	6319	0.28 : 0.72
551	In house	10241	26335	0.28 : 0.72	10043	25825	0.28 : 0.72
623	ISO18219	1598	4108	0.28 : 0.72	725	1863	0.28 : 0.72
840	In house	1319	3391	0.28 : 0.72	618	1590	0.28 : 0.72
1170	In house	1072	2756	0.28 : 0.72	732	1881	0.28 : 0.72
2115		-----	-----	-----	-----	-----	-----
2129	ISO/DIS18219	1931	4967	0.28 : 0.72	931	2393	0.28 : 0.72
2131	In house	-----	-----	-----	-----	-----	-----
2132	ISO/DIS18219	1116	2868	0.28 : 0.72	561	1442	0.28 : 0.72
2159	In house	1695	4357	0.28 : 0.72	1077	2769	0.28 : 0.72
2172	In house	1509	3879	0.28 : 0.72	741	1906	0.28 : 0.72
2247	In house	1821	4683	0.28 : 0.72	884	2274	0.28 : 0.72
2255		-----	-----	-----	-----	-----	-----
2271	ISO/DIS18219	1954	5026	0.28 : 0.72	913	2349	0.28 : 0.72
2284	ISO/DIS18219	1951	5016	0.28 : 0.72	803	2065	0.28 : 0.72
2290	ISO/DIS18219	1852	4762	0.28 : 0.72	993	2553	0.28 : 0.72
2293	ISO/DIS18219	593	1525	0.28 : 0.72	294	756	0.28 : 0.72
2300	In house	1567	4030	0.28 : 0.72	782	2011	0.28 : 0.72
2310	ISO/DIS18219	1412	3630	0.28 : 0.72	840	2161	0.28 : 0.72
2347	ISO/DIS18219	-----	-----	-----	-----	-----	-----
2350		-----	-----	-----	-----	-----	-----
2358	ISO/DIS18219	1230	3162	0.28 : 0.72	562	1445	0.28 : 0.72
2363	ISO/DIS18219	1613	4147	0.28 : 0.72	862	2216	0.28 : 0.72
2365	ISO/DIS18219	1489	3830	0.28 : 0.72	699	1799	0.28 : 0.72
2369		-----	-----	-----	-----	-----	-----
2370	EPA8082A	1344	3456	0.28 : 0.72	644	1656	0.28 : 0.72
2375	ISO/DIS18219	1517	3900	0.28 : 0.72	792	2037	0.28 : 0.72
2379	ISO/DIS18219	-----	-----	-----	-----	-----	-----
2380	CADS v4:112015	1266	3256	0.28 : 0.72	786	2021	0.28 : 0.72
2386	ISO/DIS18219	1568	4032	0.28 : 0.72	753	1935	0.28 : 0.72
2390		-----	-----	-----	-----	-----	-----
2415	In house	1122	2886	0.28 : 0.72	562	1446	0.28 : 0.72
2482	CADS v1:072015	1084	2789	0.28 : 0.72	533	1370	0.28 : 0.72
2549	ISO/DIS18219	1725	4435	0.28 : 0.72	785	2020	0.28 : 0.72
2560	In house	298	765	0.28 : 0.72	745	1917	0.28 : 0.72
2563	ISO/DIS18219	1094	2813	0.28 : 0.72	542	1393	0.28 : 0.72
2590	ISO/DIS18219	2340	6017	0.28 : 0.72	1086	2793	0.28 : 0.72
2612	In house	-----	-----	-----	-----	-----	-----
2661		395	1016	-----	-----	-----	-----
2668	ISO/DIS18219	1704	4381	0.28 : 0.72	631	1623	0.28 : 0.72
2737	In house	1445	3716	0.28 : 0.72	680	1747	0.28 : 0.72
3124	In house	955	2455	-----	-----	-----	-----
3146	In house	2026	5211	0.28 : 0.72	1042	2678	0.28 : 0.72
3149	In house	1308	3362	0.28 : 0.72	852	2191	0.28 : 0.72
3151	In house	1373	3530	0.28 : 0.72	761	1958	0.28 : 0.72
3153	In house	-----	-----	-----	-----	-----	-----
3154	In house	206	530	0.28 : 0.72	123	317	0.28 : 0.72
3163	In house	-----	-----	-----	-----	-----	-----
3172	ISO/DIS18219	1095	2816	0.28 : 0.72	587	1509	0.28 : 0.72
3197	In house	1529	3930	0.28 : 0.72	1041	2677	0.28 : 0.72
3200	In house	995	2558	0.28 : 0.72	879	2261	0.28 : 0.72
3209	ISO18219	1207	3103	0.28 : 0.72	587	1508	0.28 : 0.72
3210	In house	1649	4241	0.28 : 0.72	1000	2571	0.28 : 0.72
3220	In house	-----	-----	-----	-----	-----	-----
3225	ISO/DIS18219	1952	5020	0.28 : 0.72	821	2112	0.28 : 0.72
3237		-----	-----	-----	-----	-----	-----
average		1388	3570		766	1971	
RSD%		34%	34%		23%	23%	

APPENDIX 2

Analytical details

ion masses m/z used for the identification and quantification of SCCP

lab	2132	2159	2271	2300	2370	2612	2737	3151	3197
	LCMSMS		ECNI-MS	ECNI-MS	ECNI-MS	MSD	ECNI-MS		
m/z									
103						x			
105						x			
108						x			
116						x			
327[1]		x						x	
347[2]		x	x	x	x		x	x	
361[2]		x	x	x	x		x	x	
375[1,2]		x	x	x	x		x	x	x
389[2]		x	x	x	x		x	x	x
409[1]		x						x	x
423[1]		x						x	x
455	x								x
457	x								
469	x								
471	x								
483	x								
485	x								

ion mass[1] mentioned in Annex A of ISO/DIS18219:2012 and in literature 1
ion mass[2] mentioned in Annex A of ISO18219:2015 and in CADS V4:112014

ion masses m/z used for the identification and quantification of MCCP

lab	2132	2159	2271	2300	2370	2612	2737	3151	3197
	LCMSMS		ECNI-MS	ECNI-MS	ECNI-MS	MSD	ECNI-MS		
m/z									
403[3]		x	x	x	x	x	x	x	x
417[3]		x	x	x	x	x	x	x	x
431[3]		x	x	x		x	x	x	
434									x
438									x
445[3]		x	x	x		x		x	
450									x
497	x								
499	x								
513	x								
515	x	x						x	

ion mass[3] mentioned in CADS V4:112014

APPENDIX 3

Literature:

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