

**Supplemental Table A.** Reference Values Based on Hardener Spiked on Filters

Level	Description	ID <sup>a</sup>	Hardener Mass Spiked on Filter		Reference Values - Calculated Mass on Filter $\mu\text{g}/\text{sample}$			
			$\mu\text{g}$ hardener/sample	NCO $\mu\text{g}/\text{sample}$ <sup>b</sup>	NCO-HDI monomer <sup>c,d</sup>	NCO-IPDI Monomer <sup>c,e</sup>	NCO-HDI Oligomers <sup>c,f</sup>	NCO-IPDI Oligomers <sup>c,g</sup>
1	Zero loading	5	0	0	0	0	0	0
		11	0	0	0	0	0	0
		13	0	0	0	0	0	0
2	Very low loading or 1% UK TWA <sup>g</sup>	4	1.2	0.2	0.0004	0.0004	0.085	0.063
		12	1.2	0.2	0.0004	0.0004	0.085	0.063
		17	1.2	0.2	0.0004	0.0004	0.085	0.063
3	Low loading or 10% UK TWA	1	11.7	1.8	0.0043	0.0045	0.855	0.633
		9	11.7	1.8	0.0043	0.0045	0.855	0.633
		18	11.7	1.8	0.0043	0.0045	0.855	0.633
4a	Medium loading or 100% UK TWA	2	93.3	14.3	0.0340	0.0360	6.840	5.070
		3	93.3	14.3	0.0340	0.0360	6.840	5.070
		8	93.3	14.3	0.0340	0.0360	6.840	5.070
4b	Medium loading or 100% UK TWA	6	117	17.8	0.0430	0.0450	8.550	6.330
		15	117	17.8	0.0430	0.0450	8.550	6.330
		16	117	17.8	0.0430	0.0450	8.550	6.330
5	High loading or 100% UK STEL <sup>h</sup>	7	467	71.4	0.1710	0.1780	34.200	25.300
		10	467	71.4	0.1710	0.1780	34.200	25.300
		14	467	71.4	0.1710	0.1780	34.200	25.300

<sup>a</sup>Sample IDs were randomly and blindly assigned. <sup>b</sup>Based on titration results (NCO Mass = Mass \* 0.153; overall bulk samples has 15.30% NCO by weight). <sup>c</sup>From manufacturer's proprietary info. <sup>d</sup>HDI = 0.24% by weight. <sup>e</sup>IPDI = 0.25% by weight. <sup>f</sup>HDI oligomer = 47.90% by weight. <sup>g</sup>IPDI oligomer = 35.50% by weight. <sup>h</sup>UK TWA is 20  $\mu\text{g}$  NCO/ $\text{m}^3$  and STEL is 70  $\mu\text{g}$  NCO/ $\text{m}^3$  and levels assumed a 1  $\text{m}^3$  sample volume.

**Supplemental Table B.** NCO-HDI and NCO-IPDI Monomers and Oligomers

ID	NCO-HDI monomer µg/sample				NCO-IPDI monomer µg/sample	NCO-HDI oligomers µg/sample			NCO-IPDI oligomers µg/sample		NCO-HDI & NCO-IPDI Oligomers µg/sample
	NIOSH	LC/MS	OSHA	WA- DOSH	WA- DOSH	NIOSH	LC/MS	WA- DOSH	NIOSH	WA- DOSH	OSHA
5	0.0005 <sup>a</sup>	8.5x10 <sup>-7a</sup>	0.013 <sup>b</sup>	0.029 <sup>b</sup>	0.001 <sup>a</sup>	0.003 <sup>a</sup>	1.3x10 <sup>-5a</sup>	0.62 <sup>a</sup>	0.002 <sup>a</sup>	0.147 <sup>a</sup>	0.08 <sup>b</sup>
11	0.0005 <sup>a</sup>	8.5x10 <sup>-7a</sup>	0.013 <sup>b</sup>	0.001 <sup>a</sup>	0.025 <sup>b</sup>	0.003 <sup>a</sup>	0.012	0.62 <sup>a</sup>	0.002 <sup>a</sup>	0.147 <sup>a</sup>	0.08 <sup>b</sup>
13	0.0005 <sup>a</sup>	8.5x10 <sup>-7a</sup>	0.013 <sup>b</sup>	0.029 <sup>b</sup>	0.001 <sup>a</sup>	0.003 <sup>a</sup>	1.3x10 <sup>-5a</sup>	0.62 <sup>a</sup>	0.002 <sup>a</sup>	0.147 <sup>a</sup>	0.08 <sup>b</sup>
4	0.0006, 0.0006 <sup>d</sup>	8.5x10 <sup>-7a</sup>	0.013 <sup>b</sup>	0.029 <sup>b</sup>	0.001 <sup>a</sup>	0.119, 0.113 <sup>d</sup>	0.036	0.62 <sup>a</sup>	0.062, 0.062 <sup>c</sup>	0.147 <sup>a</sup>	0.40
12	0.0013, 0.0005 <sup>a,c</sup>	8.5x10 <sup>-7a</sup>	0.013 <sup>b</sup>	0.029 <sup>b</sup>	0.001 <sup>a</sup>	0.106, 0.113 <sup>c</sup>	0.030	0.62 <sup>a</sup>	0.069, 0.050 <sup>c</sup>	0.147 <sup>a</sup>	0.08 <sup>b</sup>
17	0.0005 <sup>a</sup> , 0.0007 <sup>c</sup>	8.5x10 <sup>-7a</sup>	0.013 <sup>b</sup>	0.029 <sup>b</sup>	0.001 <sup>a</sup>	0.076, 0.113 <sup>c</sup>	0.028	0.62 <sup>a</sup>	0.040, 0.075 <sup>c</sup>	0.147 <sup>a</sup>	0.08 <sup>b</sup>
1	0.0123	0.006	0.013 <sup>b</sup>	0.029 <sup>b</sup>	0.025	1.017	0.272	2.42	0.572	1.500 <sup>b</sup>	1.20
9	0.0060	0.006	0.013 <sup>b</sup>	0.029 <sup>b</sup>	0.025	1.110	0.280	2.61	0.580	1.500 <sup>b</sup>	1.20
18	0.0113	0.006	0.013 <sup>b</sup>	0.029 <sup>b</sup>	0.001 <sup>a</sup>	1.210	0.291	2.80	0.620	1.500 <sup>b</sup>	1.20
2	<sup>c</sup>	0.048	0.040	0.029 <sup>b</sup>	0.064	<sup>c</sup>	1.729	14.60	<sup>c</sup>	3.800	4.70
3	<sup>c</sup>	0.060	0.060	0.073	0.057	<sup>c</sup>	2.096	14.80	<sup>c</sup>	4.050	8.80
8	<sup>c</sup>	0.065	0.040	0.093	0.064	<sup>c</sup>	2.162	15.30	<sup>c</sup>	4.560	5.90
6	<sup>-d</sup>	0.065	0.070	0.153	0.076	<sup>-d</sup>	2.394	18.50	<sup>-d</sup>	4.930	12
15	0.0813	0.065	0.070	0.103	0.076	12.500	2.468	22.60	5.730	6.480	13
16	0.0813	0.065	0.070	0.123	0.110	9.1800	2.444	21.70	4.890	5.790	14
7	0.3027	0.240	0.200	0.298	0.303	34.300	7.430	74.70	17.300	19.800	59
10	0.3676	0.255	0.200	0.423	0.348	34.500	8.446	84.00	18.000	21.670	57
14	0.3557	0.235	0.200	0.343	0.326	39.500	7.710	87.17	21.100	22.400	57

<sup>a</sup>Original data below LOD and substituted for LOD/2. <sup>b</sup>Original data below LOQ and substituted for (LOQ-LOD)/2+LOD.

<sup>c</sup>NIOSH samples ID # 2, 3, and 8 were switched from the spiking level 4a (medium loading) to the spiking level 2 (very low loading) because they were mistakenly spiked at the lower loading or analyzed twice. <sup>d</sup>Sample spilled during shipping.

**Supplemental Table C.** Performance Criteria for Data with a Reference Value

Analyte	Method	Location Shift (u)	Scale Shift (v)	Accuracy (A)	Concordance (rA)	Coefficient of Variation (CV)	Precision (r)
NCO-HDI Monomer	NIOSH	-0.406	0.447	0.702	0.667	6.334	0.950
	LC/MS	-0.359	0.671	0.873	0.870	2.019	0.996
	OSHA	-0.379	0.795	0.911	0.893	1.881	0.980
	WA-DOSH	-0.789	0.476	0.625	0.599	1.577	0.958
NCO-IPDI Monomer	WA-DOSH	-0.458	0.553	0.778	0.769	0.683	0.988
NCO-HDI Oligomers	NIOSH <sup>b</sup>	-0.051	0.844	0.984	0.973	0.020	0.988
	LC/MS <sup>c</sup>	1.068	4.356	0.349	0.345	0.017	0.988
	WA-DOSH <sup>c</sup>	-0.700	0.398	0.588	0.586	0.024	0.995
NCO-IPDI Oligomers	NIOSH	0.162	1.200	0.971	0.957	0.031	0.985
	WA-DOSH	0.100	1.197	0.979	0.967	0.033	0.988
NCO- HDI and IPDI Oligomers	NIOSH	0.127	1.013	0.992	0.980	0.010	0.988
	OSHA	0.072	1.020	0.997	0.983	0.061	0.985
	WA-DOSH	-0.394	0.580	0.813	0.806	0.007	0.992
Total NCO	NIOSH <sup>d</sup>	0.237	1.207	0.956	0.945	0.008	0.988
	OSHA <sup>d</sup>	0.188	1.218	0.964	0.936	0.051	0.971
	WA-DOSH <sup>e</sup>	-0.270	0.690	0.904	0.898	0.013	0.993

<sup>a</sup>CV = root mean square/mean reference value. <sup>b</sup>Method quantified all possible HDI oligomers. <sup>c</sup>Method quantified 3 HDI oligomers: isocyanurate, uretidione, and biuret. <sup>d</sup>Total NCO mass reported by method, not including IPDI monomer. <sup>e</sup>Total NCO is the sum of NCO-HDI plus NCO-IPDI monomers and oligomers.

**Supplemental Table D.** Individual HDI Oligomer Species Results: isocyanurate, uretidione, and biuret

ID	HDI isocyanurate µg/sample			HDI uretidione µg/sample			HDI biuret µg/sample		
	NIOSH	LC/MS	WA-DOSH	NIOSH	LC/MS	WA-DOSH	NIOSH	LC/MS	WA-DOSH
5	0.012	2x10 <sup>(-5)</sup> a	2.5 <sup>b</sup>	0.012	1.97x10 <sup>(-5)</sup> a	1.4 <sup>a</sup>	0.011	2.02x10 <sup>(-5)</sup> a	0.85 <sup>a</sup>
11	0.002 <sup>a</sup>	0.057	2.5 <sup>b</sup>	0.012	1.97x10 <sup>(-5)</sup> a	1.4 <sup>a</sup>	0.011	2.02x10 <sup>(-5)</sup> a	0.85 <sup>a</sup>
13	0.012	2x10 <sup>(-5)</sup> a	2.5 <sup>b</sup>	0.012	1.97x10 <sup>(-5)</sup> a	1.4 <sup>a</sup>	0.011	2.02x10 <sup>(-5)</sup> a	0.85 <sup>a</sup>
4	0.089, 0.092 <sup>d</sup>	0.099	2.5 <sup>b</sup>	0.154, 0.158 <sup>iv</sup>	0.068	1.4 <sup>a</sup>	0.011, 0.011 <sup>iv</sup>	2.02x10 <sup>(-5)</sup> a	0.85 <sup>a</sup>
12	0.108, 0.093 <sup>d</sup>	0.096	2.5 <sup>b</sup>	0.146, 0.157 <sup>iv</sup>	0.042	1.4 <sup>a</sup>	0.011, 0.011 <sup>iv</sup>	2.02x10 <sup>(-5)</sup> a	0.85 <sup>a</sup>
17	0.075, 0.102 <sup>d</sup>	0.088	2.5 <sup>b</sup>	0.012, 0.146 <sup>iv</sup>	0.043	1.4 <sup>a</sup>	0.011, 0.011 <sup>iv</sup>	2.02x10 <sup>(-5)</sup> a	0.85 <sup>a</sup>
1	0.951	0.930	2.5 <sup>b</sup>	2.020	0.260	7.2	0.169	0.07	0.85 <sup>a</sup>
9	0.997	0.950	2.4	1.350	0.280	8.1	0.079	0.07	0.85 <sup>a</sup>
18	1.060	0.980	2.5	1.539	0.310	9	0.111	0.06	0.85 <sup>a</sup>
2	<sup>d</sup>	6.300	10.7	<sup>d</sup>	1.300	56.1	<sup>d</sup>	0.41	0.85 <sup>a</sup>
3	<sup>d</sup>	7.600	10.4	<sup>d</sup>	1.600	57.2	<sup>d</sup>	0.51	0.85 <sup>a</sup>
8	<sup>d</sup>	6.700	10.7	<sup>d</sup>	2.900	59.3	<sup>d</sup>	0.41	0.85 <sup>a</sup>
6	<sup>c</sup>	8.700	13.1	<sup>c</sup>	1.800	71.5	<sup>c</sup>	0.59	0.85 <sup>a</sup>
15	10.300	8.900	14.7	1.240	1.900	87.6	0.165	0.63	2
16	8.790	8.800	14.3	17.000	1.900	83.4	1.630	0.62	2.70
7	27.800	26	52.7	55.600	5.900	291	6.240	2.50	1.80 <sup>b</sup>
10	31.100	29	54.4	67.400	7.200	324	5.910	2.90	10.20
14	38.700	27	55.1	82.200	6.200	337	7.690	2.50	10.80

<sup>a</sup>Original data below LOD and substituted for LOD/2. <sup>b</sup>Original data below LOQ and substituted for (LOQ-LOD)/2+LOD. <sup>c</sup>Sample spilled during shipping. <sup>d</sup>NIOSH samples # 2, 3, and 8 were recoded from the spiking level 4a (medium loading) to the spiking level 2 (very low loading) because they were either mistakenly spiked at the lower loading or analyzed twice.

**Supplemental Table E.** Performance Criteria for HDI Oligomers isocyanurate, uretidione, and biuret

<b>Oligomer</b>	<b>Comparing any 2 methods</b>		<b>Location Shift (u)</b>	<b>Scale Shift (v)</b>	<b>Precision (r)</b>	<b>Accuracy (A)</b>	<b>Concordance (rA)</b>
	<b>Method <i>i</i></b>	<b>Method <i>ii</i></b>					
HDI Isocyanurate	NIOSH	LC/MS	-0.0238	1.2865	0.9780	0.9688	0.9475
	NIOSH	WA-DOSH	-0.4709	0.6726	0.7500	0.8399	0.6300
	LC/MS	WA-DOSH	-0.5146	0.5228	0.8790	0.7407	0.6510
HDI Uretidione	NIOSH	LC/MS	1.4781	11.5384	0.7240	0.1448	0.1049
	NIOSH	WA-DOSH	-0.8030	0.2758	0.7380	0.4399	0.3246
	LC/MS	WA-DOSH	-3.6306	0.0244	0.9800	0.0369	0.0362
HDI Biuret	NIOSH	LC/MS	-1.1556	0.2347	0.6980	0.3430	0.2394
	NIOSH	WA-DOSH	-4.6415	0.0203	0.9690	0.0283	0.0274
	LC/MS	WA-DOSH	-0.2982	2.6992	0.7094	0.6332	0.4492
Sum of HDI Oligomers <sup>a</sup>	NIOSH	LC/MS	-0.2982	0.8374	0.8282	0.9432	0.7811
	NIOSH	WA-DOSH	-0.8814	0.3102	0.7875	0.4640	0.3654
	LC/MS	WA-DOSH	0.5163	3.2033	0.7720	0.5288	0.4082

<sup>a</sup>Sum of HDI oligomers include isocyanurate, uretidione, and biuret