Determination of Isocyanate Concentrations in a Sample of Commercial Hardener – An Interlaboratory Study

Objectives:

- Determine the intra- and inter-laboratory variability of the isocyanate analysis of an aliquot of a commercial hardener used in the collision repair industry.
- Understand the strengths and weaknesses of the analytical methods used by different laboratories.
- Investigate and compare the ability of each method to quantify individual isocyanate species as well as the total isocyanate content of the sample based on the monomer and oligomer calibration curves.

Conditions of participation:

- The University of Washington (UW) will take the lead in coordinating the effort, including summarizing results and conclusions.
- The spike levels on individual filters will be unknown to the participating labs.
- Labs will abide by the procedures described in this document unless there are method-specific reasons for non-compliance. Any divergence from the enclosed procedures must be discussed with UW staff prior to analysis.
- We acknowledge that a comprehensive comparison of method performance must address both sampling and analytical issues. However, for the purposes of this exercise, we will concern ourselves only with analytical issues.
- Participating laboratories agree that resulting data will be reported in oral and written presentations, including technical reports and peer-reviewed publications. All participants will have the opportunity to comment on any presentation prior to release. The identities of participating labs and staff will be held confidential, upon request. Participants will be named as co-authors in any presentation of these data (unless anonymity is requested).
- The MSDS of the product to be tested will be provided in a separate communication. As requested by the manufacturer, product-specific information must not be provided in any thesis, presentation, report, or publication.

Product information:

The hardener product contains both HDI and IPDI monomers and oligomers.
According to the manufacturer:

1) %NCO should range from 16.0- 17.2, the referenced test method is ASTM D1638-74
2) Theoretical HDI: 0.24% mass monomer/total mass product and 47.9% mass oligomer/total mass product.
3) Theoretical IPDI 0.25% mass monomer/total mass product and 35.5% mass oligomer/total mass product.

4) 2 & 3 are not analyzed for each batch; values are dependant on isocyanate resin supplier data. However, total solids should range +/- 1.2% around the 83.91 wt% solids listed on the MSDS.

Note: Labs may perform their own NCO titrations, preferably in triplicate. The procedure is provided in Appendix A. The UW lab will provide their titration result to all laboratories.

Methods

Participating lab supplies required

Participating labs will ship filters and derivitizing solutions to the UW. To minimize filter handling by the UW, the participating labs will ship at least 20 filters in individual containers (these containers will be returned to the labs, when they will contain the spiked filters plus derivatizing solution). Labs will also ship a sufficient volume of prepared derivitizing solution to accommodate 20 filters.

Sample preparation

A UW analyst will dissolve the hardener in toluene to load 1, 10, 100, and 400 μg bulk product/filter (justification for these levels is provided in Appendix B). These will be prepared in triplicate. Three blank filters will be spiked with an aliquot of the toluene used to prepare the spiking solutions.

The filters will be allowed to dry at room temperature for 2-5 minutes. The loaded filters and three blanks will be placed in derivatizing solution and shipped to the participating labs on ice packs. The amount of material spiked on the filters will not be provided to the labs; each filter will be designated a code with the identification key kept by UW and SHARP.

Sample handling at the labs

Samples should be removed from shipping containers immediately and stored according to the lab's typical methodology.

Samples should be analyzed as soon as possible. If any delay is necessary, storage times should not exceed those recommended by the particular laboratory method. If analysis is delayed or exceeds established holding times, this fact should be noted on the report.

Samples should be analyzed for HDI monomer and HDI oligomers plus IPDI monomer and IPDI oligomers, as possible. It is suggested to report total NCO content of the sample. This may or may not be the sum of all individual species. Additionally, each lab should ideally provide the equivalent NCO content of each species, if the NCO content is not the primary metric used by the lab. This is required in order to make comparisons and estimate method bias.

Reporting of Results

a) Brief method description or reference to established methods,
b) Date samples received from the UW, storage conditions and duration, analysis date, and notes recording unusual situations or conditions,
c) Analytical results for the spiked filters and blanks,
d) Reporting limits,
e) Calibration range,
f) Procedural blanks and QCs,
g) Chromatogram of the bulk product and one of the each level (If possible, examine bulk material by HPLC/MS to determine the monomeric/prepolymeric profile)

Results:

The data for all laboratories will be compiled by UW and SHARP. Because the spike levels will be unknown to the labs, UW and SHARP will calculate percent recoveries for each spike level as well as variability within each level and other statistics.

A final report will be sent to the participating labs, where the labs will be identified by a code.

References

Bello, Dhimiter et al. Polyisocyanates in occupational environments: A critical review of exposure limits and metrics. American Journal of Industrial Medicine, Volume 46, Issue 5 ,June 2004, pp. 480 - 491

Liu, Youcheng; Stowe, Meredith; Bello, Dhimiter; Woskie, Susan; Sparer, Judy; Gore, Rebecca; Youngs, Fred; Cullen, Mark; Redlich, Carrie. Respiratory Protection from Isocyanate Exposure in the Autobody Repair and Refinishing Industry. Journal of Occupational and Environmental Hygiene, Volume 3, Number 5, May 2006, pp. 234-249(16).

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Appendix A

Titration of NCO

The isocyanates are unstable and so they are titrated before use in order to ensure that no polymerized species are present. This titration does not distinguish between isomers and is not specific to isocyanate.

1- Prepare a solution of dibutylamine (DBA) in toluene by mixing 60 ml (11.11%) of DBA with 480ml (88.88%) of toluene. (0.65936N)
2- Dissolve 0.1g of bromophenol blue in 100ml of methanol. Add dilute sodium hydroxide (0.1M) dropwise with stirring until the solution is blue.
3- Weigh approximately 2-3g of each *product* accurately into each of 3 flasks (3 replicates).
4- Pipette 50ml of the DBA solution into each of the sample flasks and into 3 further flasks to serve as blanks. [3 blanks + 3 replicates per each product].
5- Swirl the flasks to mix their contents. Gentle warming on a hot plate may be needed to dissolve the products and speed up the completion of the reaction.
6- Add 100ml of isopropanol and 3-4 drops of the bromophenol blue solution to each of the flasks.
7- Titrate the contents of the flasks against 1 molar hydrochloric acid. The end point is a color change from blue to pale yellow. **Blank titres should agree to within 0.1ml. If not the titration should be repeated.** The blank titre should be about 32 ml.
8- Calculate the percentage NCO in the samples as follows:

$$\%NCO = \frac{HCl\_molarity * (mean\_blank - titre) * 4.2}{sample\_weight}$$

Please contact Dr. Dhimiter Bello directly if you have any questions (Dhimiter_Bello@uml.edu).

Appendix B

Spiking Level Justification and Species Estimate

The hardener will be spiked on filters to yield concentrations based on the UK standards (Bello et al. 2004; Liu et al. 2006). Assuming a sampling time of 8 hours and a sampled air volume of 1 m^3:

- HSE 8 hr TWA =20 μg NCO/m^3 = 20 μg NCO/filter
- HSE 15-min STEL = 70 μg NCO/m^3 = 70 μg NCO/filter

(1) Very Low Level: 1% of TWA

1% of 20 μg NCO/filter = 0.2 μg NCO/filter
Assuming 17% NCO in the bulk product:
0.2/0.17 =1.176 μg bulk product/filter,
With rounding, "Very Low" spiking level is **1 μg bulk product/filter**

(2) Low Level: 10% of TWA

10% of 20 μg NCO/filter = 2 μg NCO/filter
Assuming 17% NCO in the bulk product:
2/0.17 =11.76 μg bulk product/filter,
With rounding, "Low" spiking level is **10 μg bulk product/filter**

(3) Medium Level: 100% of TWA

100% of 20 μg NCO/filter = 20 μg NCO/filter
Assuming 17% NCO in the bulk product:
20/0.17 = 117.6 μg bulk product/filter,
With rounding, "Medium" spiking level is **100 μg bulk product/filter**

(4) High Level: 100% of STEL

100% of 70 μg NCO/filter = 70 μg NCO/filter
Assuming 17% NCO in the bulk product:
70/0.17 = 412 μg bulk product/filter.
With rounding, "High" spiking level is **400 μg bulk product/filter**

Expected Masses per Filter

Level	Bulk Product μg	NCO μg (17%*)	HDI monomer μg (0.24%*)	HDI Polymer μg (47.9%*)	IPDI monomer μg (0.25%*)	IPDI oligomer μg (35.5%*)
1 (Very Low)	1	0.17	0.0024	0.479	0.0025	0.355
2 (Low)	10	1.7	0.024	4.79	0.025	3.55
3 (Med)	100	17	0.24	47.9	0.25	35.5
4 (High)	400	68	0.96	191.6	1.0	142.0

*Percentage provided by hardener manufacturer