NORA Final Report
Isocyanate SWYPE™ Surface Sampling Characterization and Validation
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Summary

Isocyanates are a leading cause of work-related asthma and workers in the auto-collision repair industry are at high risk for isocyanate exposures, particularly by the dermal route (Bello et al, 2007a and SHARP 2005). This project aims to extend and validate a rapid colorimetric surface wipe method, SWYPE™, for measuring isocyanate surface contamination in the workplace (Liu et al 2000 and 2005, and websites: CLI lab Inc. http://www.clilabs.com/, http://www.osha.gov/SLTC/autobody/docs/cdc002.html#Isocyanates, http://www.osha-slc.gov/dts/osta/otm/otm_ii/otm_ii_2.html#2). A semi-quantitative pilot study was conducted to evaluate the use of the SWYPE™ method in auto body shops and to examine the extent of contaminated surfaces. RGB (Red-Green-Blue) spectral analysis of the SWYPE™ was compared to standard quantitative method W4002 for validation purposes.

Isocyanate SWYPE™ Semi-quantitative Surface Sampling in the Puget Sound Collision Repair Industry - Pilot Study

SWYPES™ (n=122) were used for surface sampling at 20 collision repair shops in the Puget Sound region. A semi-quantitative approach was used to assess the loading of the SWYPES™ with a scale of 0 to 3, where 0 (yellow) had no contamination, and 3 (deep red) had the highest contamination (Figure 1). Semi-quantitative analysis of the field samples showed that isocyanate surface contamination in paint shops was mainly confined to the mixing room and the spray booth, with over 90% of positive samples in the paint mixing room alone (n=26). Semi-quantitative evaluation of discarded gloves showed that most (>70%) were contaminated on the outside and ~12% had detectable isocyanates inside the gloves. The semi-quantitative pilot study suggests a need for more careful examination of protective clothing and glove materials used in mixing and painting operations.

Isocyanate SWYPE™ Surface Sampling Characterization and Validation

SWYPE™ samples were collected in the laboratory and in the field. Samples were archived by recording images of the color change on a calibrated portable digital scanner. A digital image analysis algorithm was developed to quantify the surface loading on SWYPE™s. The amount of color change in field images was compared to a series of reference images collected with a known loading of the specific isocyanate-containing hardener. The algorithm allowed for quantification over a range of loadings from ~0.1 to 24.0 $\mu g/cm^2$ with reproducibility of >90% and an extraction efficiency of >90% (estimated by comparing direct loading on the SWYPE^{TM} versus wiping of controlled loading on aluminum foil). The lowest visually detected SWYPE™ in the lab (6-10ug on 10x10cm surfaces) is higher than that suggested by the manufacturer (3-5μg). We acknowledge that surface contaminants and other factors affect quantitation in the field, so detection limits might be expected to be higher (Liu et al, 2000 suggested that the field detection limit is 50μg).

Quantitative evaluation comparing duplicate laboratory analysis using method W4002 (chemical analysis OSHA method 42) on Ghost Wipe^{TM} samples, showed good accuracy (>90%), extraction efficiency (>90%), and a relatively high correlation (Swype^{TM} versus W4002 loading $R^2 > 0.69$) with the SWYPE™ samples analyzed by RGB spectral analysis. SWYPE™ RGB analysis and W4002 side-by-side field sampling of surfaces were also compared for field validation. Agreement of the two methods (Swype^{TM} versus W4002 loading R^2 ~0.5, n=5) occurred when surfaces were most uniformly loaded, such as those located inside the spray booth, e.g., panel surface after being sprayed painted. SWYPE™ RGB analysis and W4002 side-by-side field sampling compared poorly (Swype^{TM} versus W4002 loading R^2~0.3, n=5) when surfaces were not uniformly loaded, such as those located inside the mixing room, e.g., mixing balance surface. Regardless of the difficulty comparing the SWYPE™ RGB analysis and W4002 methods in the field because of the lack of uniformity, SWYPE™ RGB analysis is faster and more economical than W4002. Furthermore, SWYPE™ RGB analysis has the advantage of being objective. Using the traditional SWYPE™ semi-quantitative approach, the investigator's color perception is subjective and variable. For example, when comparing color scale from field observation versus the same samples after being scanned, color scale assignment only agreed up to 80%.

Standard Methods

Colorimetric SWYPE™ Sampling Procedure

1) Load surface of interest with 2-3 sprays of mineral oil (developing solution), wait 30 sec.
2) Wipe the interested surface with a Surface SWYPE™ pad (CLI for aliphatic isocyanate #1023). Try to be consistent from sample to sample: wipe surface in circles starting in the borders and working in with constant pressure. Only wipe the circle within the 10x10 cm area.
3) Wrap wipe with plastic wrap and label sample.
4) Take a photo of the sample against a white background with a calibrated Flatbed HP ScanJet G4010 Photo Scanner ideally between 3 to 20 minutes after sampling to assure color development.

W4002 Method Sampling Procedure

1) Withdraw a Ghost Wipe ™ (Environmental Express Cat#4210) from a Ziploc™ bag with gloved fingers or clean tweezers. Use the disposable pipette to moisten the medium with 0.5 mL of the wetting reagent (50:50 isopropyl alcohol:water solution).
2) Apply firm pressure when wiping. Start at the outside edge and progress toward the center making concentric squares of decreasing size. Fold the medium with the contaminant side inward and repeat.
3) Without allowing the medium to come into contact with any other surface, fold the medium with the exposed side inward. Place the medium in a sample vial containing the derivatizing solution (50:50 dimethyl sulfoxide : ethyl acetate and 0.025 M 1-(2-pyridyl) piperazine (1- 2PP), secure the cap and shake vigorously for one minute.
4) Store vials in a cooler and send them to the EH Lab for OSHA 42 analysis. In the lab, the wipes were gently compressed to remove derivatizing solution and transferred to a GC vial.

Results

Calibration Results

Loaded aluminum foil surfaces were used as references for both SWYPE™ and W4002 calibrations. Calibration of the SWYPE™ is possible (up to R^2 of 0.97) by associating loading with green plus blue RGB histogram signals. Loading of the SWYPE™ is proportional to color because the SWYPE™ reacts proportionally to isocyanate groups. However, because the SWYPE™'s color is proportional to the NCO bonds (and not to the mass of isocyanates), color gradient is different for every hardener. Ideally, a calibration should be performed for every hardener of interest. This can be a limitation of the method, especially when a shop uses several hardeners simultaneously.

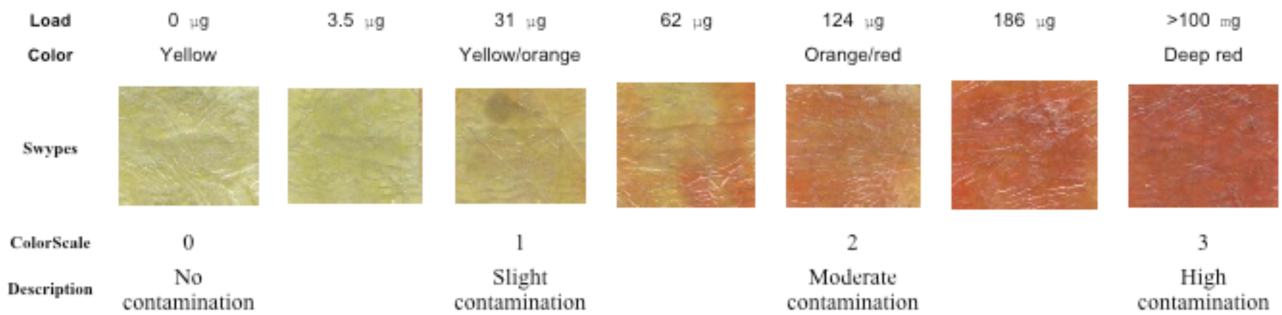

Figure 1. Color gradient in Scanned Pictures of the SWYPE™.

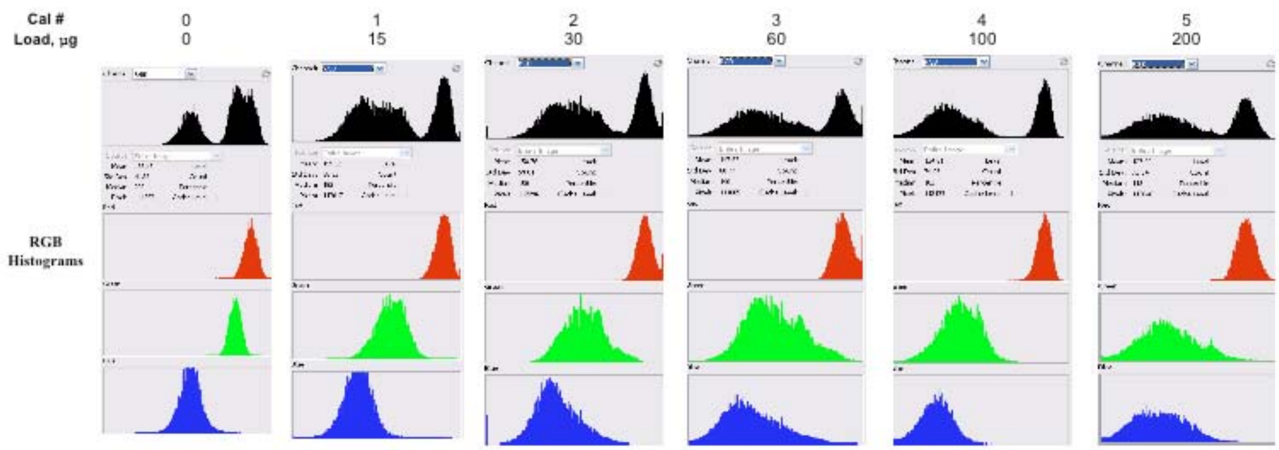

Figure 2. SWYPE™ RGB Analysis with Adobe Photoshop CS2. Increasing red intensity is clear when looking at the RGB histograms, green color starts separating from the red, also moving with the blue while the red stays basically the same.

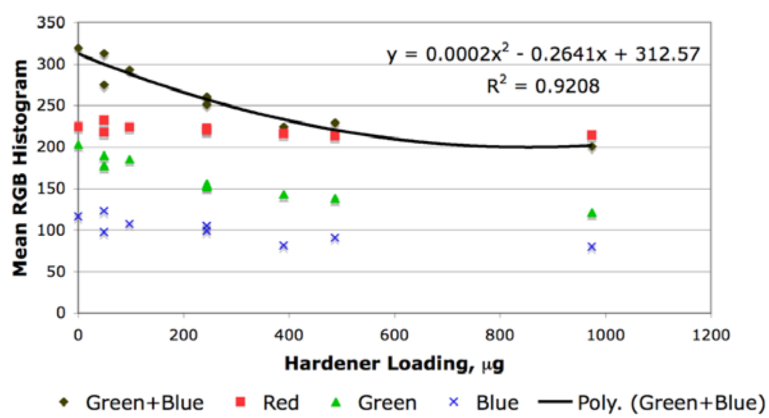

Figure 3. SWYPE™ Calibration Results. Notice some flattening to the right side of the quadratic curve, this can be attributed to the 10% variance of the method.

Calibration of the Ghost Wipe™ W4002 method is possible (up to R^2 of 0.99) by associating loading with total mass of isocyanate species analyzed, which are proportional to the total functional group number in the particular hardener. W4002 method had a good surface recovery >90% (estimated by comparing direct loading on the Ghost Wipe™ versus wiping of controlled loading on aluminum foil).

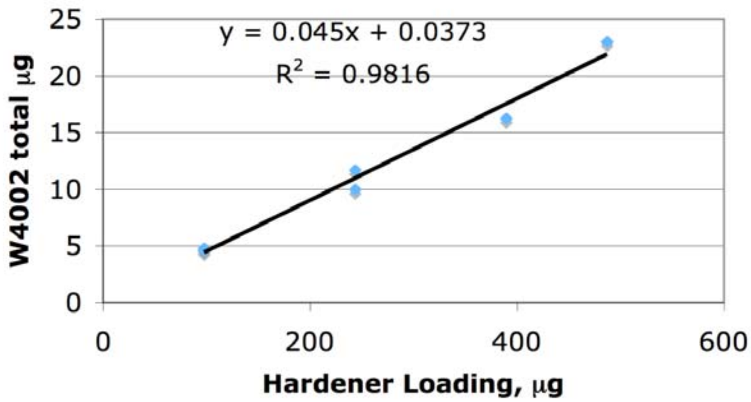

Figure 4. W4002 Calibration Results.

Jackknife Cross Validation

Duplicate calibration standards were used in a Jackknife approach, which is similar to bootstrapping. The jackknife estimator systematically recomputed the statistic estimate while omitting one observation at a time from the sample. From this new set of "observations" for the statistic, both an estimate of the bias and the variance of the statistic can be calculated. Figure 5, for example, relates the predicted values of each method and the true loading applying the jackknife approach. Figure 5 slope similarities suggest good agreement between the two methods. The correlation of the SWYPE™ versus W4002 jackknife predictions was R^2=0.69 (Figure not shown). This correlation was perhaps not higher due to the lack of dual replicates available for the jackknife approach.

The only SWYPE™ quantitative validation efforts in the literature that we are aware of is by Bello et al, 2007b and Liu et al, 2007. Liu et al published a graph where spiked SWYPETM are compared with spiked quantitative wipes analyzed by method NIOSH 5525. Data had a quadratic shape, just like our SWYPETM calibration using the RGB methodology. Bello et al reported that auto spray paint takes several days to cure completely. In this publication, SWYPE™ semi-quantitative color scale data agreed with quantitative wipes analyzed by method NIOSH 5525 (R^2 0.85).

Conclusions

The SWYPE™ method has the advantage of being portable, fast, economical, visual, and easy to use. However, this surface sampling technique has the disadvantage of not being specific for a particular isocyanate but general to isocyanate functional groups. Another disadvantage is that mineral oil (the developing solution) can be a workplace hazard if not cleaned after sampling.

In the Puget Sound Region surface sampling pilot study, most isocyanate-contaminated surfaces were inside the paint mixing room. Consequently, efforts should be concentrated on improving work practices and dermal protection of workers while mixing and spraying paints. Evidence of isocyanate contamination on glove's surfaces suggests that workers are in direct contact with unpolymerized isocyanates. We recommend that painters improve mixing and spraying practices and change gloves after each mixing or painting task. Furthermore, research evaluating protective clothing efficacy is needed.

SWYPE™ surface sampling has great potential when combined with the RGB analysis method. Even though reliable and objective, many variables still affect the quantification of the SWYPE™ color, such as wetting agent (oil), light, time, loading, type of surface and isocyanate, roughness, and other interferences. Laboratory RGB method characterization determined that the SWYPE™ detection limit (LOD) is ~0.1 µg/cm², replicates with a coefficient of variation < 9%, and extraction efficiency > 90%.

The SWYPE™ RGB analysis and W4002 wipe method compared well. Duplicate laboratory analysis using W4002, showed good accuracy (>90%), extraction efficiency (>90%), and a relatively high correlation ($R^2 > 0.69$) with the SWYPE™ samples with RGB analysis. During side-by-side field comparison, SWYPE™ RGB analysis and W4002 compared better when surfaces were uniformly loaded, such as those located inside the spray booth. These results and the work of others (Bello et al, 2007b) suggest that SWYPE™ is a promising tool for identification of uncatalyzed isocyanates contamination in the workplace, and if used properly it provides quantitative information.

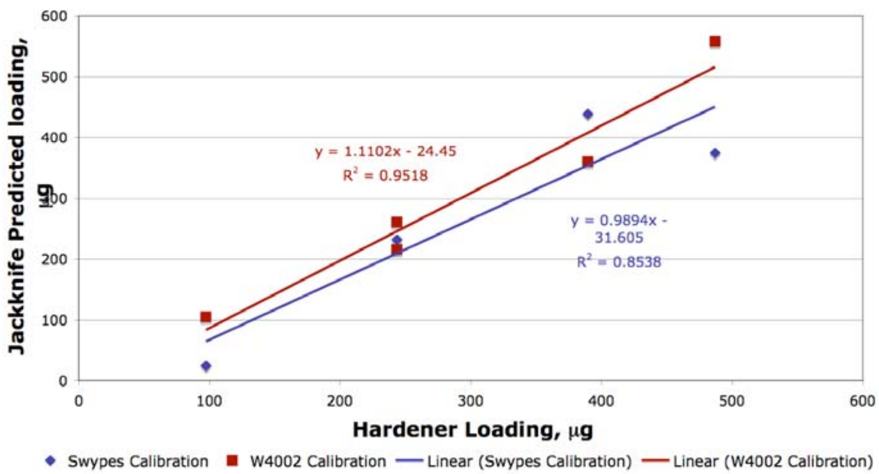

Figure 5. SWYPE™ and W4002 predicted values versus known loading masses

References

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