A Novel Analytical Scheme for Measuring Total Reactive Isocyanate Group based on 1,8-Diaminonaphthalene

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Research Purpose: Commercial isocyanate products are often complex mixtures of isocyanate species and analytical standards exist only for a few species. Quantitation of individual species is therefore difficult and labor intensive. Furthermore, current methods cannot measure unreacted isocyanate groups bound to non-chromatographable species, such as high molecular weight prepolymers or partial reaction products formed, for example, during spray foam applications of fast curing formulations. A new analytical method has been developed to overcome these issues.

Relevance: The new method offers unique advantages for airborne and surface sampling of fast curing aerosols of aromatic isocyanates, and the only practical way for monitoring unreacted isocyanate groups attached to non-chromatographable species. Since the method involves only a single analyte and offers minimal sample workup with short analysis run time, it offers an economical and unambiguous technique for conducting total isocyanate group determinations. When combined with existing analytical techniques, unique insights can be gained on the chemical composition of complex samples and for studying the health relevance of exposure to such species.

Methods: The analytical method utilizes 1,8-diaminonaphthalene (DAN) as the derivatizing reagent. Isocyanates are first converted into ureas during sample collection, analogous to established isocyanate methods. In a second post-collection step, the different DAN ureas are converted into a single analyte, perimidone. This step results from an intramolecular cyclization reaction in which the carbonyl (C=O) group that was a part of the original isocyanate group (-N=C=O), is effectively extracted to yield perimidone and the amine corresponding to the original isocyanate species. The amount of perimidone is proportional to the amount of total isocyanate contained in the sample.

Air sampling is accomplished using impingers containing DAN in DMSO. A small aliquot of impinger solution (0.5 ml) is mixed with an equal volume of formic acid (a catalyst for cyclization). After 30 min, 10 µL acetone is added to the sample to consume excess DAN, followed by the addition of an internal standard, d6-perimidone (10 ng/mL). The sample is analyzed in 15 min runs by liquid chromatography – tandem mass spectrometry (LC-MS/MS) using a C18 column and mobile phase gradient. Perimidone is monitored via three transitions in the positive ion mode.

Results: Laboratory validation of the DAN analytical scheme was performed via spikes of known amounts of several aromatic isocyanate bulk products in DAN/DMSO. The yield of perimidone averaged 98% (range 88-108%) of the theoretical isocyanate content determined via dibutylamine titration. The method is also highly reproducible and sensitive (limit of detection <100 pg/mL).

Conclusions: The DAN isocyanate chemistry has been developed into a working analytical method and its performance in laboratory testing has been satisfactory. An initial field study comparing DAN with several established methods has been completed and will be summarized. Field testing results showed that the total reactive isocyanate group (TRIG) values found with DAN were higher than those found with other TRIG determination methods, highlighting the ability of the DAN method to more fully assay isocyanate groups present.

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Particle Size Fractionated Sampler for Isocyanates

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Objective: To advance the denuder cascade impactor technology for respirable airborne isocyanate particles and to study the performance of the sampler in an environmental chamber containing gas and particle-borne isocyanates.

Methods: An isocyanate atmosphere was generated by wet permeation of 2,4-, 2,6-toluene diisocyanate (TDI), 1,6-hexamethylene diisocyanate (HDI) and Isophorone diisocyanate (IPDI). MDI particles were generated by heating of technical MDI and condensing the mixture of gas and particle-borne MDI in an atmosphere containing mixed salt particles. The study was performed in a 0.85 m3 environmental chamber with stainless steel walls.

An advanced design of a denuder impactor (DI) sampler was developed with a section comprised of 12 different parallel denuder tubes, 4 impaction stages with the cut-off values (d50): of 9.5, 4, 2.5 and 1 µm, and an end filter that collects particles < 1 µm. All collecting parts were impregnated with di-n-butylamine (DBA) as the reagent in a mixture with acetic acid. For comparison, a dry isocyanate sampler based on DBA derivatisation was used as a reference sampler. A scanning mobility particle sizer (SMPS) was used to separate a flow of selected fractions containing MDI particles from mixed MDI and salt particles. The particle-size distribution had a maximum at about 300 nm, but later in the environmental chamber 1 µm dominated. The distribution was very different as compared to with only NaCl or MDI present.

Results: The denuder collection efficiency for HDI and IPDI ranged between 94.5 – 96.7%. For MDI aerosols gas and particle distribution was affected by the humidity. At low humidity the small particles (<1 µm and 1 µm fraction) dominated. For a relative humidity of 50% and 90% the particle sizes 1 µm – 4 µm dominated.

During sampling for 20 – 320 min in the environmental chamber at 50 % RH, the dry isocyanate sampler and the DI sampler in total collected about the same amounts of isocyanates. The predominately isocyanate gas-phase air concentrations were in the range of 14-29 µg/m3 for HDI, 80-105 µg/m3 for IPDI1, 33-41 µg/m3 for IPDI2, and 9-11 µg/m3 for 2,4-TDI. The 2,6-TDI concentration was about 2 µg/m3. MDI was present predominately in the particle phase in the range of 45-72 µg/m3.

Conclusion: With the advancement of the DI sampler it is now possible to collect isocyanate particle samples for 320 min. The performance of the DI sampler is essentially unaffected by the humidity. The DI sampler and the isocyanate air sampler gave similar results. Sample losses within the DI sampler are low. In the environmental exposure chamber it was observed that the particle distribution may be affected by the humidity and ageing. SMPS and isocyanate air sampling can be used for the investigation of nano isocyanate particles.

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