Welcome to News on Air
2014 Volume 3

This edition will cover the recent developments in sampling of isocyanates with the ASSET™ EZ4-NCO Dry Sampler.

This new and easy to use sampling device for the determination of Isocyanate monomers and oligomers in air offers

- Low detection limits and high capacity, with sampling times from 5 minutes up to 8 hours for true TWA determinations
- Stable derivatisation using Dibutylamine (DBA) - no refrigeration or infield extraction is needed
- Complete derivatisation of particles, preventing underestimation of isocyanate exposure
- Compliance with ISO17734-1 “Determination of organonitrogen compounds in air using liquid chromatography and mass spectrometry —Part 1: Isocyanates using dibutylamine derivatives”

The sampler is supported by a set of calibration standards including a deuterated internal standard mix for LC-MS/MS.

Isocyanates are used in the production of polyurethane (PUR) materials, one of the most widely used plastics in the world. Workers who are exposed to these compounds either in a production or by treating/handling PUR coated materials (e.g. welding or spray coating) are at risk for respiratory disorders, asthma and other health conditions. Particulate isocyanates often show incomplete reactions with the used reagent using common sampler types, which can result in underestimation of exposure. Additionally filter samples often show very limited capacity allowing only for short sampling times.

The ASSET EZ4-NCO sampling device is a unique dry sampler based on derivatization of isocyanate groups with di-n-butyamine. The sampler consists of a denuder and a filter, both impregnated with DBA. The sampler extract is analyzed using LC-MS or LC-MS-MS offering the ultimate sensitivity and low detection limits not achievable with other methods.

For more information and to watch a video on the sampler’s functionality and use, visit sigma-aldrich.com/asset
Sampling of Isocyanates

Field Sampling Recommendations
Flow Rate: 200 mL/min (suggested)
Range (100 to 250 mL/min)
Low back-pressure (suitable for most air sampling pumps):
9 inches of water @ 200 mL/min
Sampling Time: 15 minutes is typical,
(range can be 5 minutes to 8 hours)

Analysis of the sampler

Extraction of Sampler.
The denuder & filter section of the sampler are extracted with solvent. For a step by step procedure on the extraction of the ASSET sampler, including an equipment and reagents list, please visit www.sigmaaldrich.com/asset

LC-MS/MS Analytical Conditions for Isocyanate Analysis Using ASSET Sampler
While a range of air monitoring applications use GC for analysis, the analysis of the ASSET sampler uses a liquid.
ASSET™ EZ4-NCO Standards

This set of analytical standards supports the LC/MS Analysis of the Isocyanates collected with the ASSET sampler:

### 40141-U DBA Isocyanate Mix (acetonitrile:methanol, 99:1, varied conc) 6 x 1 mL

<table>
<thead>
<tr>
<th>Isocyanate</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isocyanic acid-di-n-butylamine (ICA-DBA)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>Ethyl isocyanate-di-n-butylamine (EIC-DBA)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>Hexamethylene diisocyanate-2(di-n-butylamine) (HDI-2(DBA)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>Isophorone isocyanate-2(di-n-butyl amine) isomer 1 (IPDI-2(DBA)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>Isophorone isocyanate-2(di-n-butyl amine) isomer 2 (IPDI-2(DBA)</td>
<td>0.4 μg/mL</td>
</tr>
<tr>
<td>4,4’-Methylene diphenyl diisocyanate-2(di-n-butylamine) (4,4’-MDI-2(DBA)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>Methyl isocyanate-di-n-butylamine (MIC-DBA)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>Phenyl isocyanate-di-n-butylamine (Phi-DBA)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>Propyl isocyanate-di-n-butylamine (PIC-DBA)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>2,4-Toluene diisocyanate-di-n-butylamine (2,4-TDI-2(DBA)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>2,6-Toluene diisocyanate-2(di-n-butylamine) (2,6-TDI-2(DBA)</td>
<td>1 μg/mL</td>
</tr>
</tbody>
</table>

### 40142-U Isocyanate Internal Standard Mix 6 x 1 mL

<table>
<thead>
<tr>
<th>Isocyanate</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isocyanic acid-di-n-butylamine-d9 (ICA-DBA-d9)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>Ethyl isocyanate-di-n-butylamine-d9 (EIC-DBA-d9)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>Hexamethylene diisocyanate-2(di-n-butylamine-d9) (HDI-2(DBA-d9)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>Isophorone diisocyanate-2(di-n-butylamine-d9) isomer 1 (IPDI-2(DBA-d9)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>Isophorone diisocyanate-2(di-n-butylamine-d9) isomer 2 (IPDI-2(DBA-d9)</td>
<td>0.28 μg/mL</td>
</tr>
<tr>
<td>4,4-Methylene diphenyl diisocyanate-2(di-n-butylamine-d9) (4,4’-MDI-2(DBA-d9)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>Methyl isocyanate-di-n-butylamine-d9 (MIC-DBA-d9)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>Phenyl isocyanate-di-n-butylamine-d9 (Phi-DBA-d9)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>Propyl isocyanate-di-n-butylamine-d9 (PIC-DBA-d9)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>2,4-Toluene diisocyanate-2(di-n-butylamine-d9) (2,4-TDI-2(DBA-d9)</td>
<td>1 μg/mL</td>
</tr>
<tr>
<td>2,6-Toluene diisocyanate-2(di-n-butylamine-d9) (2,6-TDI-2(DBA-d9)</td>
<td>1 μg/mL</td>
</tr>
</tbody>
</table>

### 40143-U DBA Isocyanate Standard Kit 2 x 1 mL

Includes 1 mL of DBA Isocyanate Mix and 1 mL of d9-DBA Internal Standard Mix

Analytical Service

An range of international contract laboratories offer an analytical service for the ASSET-EZ4 NCO sampler. Please visit our website sigma-aldrich.com/asset to find more details.

We recently launched Certified Reference Material (CRM) Standards for analysis of new monomers HMDI and TMX diisocyanates and HDI adducts are also available. IPDI adducts and pMDI are coming soon. For more information on availability, please contact Kristen Schultz at kristen.schultz@sial.com.

World Regulatory Update

Piperazine compounds are commonly used in isocyanate sampling devices as derivatives to convert the reactive isocyanates into stable compounds that can be analyzed by HPLC. In the United Kingdom, early in 2013, piperazine compounds were declared controlled substances as a result of these compounds being used for the manufacturing of illegal designer drug formulations. Therefore the 1,2-pyridyl piperazine (PP) wet sampler for OSHA methods 42 & 47 cannot be used as well as the impinger solution containing 1-(9-anthracenylmethyl) piperazine (MAP) for NIOSH 5525 and the UK MDHS 25/3 methods. In addition, the ISO-CHEK® back-filter containing 1-(2-methoxyphenyl) piperazine (MOPIP) can also not be used for sampling and analysis of isocyanates

Since ASSET EZ4-NCO Dry Sampler does not contain any piperazine compounds, it does not face regulatory or compliance issues in the UK.

OSHA National Emphasis Program (NEP) on Isocyanates

In June 2013, OSHA announced a new National Emphasis Program (NEP) for occupational exposure to isocyanates that will focus on workplaces in the general, construction and maritime industries in which isocyanate compounds are used. Over a 3-year period, OSHA will focus outreach efforts and inspections on isocyanate hazards in an effort to reduce occupational illnesses, injuries and deaths, and to
raise awareness of the health effects associated with exposure to isocyanates, which can cause occupational asthma, irritation of the skin, eyes, nose, and throat and cancer. Workers in jobs such as painting, blowing foam insulation, and the manufacture and thermal degradation of polyurethane products may be exposed to these hazardous chemicals.

Within this program, OSHA issued an official statement that it is now their recommendation that all isocyanates regardless of physical state (vapor or aerosol) shall be field desorbed. The rationale behind this decision is confirmed by the article from Karoly, American Industrial Hygiene Journal 59:645-647, 1998, which showed under reporting of MDI when samples were not field desorbed. There is a consensus in the industry that the majority of the isocyanate sampling, especially when aerosols reach a certain size (> 2 μm) the sample collected will underestimate the airborne concentration.

Basically, OSHA is now recognizing that using a wet sampler underestimates isocyanate exposures because it does not discern collection of vapors from aerosols. This means that field desorption will be required for wet samplers such as 1,2-PP coated filters and the ISO-Chek back-filter. As a result, other sampling techniques must be used to avoid this inconvenience, complexity and reliability issues associated with field desorption. Therefore impinger methods or the Supelco ASSET EZ4-NCO dry sampler must be used.

If you want to be in compliance with the OSHA NEP you will either need to sample with glass impingers, derivatize your wet samplers in the field, or collect your samples on the easy to use ASSET sampler.

Publications:
ISO 17734-1:2006, Determination of Organonitrogen Compounds in Air Using Liquid Chromatography and Mass Spectrometry

Authors: Gunnar Skarping, Marianne Dalene and Daniel Karlsson

Isocyanates, Amines and Alkanolamines: Sampling, Chromatography and Detection
Author: Riddar, Jakob B,
Affiliation: Department of Analytical Chemistry, Faculty of Science, Stockholm University, P.O. Box 460, S-28124 Hassleholm, Sweden
Journal: Doctoral thesis, comprehensive summary (Other academic), 2013

Dry Sampling of Gas-Phase Isocyanates and Isocyanate Aerosols from Thermal Degradation of Polyurethane
Authors: Daniel Gylestam, Jakob B Riddar, Marianne Dalene and Gunnar Skarping
Affiliation: Department of Analytical Chemistry, Work Environment Chemistry, Stockholm University, P.O. Box 460, S-28124 Hassleholm, Sweden

Solvent-Free Sampling with Di-n-Butylamine for Monitoring of Isocyanates in Air
Authors: Asa Marand, Daniel Karlsson, Marianne Dalene and Gunnar Skarping
Affiliation: Department of Analytical Chemistry, Work Environment Chemistry, Stockholm University, P.O. Box 460, S-28124 Hassleholm, Sweden
Journal: Journal of Environmental Monitoring, 2005, 7, 335-343

Determination of Airborne Isocyanates as Di-n-Butylamine Derivatives Using Liquid Chromatography and Tandem Mass Spectrometry
Authors: Daniel Karlsson Jakob Dahlin, Asa Marand, Gunnar Skarping, Marianne Dalene
Affiliation: Department of Analytical Chemistry, Work Environment Chemistry, Stockholm University, P.O. Box 460, S-28124 Hassleholm, Sweden