

ASSET™ EZ4-NCO Dry Sampler

For Isocyanate Measurements in Air

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Topics

- Introduction to the ASSET Sampler
- Design Features
- Benefits
- Performance LC-MS/MS vs. LC-MS
- Comparison to Existing Sampling Devices
- Collateral



Partnership with Institutet för Kemisk Analys Norden AB (IFKAN)

- Supelco partnered with IFKAN in November 2011 to commercialize the ASSET EZ4-NCO Dry Sampling Device
- IFKAN is recognized as a leader in occupational exposure investigations.
- Expertise – Exposure to airborne thermal degradation compounds, over 30 years



Drs. Gunnar Skarping (L) and Marianne Dalene (R)

IFKAN



Institutet för Kemisk Analys Norden AB



ASSET™ EZ4-NCO Dry Sampler

Filter

Denuder

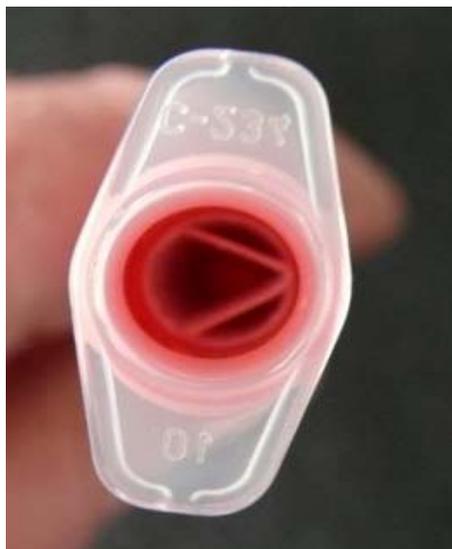


Unique design efficiently retains both the vapor and particulate isocyanates from air



Dibutylamine Impregnated Media

Vapor phase isocyanates are collected in the denuder (syringe barrel)



The isocyanate particles are collected on the filter (filter cassette)



A higher concentration of DBA is impregnated on the denuder that continuously refreshes the filter with fresh reagent during sampling. This reduces the risk of analyte breakthrough from occurring. It also prevents the loss of isocyanates particles, which can occur with other samplers because fresh DBA is able to derivatize the particles.



Vapor Phase & Particulate Isocyanates

MDI is a particulate isocyanate and is commonly underestimated. Why?

The particles lay on the surface of the filter consuming reagent, therefore using up the capacity of the reagent for derivatization.

The patented design of the ASSET-EZ4 collects the vapor phase isocyanates in the denuder allowing for the particle phase isocyanates to collect onto the filter.

The high loading of the DBA-acetic acid mixture onto the filter allows for constant refreshing of the reagent resulting in high capacity.



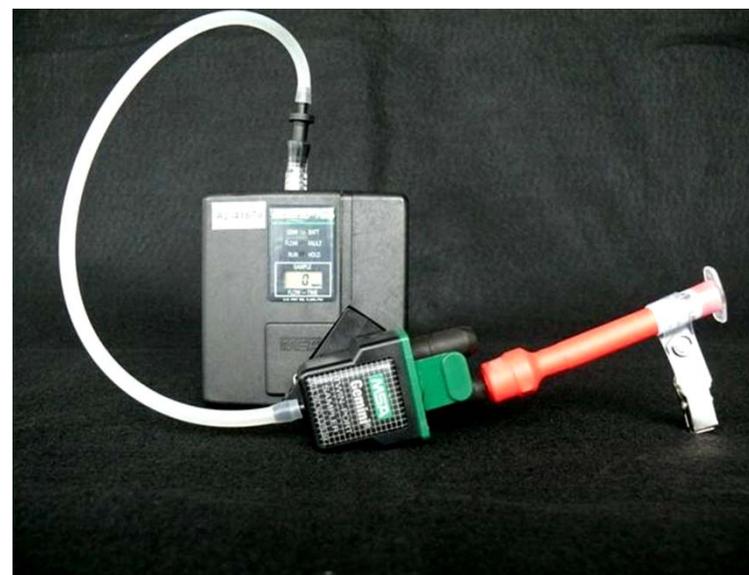
Field Sampling

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 (5 minutes to 8 hours)
- Single sampler can be used for 8 hour sampling





Connecting ASSET to a Sampling Pump

Tubing Adapters

- Adapter will fit most tube holders
- Included with each pack of samplers



Assortment of Luer to Hose-Barb Fittings

- Will be available soon



Calibrating the Sampling Flow Rate

A Flow Calibration Fitting is included with each pack of samplers



Flow Calibration Fitting





Securing the ASSET





Storage of ASSET EZ4-NCO

- After sampling, just put the caps back on the sampler.
- ASSET (new and sampled) can be stored at room temperatures.
- Recommendation: ASSET should be analyzed within **4 weeks** after sampling; *however, preliminary studies indicate that long-term storage may be possible.*



Preparing ASSET for Extraction – At the Lab...





Preparing ASSET for Extraction – At the Lab...



Remove the filters from the denuder and the 13 mm filter housing and place into a centrifuge tube; then rinse both the sample tube and filter housing with extraction solvent into the centrifuge tube.



Extracting the Filters – At the Lab...



Filters w/ extraction solvents on the shaker

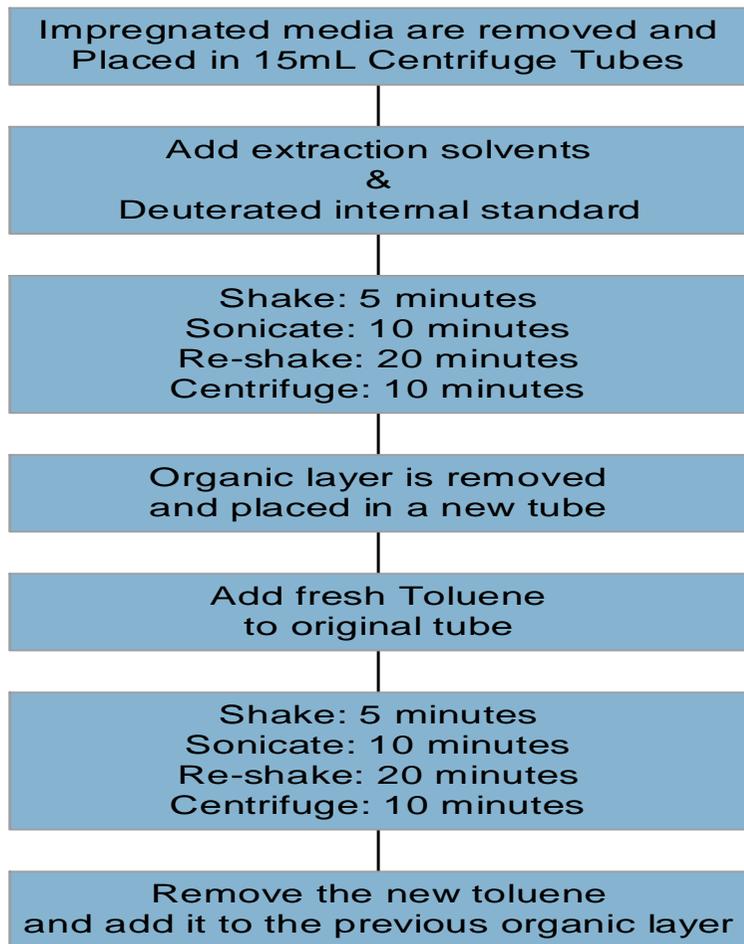


Filters after shaking and sonication

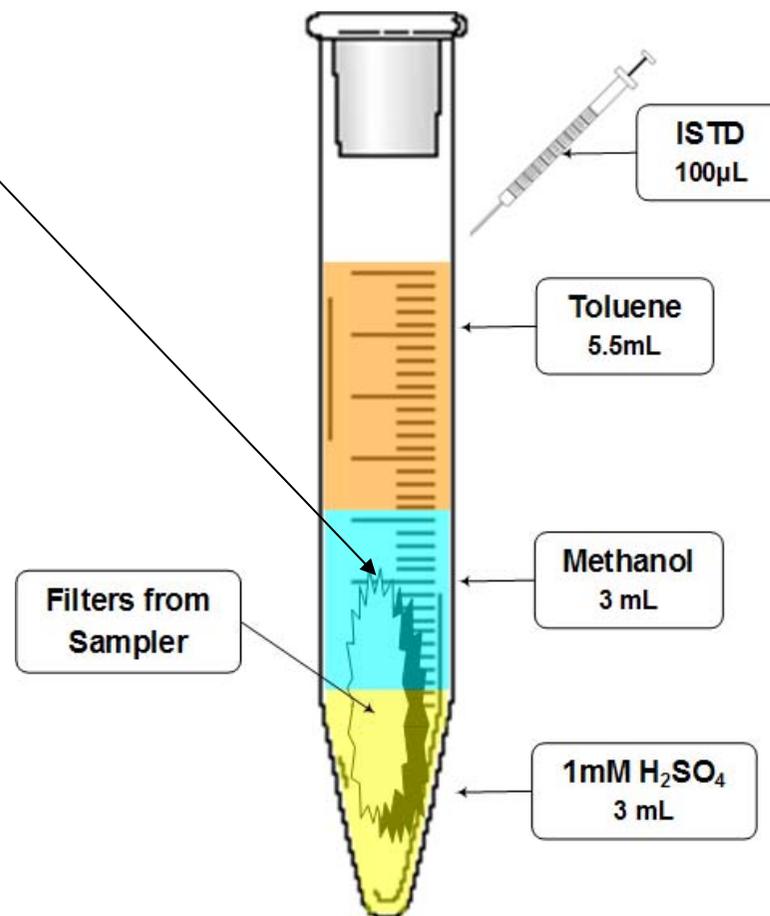


Extraction of the ASSET

Double extraction



Extraction solvents





Removal of the Extract for LC-MS/MS or LC-MS Analysis





Comprehensive Analytical Calibration Standards

Derivatized - Calibration Standard

- Isocyanic acid-DBA
- Ethyl isocyanate-DBA
- Methyl isocyanate-DBA
- Phenyl isocyanate-DBA
- Propyl isocyanate-DBA
- Hexamethylene diisocyanate-DBA
- cis-Isophorone diisocyanate-DBA
- trans-Isophorone diisocyanate-DBA
- 4,4-Methylenediphenyl diisocyanate-DBA
- 2,4-Toluene diisocyanate-DBA
- 2,6-Toluene diisocyanate-DBA



Deuterium Labeled - Internal Standard

- Isocyanic acid-(d₉-DBA)
- Ethyl isocyanate-(d₉-DBA)
- Methyl isocyanate-(d₉-DBA)
- Phenyl isocyanate-(d₉-DBA)
- Propyl isocyanate-(d₉-DBA)
- Hexamethylene diisocyanate-2(d₉-DBA)
- cis-Isophorone diisocyanate-2(d₉-DBA)
- trans-Isophorone diisocyanate-2(d₉-DBA)
- 4,4-Methylenediphenyl diisocyanate-2(d₉-DBA)
- 2,4-Toluene diisocyanate-2(d₉-DBA)
- 2,6-Toluene diisocyanate-2(d₉-DBA)



New Standards Coming Soon ***April 2013***

- HMDI (total isomers)
- TMXDI

Oligomers

- HDI Adducts
 - HDI biuret
 - HDI isocyanurate
- IPDI Adducts
 - IPDI Isocyanurate
- Polymeric MDI mix (pMDI)
 - 2 ring, 3 ring, 4 ring, 5 ring



Limit of Quantification: LC-MS/MS vs. LC-MS

Calibration concentration range: 5-280 ng/mL

Compound	MS (ng/mL)	MS/MS (ng/mL)
ICA	5.00	1.000
MIC	25.00	3.000
EIC	15.00	4.000
PIC	10.00	10.000
PhI	3.00	0.400
HDI	2.00	0.500
2,6-TDI	3.00	0.030
2,4-TDI	3.00	0.030
IPDI-1	4.00	0.400
IPDI-2	4.00	0.400
MDI	3.00	2.000



LC-MS/MS System Configuration

Instrument: Agilent 1100

Column: Ascentis Express C18, 15 cm × 4.6 mm, 2.7 μm particles (53829-U)

Flow rate: 1 mL/min

Temperature: 35 °C

Injection volume: 2 μL

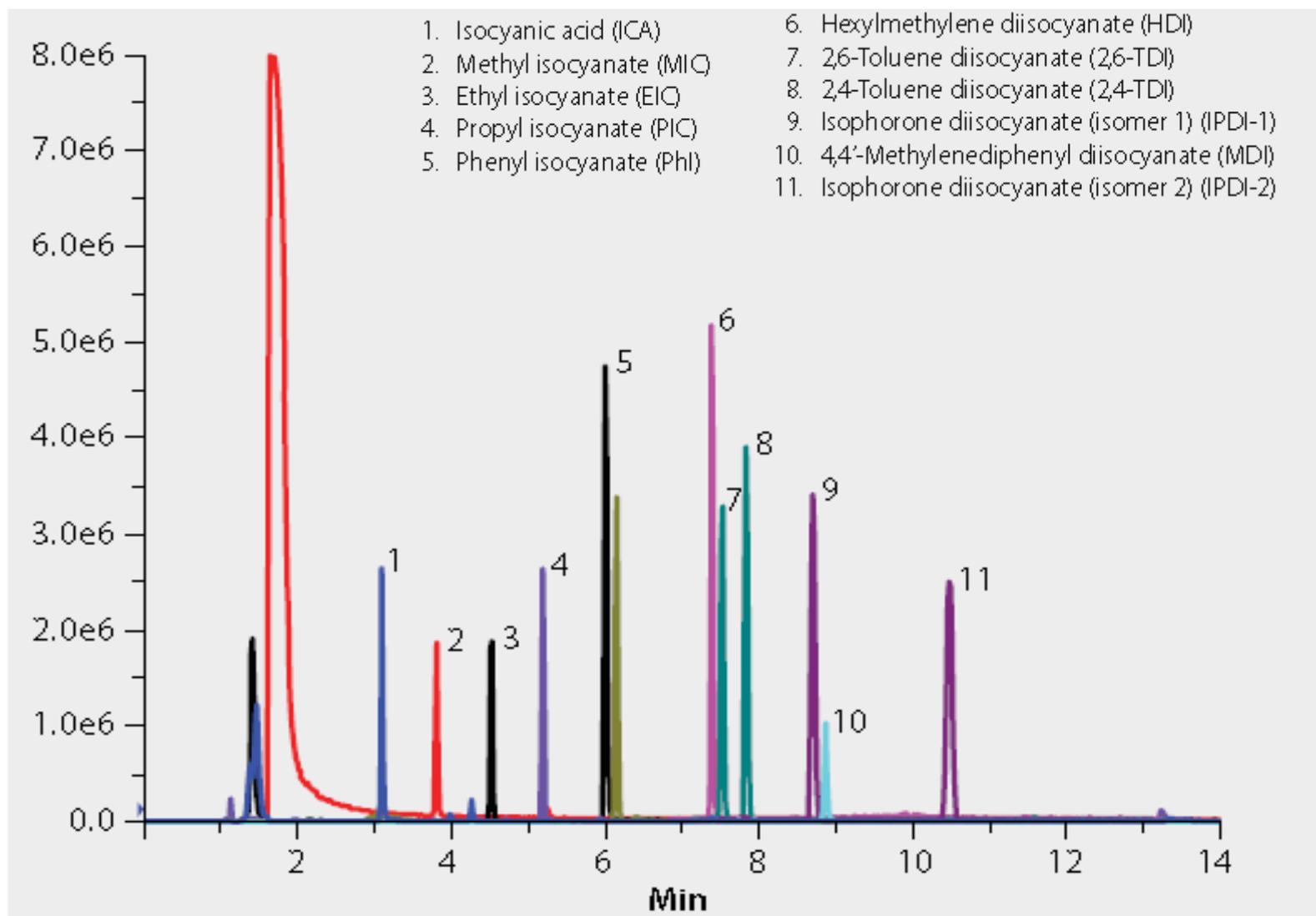
Detector: AB3200 QTrap MS, ESI(+), SIM

Mobile phase composition: (A) 5:95 acetonitrile:water w/ 0.05% formic acid; (B) 95:5 acetonitrile:water w/ 0.05% formic acid

Gradient: 40% to 70% B in 3 min; 70% to 90% B in 2 min; hold at 90% for 6 min, 90% to 40% in 0.1 min, hold at 40% for 3.9 min



Isocyanate Monomers Analyzed by LC-MS/MS





Chamber Validation Correlation of Sampling Time with Amount of Sampled Isocyanate

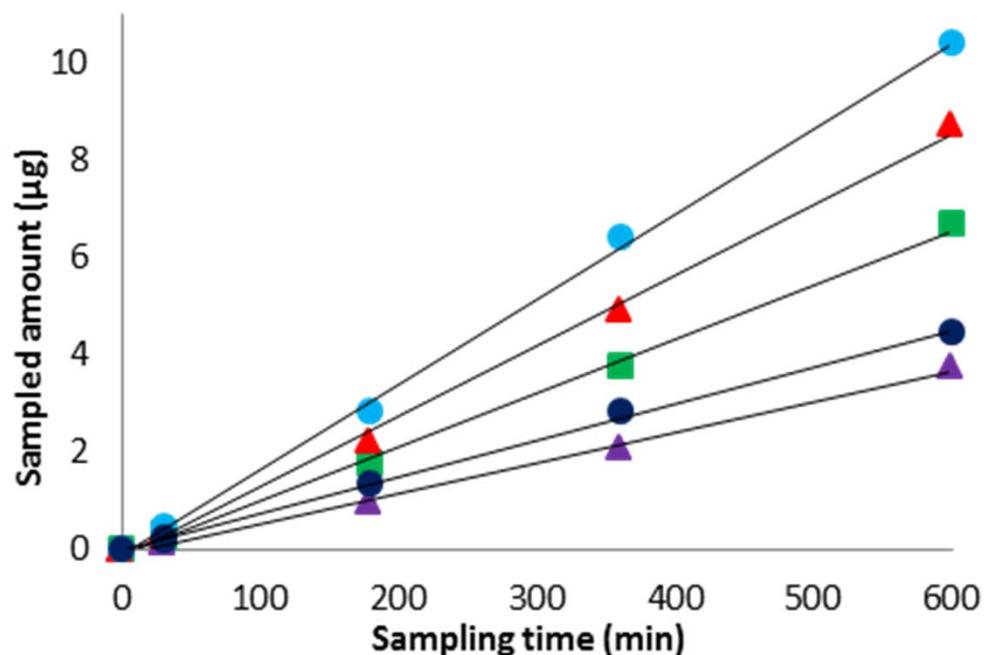
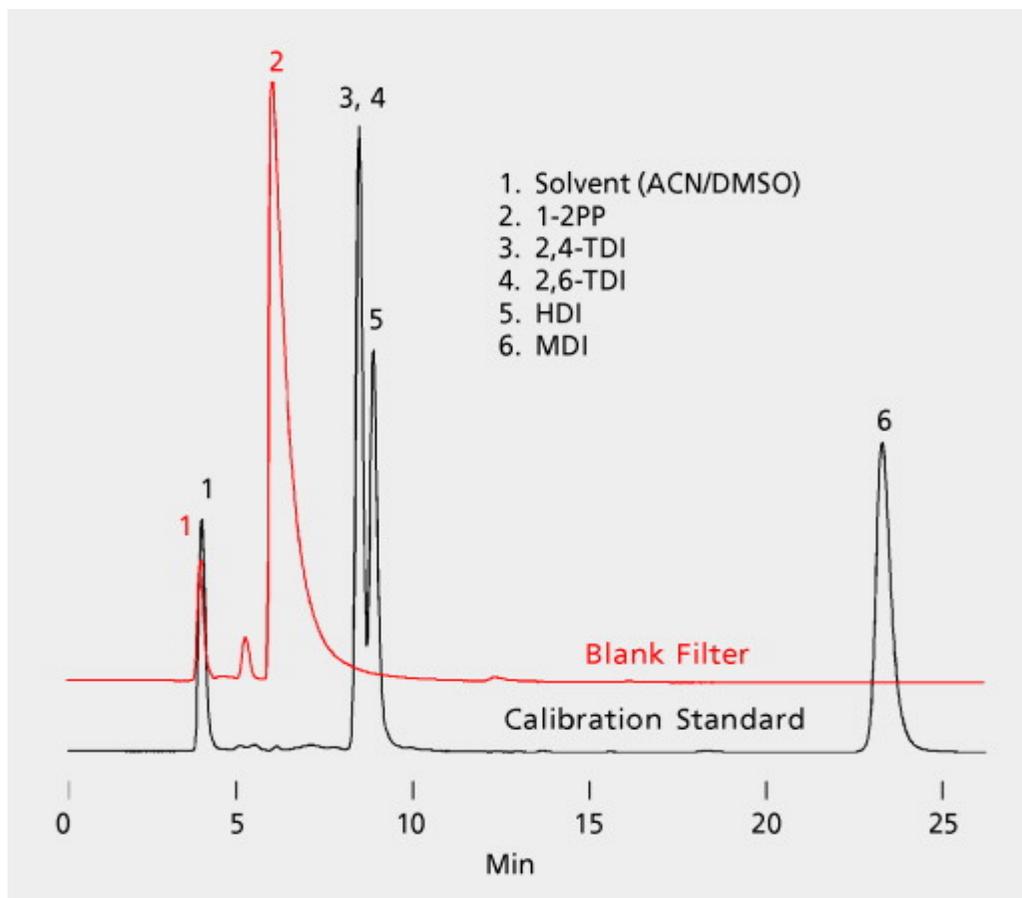


Figure 3. Correlation of sampling time with amount of sampled isocyanate.
HDI (■): $y = 0.011x - 0.0802$, $R^2 = 0.998$; IPDI1 (●): $y = 0.0175x - 0.0732$, $R^2 = 0.999$; IPDI2 (●): $y = 0.0075x + 0.0017$, $R^2 = 0.999$; 2,4-TDI (▲): $y = 0.0145x - 0.1319$, $R^2 = 0.9977$; 2,6-TDI (▲): $y = 0.0062x - 0.063$, $R^2 = 0.9977$.



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Alternative Sampling Devices



3-piece 25 mm cassette with glass fiber filter coated with 1,2-pyridyl piperazine (PP) reagent.

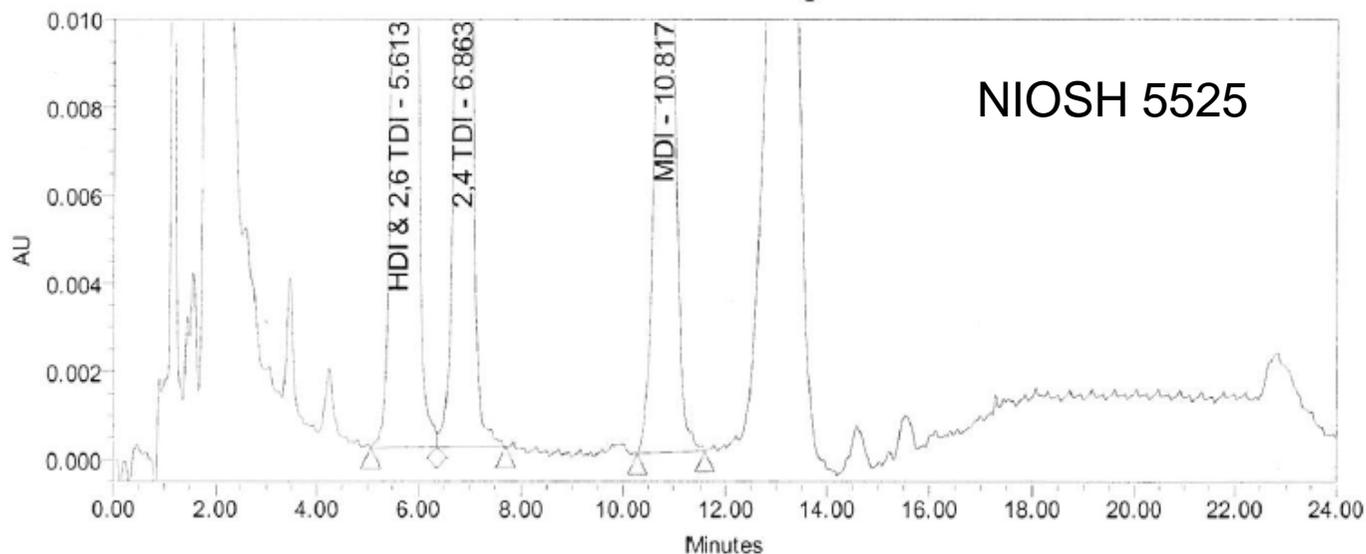
Suitable for TDI, HDI, MDI only

OSHA 42/47 Method: Run time 25 minutes
Analysis: HPLC-UV



Environmental

Alternative Sampling Devices



Glass Impinger/Bubbler: filled with reagent solution: multiple methods

NIOSH

5521: solution 1-(2-methoxyphenyl) piperazine in toluene
Suitable for monomers TDI, HDI, MDI, NDI

5522: solution tryptamine in DMSO
Suitable for monomers TDI, HDI, MDI

5525: solution 1-(9-anthracenylmethyl)piperazine (MAP) or coated on glass fiber filter
Suitable for Total -NCO functional groups



Issues with Alternative Methods

- Underestimate exposure
- Impingers are not safe for the worker to wear
- Cannot ship devices and/or necessary reagents across borders for compliance reasons.
- Other coated filter methods must be field desorbed for MDI
- Limited range of isocyanates sampled, and accuracy is in question
- Workflow is disrupted installing samplers on workers for 15-minute increments several times per day for specific job functions



Benefits

- The Most Field Use Friendly Device
- No Lost Time – can be worn for 8 hours
- Amenable to Global Distribution
- Safe to wear
- High sensitivity / low detection limits
- *Does not underestimate exposure*



Environmental

Benefits

The ASSET EZ4-NCO Dry Sampler for Isocyanates is the **easy-to-use** sampler offering the **ultimate sensitivity** for collection and measurement of **vapor phase and particulate isocyanates**.

Ultimate Sensitivity

Achieves detection limits 50-100x below existing methods

Suitable for aliphatic and aromatic isocyanate monomers and oligomers



ASSET on the Web

www.sigmaaldrich.com/asset

Analytical / Chromatography > Air Monitoring > ASSET™ EZ4-NCO Dry Sampler



Analytical / Chromatography Products

Air Monitoring

Air Monitoring Products

Learning Center

Air Monitoring Applications

Overview

Carbon Adsorbents

Active Sampling

Passive Sampling

radiello Diffusive Sampling

Whole Air Sampling

Gas Sampling Bags

Air Monitoring Standards

Air Sampling Pumps

Custom Capabilities

Regulatory Agencies

Literature

Cross Reference for SKC Products

ASSET™ EZ4-NCO Dry



Air Monitoring

ASSET™ EZ4-NCO Dry Sampler for Isocyanates

Providing Ultimate Sensitivity for Vapor Phase and Particulate Isocyanates

The ASSET EZ4-NCO dry sampler for isocyanates is the easy-to-use sampler offering the ultimate sensitivity for collection & measurement of vapor phase and particulate isocyanate monomers and oligomers.

Key Features and Benefits

- Ability to achieve reliable, low detection limits
- Only device to measure vapor phase and particulate isocyanates
- Sampling for > 8 hrs
- No special storage conditions required for the sampler, before or after sampling
- No interferences, no field extraction
- 2 year shelf life



ASSET™ EZ4-NCO Dry Sampler for Isocyanates flyer

[Technology Overview](#)

[Supporting Data](#)

[References](#)

[Analytical Service Laboratories](#)

[Ordering Information](#)

Interested in evaluating this new technology? Contact: kristen.schultz@sial.com

Technology Overview

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 are at risk for respiratory disorders, asthma and other health conditions. With current isocyanate sampling devices, there are certain disadvantages to deploying the samplers in the field; such as the need to ship reagents to the sampling location, and also the need for field desorption. It is also known that particulates form incomplete reactions, with the reagent as well as the isocyanate monomers and oligomers being measured, which results in underestimation of exposure.



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Analytical Service

US Analytical Service

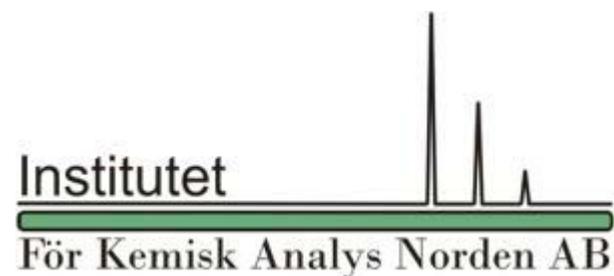
- [Bureau Veritas IH Lab](#), Novi MI US

Europe Analytical Service

- [IFKAN](#), Hasselholm, Sweden



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VERITAS



We are recruiting analytical test labs that have the capability of LC-MS/MS. The Analytical Protocol is available to send to interested laboratories.



References

Sampler technology protected by patent (US) *Patent number US 7,700,045 B2; Apr. 20, 2010.*

Dry sampling system is an ISO standard:

Gunnar Skarping, Marianne Dalene and Daniel Karlsson

ISO 17734-1:2006, Determination of organonitrogen compounds in air using liquid chromatography and mass spectrometry — Part 1: Isocyanates using dibutylamine derivatives.

Gunnar Skarping, Marianne Dalene and Daniel Karlsson

ISO 17734-2:2006, Determination of organonitrogen compounds in air using liquid chromatography and mass spectrometry — Part 2: Amines and aminoisocyanates using dibutylamine and ethyl chloroformate derivatives.

In a technical ISO report, the technology is described as the only methodology that covers all situations.

Gunnar Skarping, Marianne Dalene and Daniel Karlsson

ISO/TR 17737:2007, Workplace air – Guidelines for selecting analytical methods for sampling and analyzing isocyanates in air



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Results Delivered.

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