Measurement of the Potential Exposure to Isocyanate Monomers and Oligomers During Spray Painting

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Solutions within.

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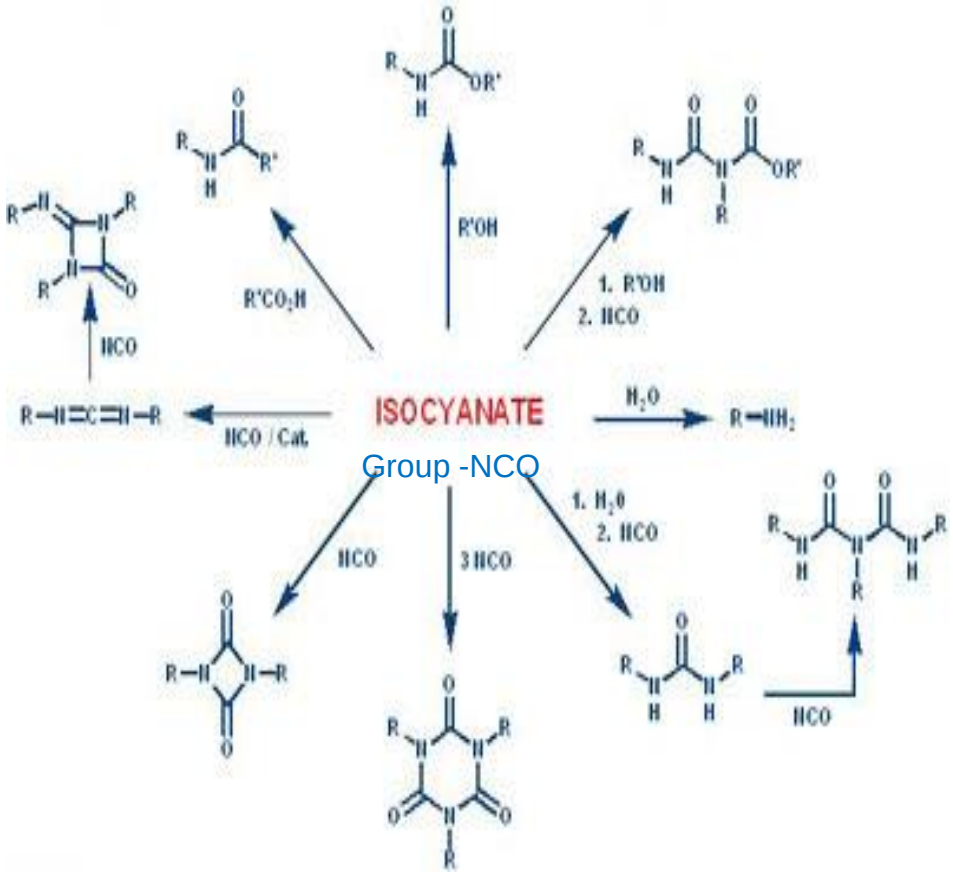
What is an isocyanate? (chemistry)



Isocyanate + polyol (compound with many alcohol groups) = polyurethane

$$R^1\text{-}N{=}C{=}O \;+\; R^2\text{-}O\text{-}H \longrightarrow R^1\text{-}\overset{\displaystyle H}{\underset{|}{N}}\text{-}\overset{\displaystyle O}{\underset{\|}{C}}\text{-}O\text{-}R^2$$

Isocyanates In the News:

January 8, 2015 – US EPA issues rule proposal limiting the US of TDI chemicals in consumer products.

2014 – Worker exposure to TDI at Automotive manufacturing plant in Selma, LA gains national attention

June 25, 2013 – OSHA NEP on isocyanate exposure in the workplace

April 2013 – 1,2-MP and other piperazine banned in UK as Class C drugs of abuse.

April 13, 2011 – EPA Action Plan on MDI & TDI

Isocyanates Exposure

Isocyanates exposure is universal

Health Risks

- Respiratory: Asthma ***- leading cause of occupational asthma***; difficulty breathing [Johnson et al. 2004; Wisnewski et al. 2006]
- Musculoskeletal: Chest pains
- Irritation of mucous membranes; dermatitis
- Cancer: Aromatic isocyanates (Europe)
- Death: MIC, Union Carbide (Bhopal, India)

NIOSH Pocket Guide to Chemical Hazards

Hexamethylene diisocyanate (HDI) (CAS No. 822-06-0)
Isophorone diisocyanate (IPDI) (CAS No. 4098-71-9)
Methyl isocyanate (MIC) (CAS No. 624-83-9)
Methylenebis(phenyl isocyanate)(MDI) (CAS No. 101-68-8)
Naphthalene diisocyanate (NDI) (CAS No. 3173-72-6)
Toluene-2,4-diisocyanate (TDI) (CAS No. 584-84-9)

Isocyanate Species	NIOSH REL (ug/m3)	ACGIH TLV (ug/m3)
TDI	CA (lowest feasible)	36
MDI	50	51
HDI	35	34
HMDI	None	54
IPDI	45	45
NDI	40	None
TRIG (total reactive isocyanate group)	None	None

Facts

Isocyanates are a main component in the production of polyurethane (PUR) materials

Exposure to isocyanates can put workers at risk for respiratory disorders like “occupational asthma”

Not only monomers pose a health risk

How Isocyanate Exposure Occurs

Application – before curing is complete

Thermal degradation – Grinding, Cutting, Welding

Current Test Methods

NIOSH Method 2535 – TDI

- Glass tube with (N-[(4-nitrophenyl)methyl]-propylamine on glass wool
- HPLC UV

ASTM D5932 – TDI

- Segregating device containing with a glass fiber filter impregnated with 9-(N-methylaminomethy) anthracene
- HPLC UV/Fluorescence

ASTM D6561 – oligomeric HDI

- Segregating device containing a polytetrafluoroethylene (PTFE) filter
- HPLC UV

OSHA 42/47 - TDI, HDI, MDI

- Filter cassette with glass fiber filter impregnated with 1-(2-pyridyl)piperazine
- HPLC UV

ISO 17734-1:2013 – monomeric and oligomeric

- Filter cassette + denuder with glass fiber filter impregnated with dibutylamine
- LC-MS/MS

Experiment-Overview

Spray painting using an automotive clear coat

Painting was done for a continuous length of time

Collect personal and area samples

Quantitative analysis was performed accordingly to the specific sampler

Spray Booth Samples

Two part clear coat was used to spray paint a car hood

Spray Booth Samples

Two different types of “dry” samplers

ORBO-80

1-(2-pyridyl)piperazine (1-2PP) coated glass fiber filter
1L/min per OSHA 42/47

Asset EZ4-NCO

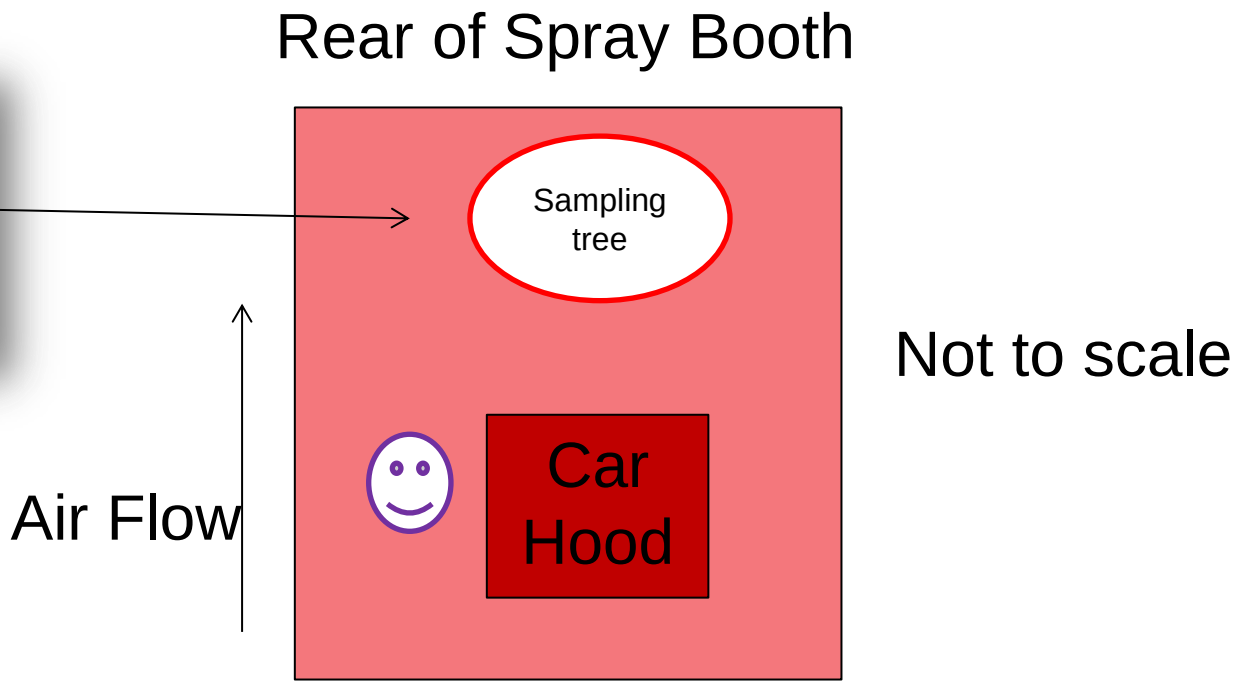
Dibutylamine (DBA) coated glass fiber filters
100ml/min

Spray Booth Samples

Two types of samples (Personal and Area)

Spray Booth Samples

The sampling tree was placed in the rear of the spray booth

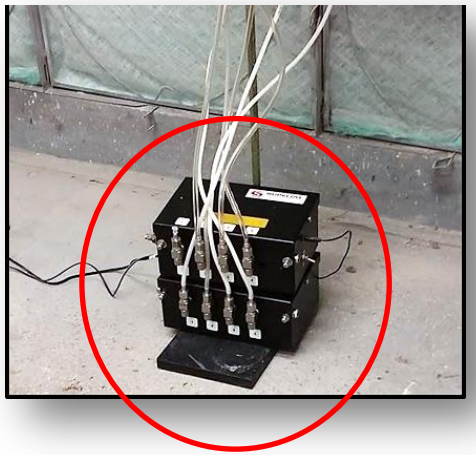


Spray Booth Samples

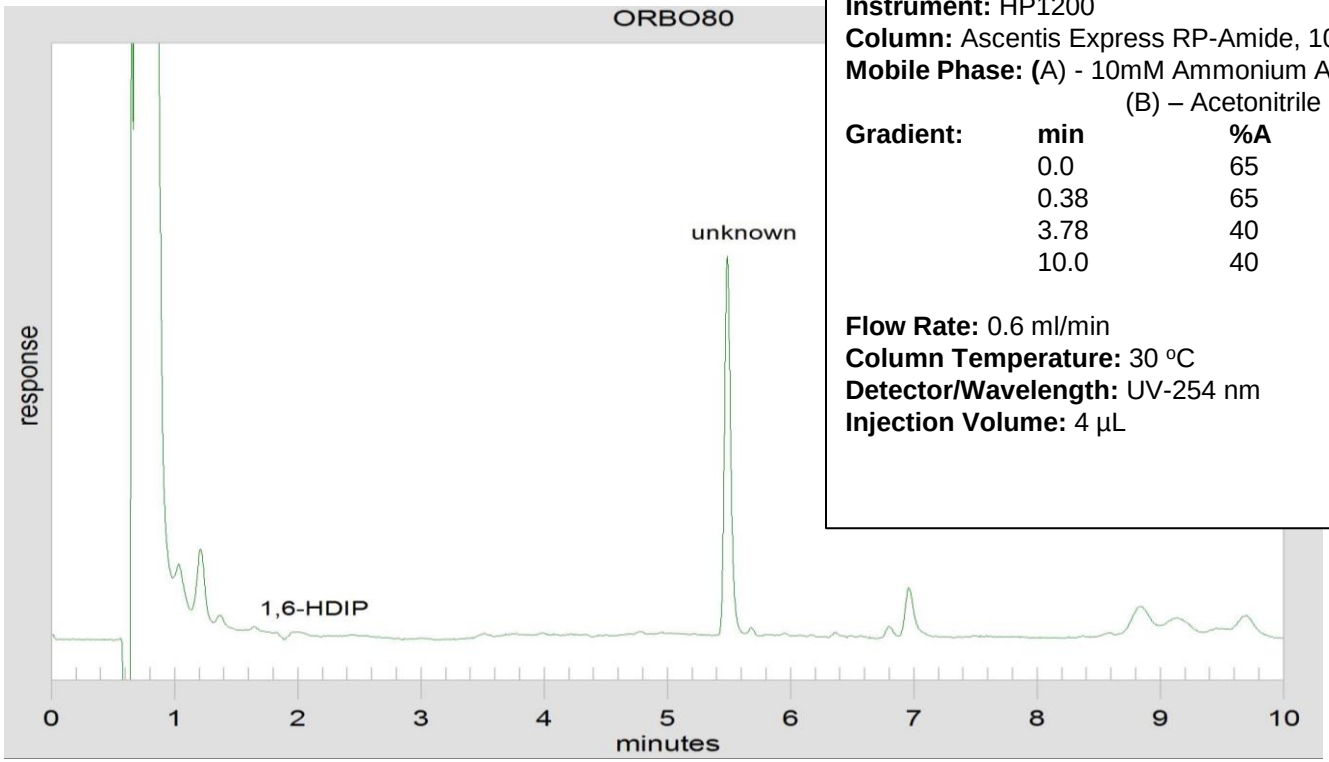
Sampling rates:

- ORBO-80 – 1 L/min per OSHA 42/47
- Asset EZ4-NCO – 100 ml/min

- Sampling Time: 15 minutes



Chromatogram – ORBO-80



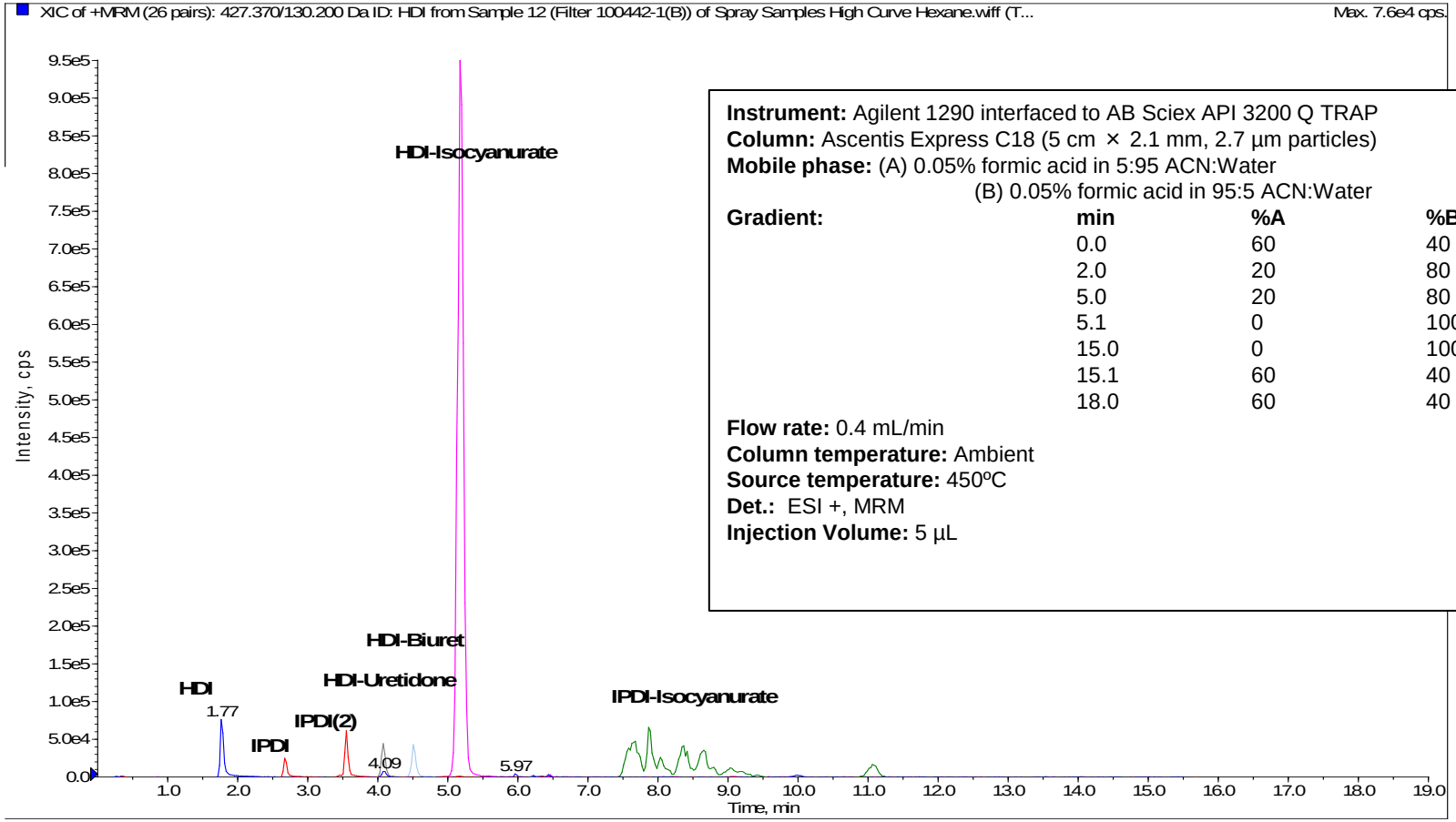
Instrument: HP1200
Column: Ascentis Express RP-Amide, 10cm x 3.0mm x 2.7um
Mobile Phase: (A) - 10mM Ammonium Acetate pH 6
(B) – Acetonitrile

Gradient:	**min**	**%A**	**%B**
	0.0	65	35
	0.38	65	35
	3.78	40	60
	10.0	40	60

Flow Rate: 0.6 ml/min
Column Temperature: 30 ºC
Detector/Wavelength: UV-254 nm
Injection Volume: 4 µL

LC-UV chromatogram of the resulting extract from the ORBO-80 sampler used for spray booth sampling.

Chromatogram - ASSET



Instrument: Agilent 1290 interfaced to AB Sciex API 3200 Q TRAP
Column: Ascentis Express C18 (5 cm × 2.1 mm, 2.7 µm particles)
Mobile phase: (A) 0.05% formic acid in 5:95 ACN:Water
(B) 0.05% formic acid in 95:5 ACN:Water

Gradient:

min	%A	%B
0.0	60	40
2.0	20	80
5.0	20	80
5.1	0	100
15.0	0	100
15.1	60	40
18.0	60	40

Flow rate: 0.4 mL/min
Column temperature: Ambient
Source temperature: 450ºC
Det.: ESI +, MRM
Injection Volume: 5 µL

LC-MS/MS chromatogram for an ASSET area sampler used for spray booth sampling

Calibration Standards

ASSET - CRM

Monomer: Dibutylamine derivative

- EIC (Ethyl isocyanate)
- HDI (Hexamethylene diisocyanate)
- HMDI (Dicyclohexylmethane 4,4'-diisocyanate)
- ICA (Isocyanic acid)
- IPDI (Isophorone diisocyanate)
- MIC (Methyl isocyanate)
- 4,4' -MDI (Methylenediphenyl diisocyanate)
- PhI (Phenyl isocyanate)
- PIC (Propyl isocyanate)
- 2,4 and 2,6 -TDI (Toluene diisocyanate)
- m-TMXDI (m-tetramethylxylene diisocyanate)

Oligomers: Dibutylamine derivative

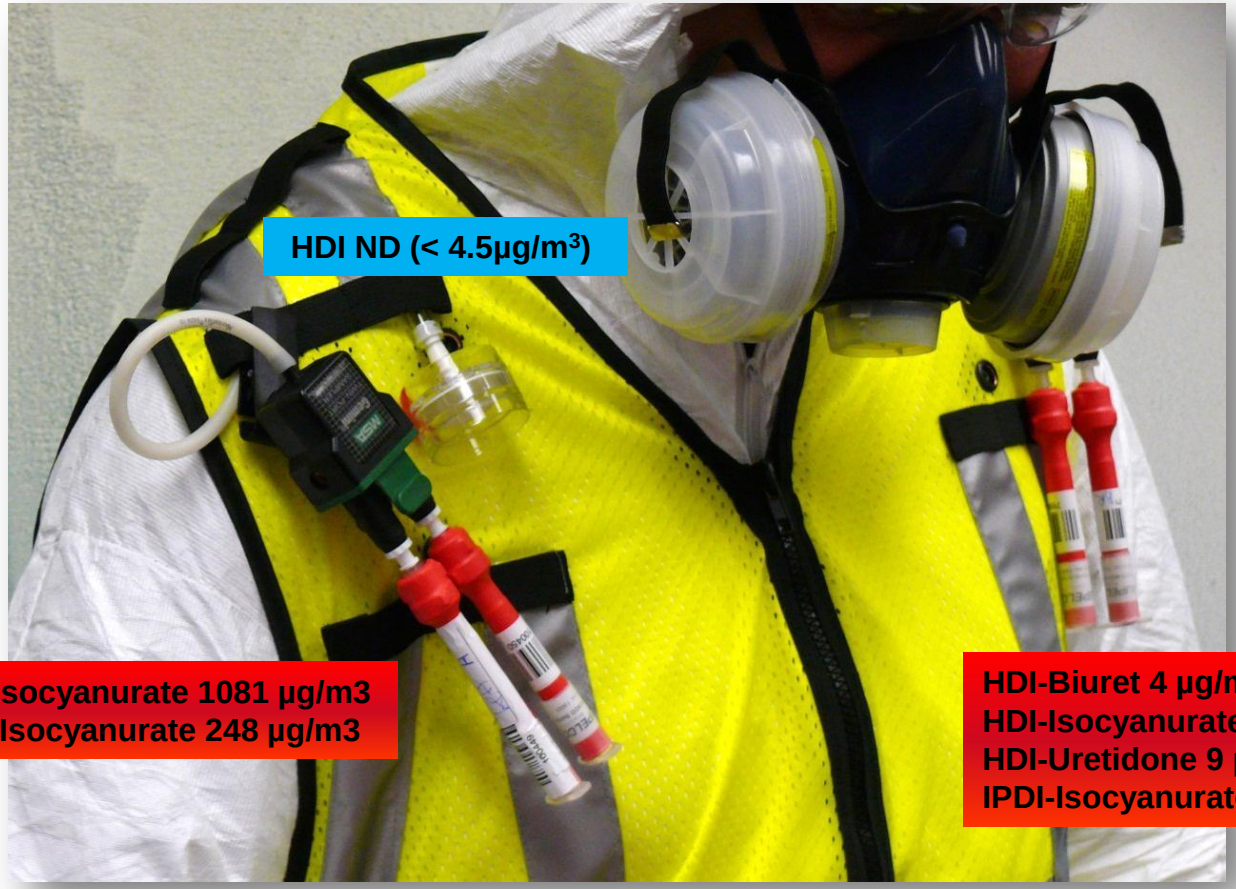
- HDI-Biuret
- HDI-Isocyanurate
- HDI-Uretdione
- IPDI-Isocyanurate
- MDI-Trimer
- MDI-Tetramers

ORBO-80

Monomers: 1-(2-pyridyl)piperazine derivative

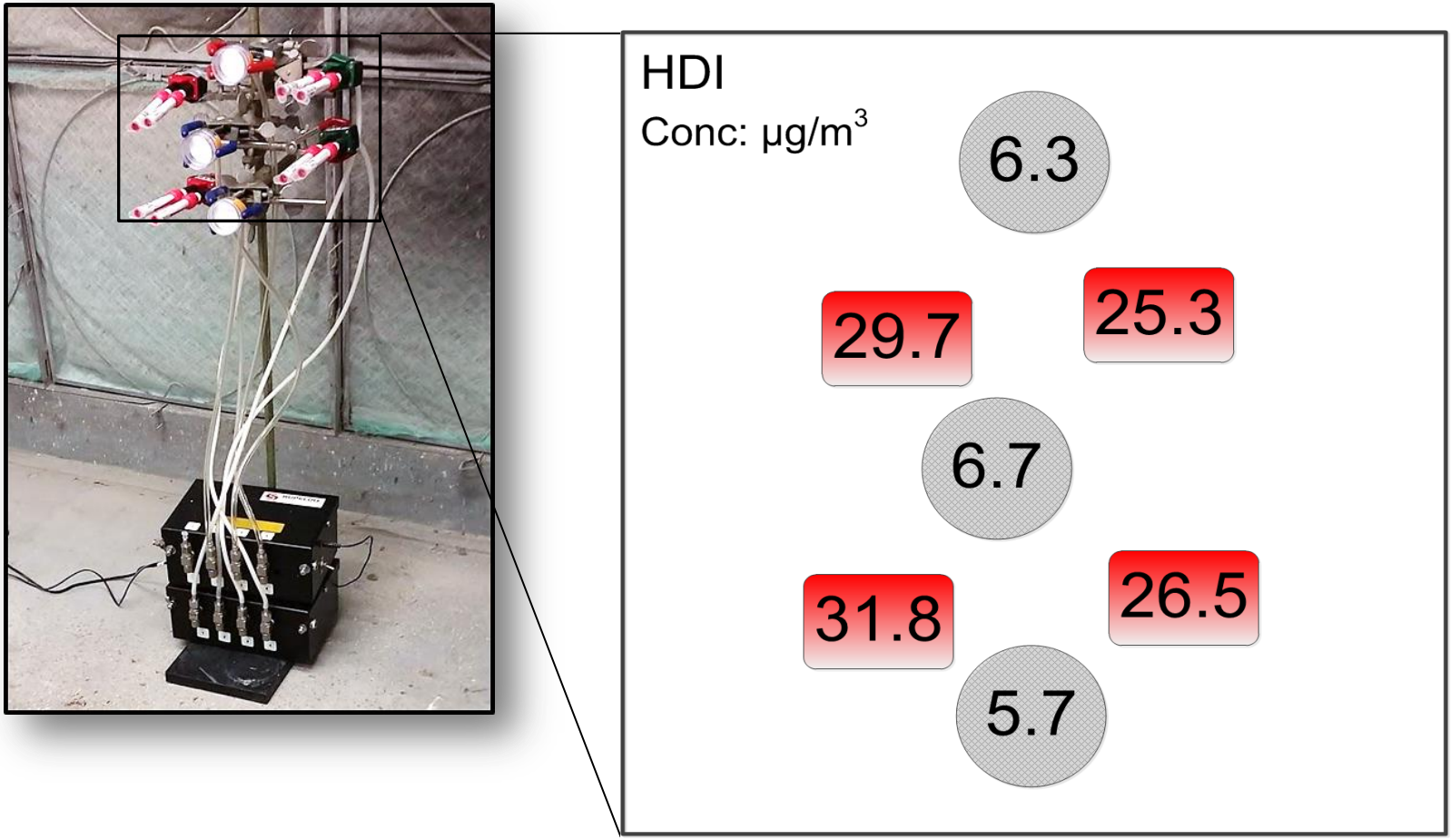
- HDI (Hexamethylene diisocyanate)
- 4,4' -MDI (Methylenediphenyl diisocyanate)
- 2,4 and 2,6 -TDI (Toluene diisocyanate)

Results from Personal Samples



ASSET ORBO-80

Results from Area Samples



Red squares represent ASSET samplers, grey circles are ORBO-80 samplers.

Results (µg/m^3) from Area Samples(ASSET)

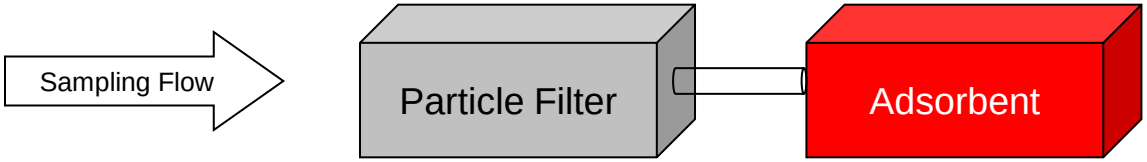
Analyte	M.W.	Sample 1	Sample 2	Sample 3	Sample 4
HDI	168.2	25.3	29.7	26.5	31.8
HDI-Biuret	478.6	21.5	26.9	22.8	27.1
HDI-Isocyanurate	504.6	7022.4	8602.1	7796.8	9866.4
HDI-Uretidone	336.4	50.2	61.3	51.5	66.4
IPDI	222.3	8.6	8.9	8.5	10.0
IPDI(2)	222.3	2.3	2.6	2.4	3.0
IPDI-Isocyanurate	666.9	5160.8	5801.4	5177.9	6887.9

Results (µg/m^3) from Area Samples(ORBO-80)

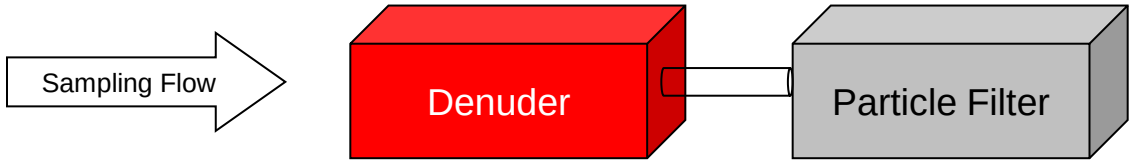
Analyte	Sample 1	Sample 2	Sample 3
2,6-TDI	ND<4.5	ND<4.6	ND<4.5
1,6-HDI	6.3	6.7	5.7
2,4-TDI	ND<4.5	ND<4.6	ND<4.5
4,4-MDI	ND<5.6	ND<5.7	ND<5.6

The ASSET Sampler Works Differently

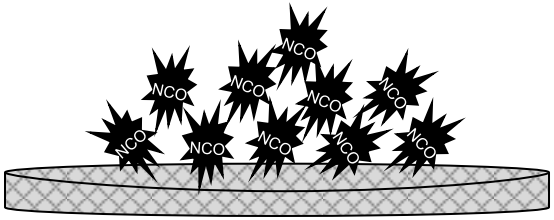
Typically the filter is placed before the vapor collection device when sampling for both vapors and particulates.



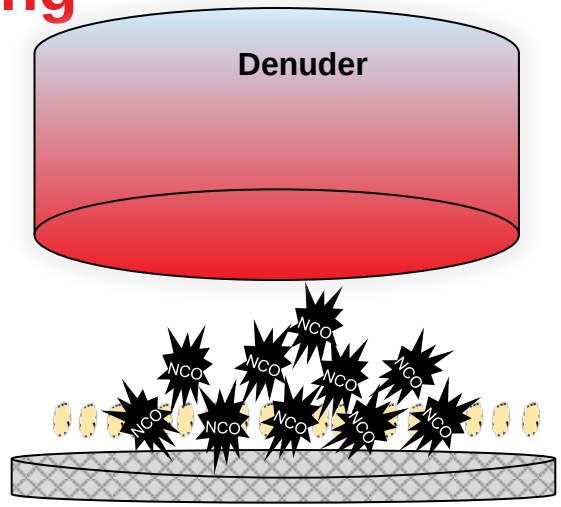
The ASSET Sampler works Differently.....the filter is placed after the vapor collection device (denuder). The vapors collect in the denuder, while the particles pass through to the filter.



Reagent Depletion – During Sampling



Filter



37mm Filter Cassette

Denuder

Filter

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

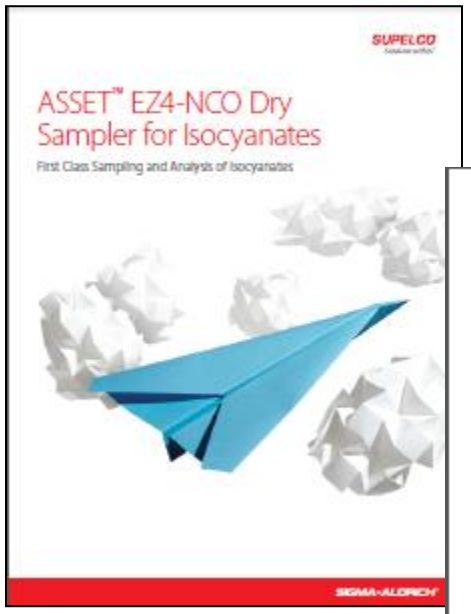
Key Differences

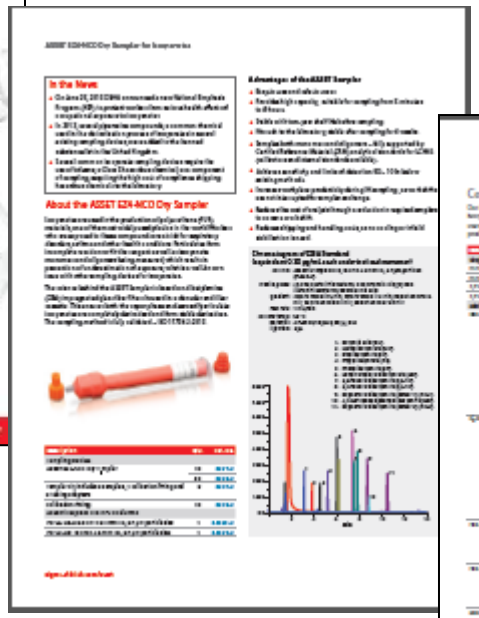
- Calibration standards
- Analytical technique
- Sampler design

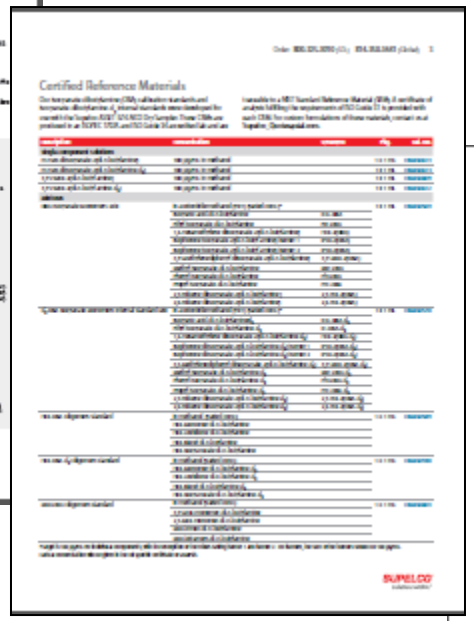
For More Information on the Dry Sampler, visit our website or request the flyer.

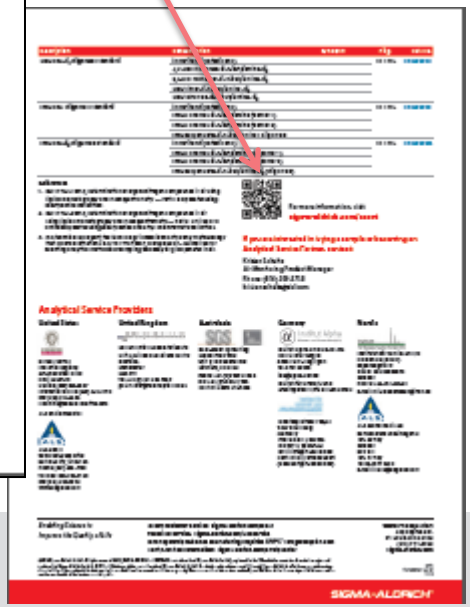
4-Page Flyer – T412089 (OTB)

On the web at: www.sigmaaldrich.com/as









For more information, visit
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Conclusions

- The possible improvement that sampler design could provide
- The LC-MS/MS analysis detected and confirmed the identity of isocyanate compounds and provided accurate quantitation with the use of derivative specific and deuterated derivative standards
- Predominant airborne species (oligomers) were HDI-isocyanurate and IPDI-isocyanurate
- Higher levels of oligomers in comparison to monomer levels

Thank You !

Questions ?

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