A NEW APPROACH TO SAMPLING ISOCYANATES MONOMER AND OLIGOMERS IN AIR USING A DRY SAMPLER

BACKGROUND

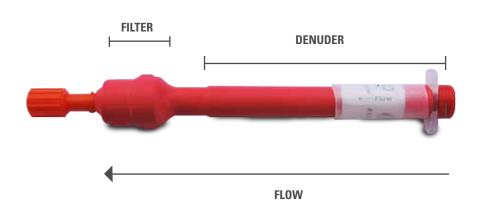
Isocyanates are highly reactive, low molecular weight compounds which contain the isocyanate functional group. These chemicals are commonly used in the production of paints/protective coatings, building materials (foams and adhesives), manufactured goods (furniture, electronics and shoes) and the automotive repair industry.

Human exposure to isocyanate compounds is typically by inhalation and dermal contact, and can have adverse health effects including irritation (skin, eyes, gastrointestinal and respiratory tracts), sensitisation and asthma, hypersensitive pneumonitis and possibly cancer.

To be compliant with the United States' Occupational Safety and Health Administration's recommendation that all isocyanates, regardless of physical state (vapour or aerosol), be field desorbed, sampling needs to be undertaken with glass impingers and derivatised in the field (the traditional wet impinger method) or collected using a dry sampler, such as the new ASSETTM EZ4-NCO sampler.

OVERVIEW

The ASSETTM EZ4-NCO Dry Sampler is an alternative to the traditional 'wet' impinger methods that is easy to use and offers high sensitivity for the collection and measurement of vapour phase and particulate isocyanates. It is an active sampling device for the collection of isocyanates using a pump to pull air through the device at a known rate. The sampler has two points of collection – a denuder for collecting isocyanates in vapour form and a filter for collecting particulates. As the isocyanates pass through the device, they react with di-n-butylamine (DBA) to form stable isocyanate derivatives.





1.1 COMPARISON BETWEEN WET SAMPLER AND DRY SAMPLER

There are numerous documented health and safety, transport and handling issues associated with the traditional impinger sampling for isocyanates that using a dry sampler avoids.

WET IMPINGER	DRY SAMPLER
Impinger solution needs to be transferred into a clean vial to be transported	No contact with sample media in the field so there is no risk of human exposure to the solution or contamination of the solution
The impinger solution for NIOSH method 5522 contains dimethyl sulfoxide which is readily absorbed into the skin and not suitable for personal exposure sampling	Safe to wear so suitable for workplace personal exposure sampling
Toluene in the impinger solution for NIOSH method 5521 is flammable and may cause issues with transportation.	No shipping compliance issues
Literature suggests that wet samplers may underestimate isocyanate exposure as they do not discern vapours from aerosols.	Measures vapour phase and aerosols separately with lower detection limits
The preparation of the glass fibre filter in the field for OSHA method no. 42/OSHA method no. 47 can be difficult, increase the risk of contamination and delay sampling	No leaking or breaking impingers
NIOSH method 5521 and OSHA method no. 42/OSHA method no. 47 use an impinger solution containing piperazine, which is a controlled substance in the United Kingdom and cannot be used.	Sampler uses DBA which has no restrictions
It is recommended that the glass fibre filter used in OSHA method no. 42/OSHA method no. 47 are stored at reduced temperatures until used for sampling	No specific storage requirements
Sampling time is limited	DBA replenishment from denuder means longer sampling periods and is therefore capable of true time weighted average sampling

1.2 SAMPLE COLLECTION PROCEDURE

The ASSETTM EZ4-NCO Dry Sampler is supplied with caps on the inlet and outlet, which are removed just prior to sampling. The Dry Sampler should be labelled prior to the connection to the air sampling pump, flow set to the recommended rate of 0.2 litres per minute and secured to the person to be sampled using an optional label clip. At the completion of sampling, check the flow, record the flow rate and time, disconnect the sampler from the pump, replace the caps on each end of the sampler and package ready for shipping to the laboratory. Recommended holding time is two weeks. The samplers can be stored in an airtight container and shipped at room temperature, but can also be stored in the refrigerator and transported with cooler bricks if warmer temperatures are anticipated.

1.3 EXTRACTION AND ANALYSIS PROCEDURE

At the laboratory, the filter media is extracted into an acidified methanol solution, which undergoes a liquid/liquid extraction with toluene, the toluene is then evaporated and is reconstituted into acetonitrile, and this acetonitrile extract is then analysed by the Liquid Chromatography – Tandem Mass Spectrometry (LC MSMS). This is in accordance with ISO Method 17734-1:2013 – Determination of Isocyanate Compounds in Air using Dibutylamine Derivatives.

The validated compounds include a range of monomers and oligomers including Isocyanic acid, Methyl isocyanate, Ethyl isocyanate, Propyl isocyanate, Phenyl isocyanate, Hexamethylene diisocyanate, 2,4-Toluene diisocyanate, 2,6-Toluene diisocyanate, Isophorone diisocyanate (isomer 1), Isophorone diisocyanate (isomer 2), 4,4' –Methylenediphenyl diisocyanate and Dichlohexylmethane 4,4'-diisocyanate.

1.4 VALIDATION

The validation carried out by SGS Environment, Health and Safety found that all compounds were less than $0.005 \, \mu g/s$ ampler on blank samplers, with the exception of Isocyanic acid and Propyl isocyanate which are $0.3 \, \text{and} \, 0.02 \, \mu g/s$ ampler respectively.

Therefore, based on a sample volume of 3 litres, the detection limit for Short Term Exposure Limit sampling would be 1.6 μ g/m3 and based on a sampling volume of 96 litres the detection limit for Time Weighted Average sampling would be 0.05 μ g/m3 achieved for all compounds other than Isocyanic acid and Propyl isocyanate (due to the higher background levels on the blank samplers). This would be based on using a detection limit of 0.005 μ g total as the limit of detection.

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