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Comparison of air samplers for determination of isocyanic acid and applicability for work environment exposure assessment

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Isocyanic acid (ICA) is one of the most abundant isocyanates formed during thermal decomposition of polyurethane (PUR), and other nitrogen containing polymers. Hot-work, such as flame cutting, forging, grinding, turning and welding may give rise to thermal decomposition of said polymers potentially forming significant amounts of ICA. A newly launched dry denuder sampler for airborne isocyanates using di-*n*-butylamine (DBA) demonstrated build-up of background ICA-DBA over time. Build-up of background ICA-DBA was not observed when stored at inert conditions (Ar atmosphere) for 84 days. Thus, freshly prepared denuders were used. The sampling efficiency of ICA using freshly prepared denuder samplers (0.2 L min^{-1}), impinger + filter samplers (0.5 L min^{-1}) using DBA and 1-(2-methoxyphenyl) piperazine (2MP)-impregnated filter cassette samplers (1 L min^{-1}) was investigated. PTR-MS measurements of ICA were used as a quantitative reference. Dynamically generated standard ICA atmospheres covered the range 5.6 to 640 ppb at absolute humidities (AH) 4.0 and 16 g m^{-3} . Recovered ICA was found to be 73–115% (denuder), 89–115% (impinger + filter) and 62–100% (2MP filter cassette). The method limit of detection (LOD) was equal to an amount of ICA of 24 ng (denuder), 8.9 ng (impinger + filter) and 9.4 ng (2MP filter cassette). The PTR-MS LOD for ICA was 1.8 and 2.8 ppb in atmospheres with an AH of 4 and 16 g m^{-3} . Denuder samplers were used for personal ($n = 176$) and stationary ($n = 31$) air sampling during hot-work at six industrial sites ($n = 23$ workers). ICA was detected above method LOD in 66% and 58% of the personal and stationary samples, respectively. ICA workroom air concentrations were determined to be 1.8–320 ppb (median 12 ppb) (personal samples), and 1.5–44 ppb (median 6.6 ppb) (stationary samples).

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Environmental impact

Personal sampling of airborne isocyanates generated during hot-work demands a sampling device which can efficiently collect isocyanates that potentially can be present in multiple phases and offers practical employment in terms of usage and safety. A chemisorptive denuder sampler for airborne isocyanates has been made available, which is solvent-free and requires no special treatment prior to or after air sampling. In this study, the applicability of different air sampling methods for field sampling of isocyanic acid was investigated by initial comparison. Real-time continuous PTR-MS was used as a quantitative reference in order to disclose any potential sampling bias of the sampling devices. The denuder sampler was employed in field for determination isocyanic acid during hot-work processes.

Introduction

Isocyanic acid (ICA) is emitted during thermal decomposition of polyurethanes (PUR).¹ Formation of ICA also occurs during thermal decomposition of other polymers such as phenol-formaldehyde (PF) and urea-formaldehyde (UF) resins^{2,3} and biomass.^{4,5} Studies have shown that thermal decomposition of PUR and epoxy resin materials form ICA in larger quantities than other isocyanates.^{2,6,7} Thus, hot-work such as welding, metal casting and flame cutting, if performed on materials

coated with or containing *e.g.* PUR or UF-resins, may present a risk of exposure to ICA to workers.

It is well documented that exposure to isocyanates may pose health risks to workers.^{8,9} Exposure to ICA is linked to the development of several adverse health effects, such as atherosclerosis,^{10–12} cataracts¹³ and rheumatoid arthritis.⁵ However, occupational toxicological data regarding ICA is lacking and a link between potential adverse health effects and occupational exposure to ICA is, to the authors' knowledge, not described in the literature. Nevertheless, ICA is readily water soluble at physiological pH⁵ and hydrolyzes at a relatively slow rate, which is influenced by pH and temperature.^{5,14} Based on the model published by Borduas *et al.*¹⁴ the half-life ($t_{0.5}$) of ICA in human

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blood *in vivo* can be estimated to be approximately 3 months (assuming hydrolysis as the governing reaction), which might allow ICA to interfere with biological systems. ICA may also readily participate in a protein carbamylation process.¹⁰ In a recent review, Annema *et al.* describe a close relationship between carbamylated high-density lipoprotein (HDL) and the development of atherosclerosis.¹¹ Therefore, measuring the occurrence of ICA in air during hot-work occupations is important.

Measurements of airborne isocyanates are usually performed by pumped personal air sampling, followed by liquid chromatographic mass spectrometric (LC-MS) analysis of desorbed derivatized solutes. Air sampling of ICA has mainly been done by use of filter cassettes, impingers or sampling tubes through derivatization of isocyanates by use of a nucleophilic reagent (usually an amine), due to their reactive nature.¹⁵ Thermally decomposing materials might result in the formation of an aerosol, which requires the application of a sampling device which can collect and permit a complete derivatization of any isocyanate present in potential multiple phases. Sampling efficiencies of methods in use of at least 75% has previously been described in the literature as satisfactory.¹⁶ Ideally, the sampling device and the subsequent analytical method in use should provide a detection limit which corresponds to at least 1/10 of an occupational exposure limit (OEL).^{16,17} For occupational exposure assessment, personal air samples collected in the breathing zone are preferred over stationary sampling, providing individual exposure data of relevance for health.¹⁷ Furthermore, thermal processes producing heat over short time frames (*e.g.* welding) may result in the formation of high concentrations of ICA as transient events.¹⁸ Task-based short-term personal air sampling is thus important to reveal exposure variance. Air sampling methods for isocyanates have been reviewed by Streicher *et al.*¹⁹ and Levine.²⁰

Occupational air sampling of ICA has traditionally been performed by use of impinger-filter samplers using di-*n*-butylamine (DBA) as reagent.^{2,6,21} Other reagents such as 1-(2-methoxyphenyl)piperazine (2MP) has also been successfully applied,²² but DBA is preferred in impingers due to a higher reactivity towards isocyanates.^{23,24} A downstream filter combined with an impinger makes possible collection of particulate matter smaller than about 1.5 μm , which is not effectively collected by impingers.²⁵ Additionally, the use of a volatile reagent like DBA will continuously provide the filter with reagent during sampling, making available the use of DBA as reagent also on filters using this set-up. Furthermore, the relatively large amount of reagent used provides high sampling capacity and efficient derivatization of isocyanates. However, the collection efficiency of ICA using impinger-filter samplers is adversely affected by sample air humidity,^{26,27} most likely due to water condensation in the samplers. Due to the fragile and bulky nature of impinger flasks, sampling of ICA using impingers has mostly been performed by stationary air sampling. Furthermore, the organic solvent in impingers presents risk of exposure and is a potential fire hazard near heat-sources. Thus, dry methods are to be preferred during hot-work.¹⁷

Filter methods offer a solvent-free and user-friendly collection of airborne isocyanates in the vapour and liquid phase. The use of 2MP impregnated glass fibre (GF) filters and personal air sampling for measurement of ICA in workroom air have been reported.^{28,29} For sufficient collection of ICA (and MIC) larger amount of reagent, by use of two or thicker filters, is required, as compared to sampling of less volatile diisocyanates.²⁸ However, filter methods in general may suffer from the possibility of local reagent depletion, especially long-term sampling, leading to sampling loss.^{28,30} Furthermore, filter methods provide poor mixing kinetics between isocyanates and reagent, compared to impingers.³⁰ In addition, filters need to be transferred to a reagent containing solvent shortly after sampling to ensure derivatization of unreacted isocyanates, making the field procedure more complicated and demanding.

In accordance with recommendations by a Nordic expert group regarding sampling of airborne isocyanates,¹⁷ a denuder sampling device with an end filter using DBA as a derivatization agent has been developed for collection of airborne isocyanates by Skarping and co-workers,²⁷ which is capable of sampling isocyanates from a multiphase matrix without being affected by air humidity.²⁶ The reagent is present in a relatively large amount and is immobilized using an equimolar amount of acetic acid. Thus, the sampler is solvent-free and user-friendly, and represents an attractive choice for collection of isocyanates in mixed phases, including ICA, during hot work. Additionally, no field extraction procedure or special storage conditions are claimed to be required. The denuder sampling method is fully validated according to ISO 17737:2012 (workplace atmospheres – guidelines for selecting analytical methods for sampling and analyzing isocyanates). The application of the denuder is however so far limited to controlled laboratory environments, to the authors' knowledge. Thus, there is a need for further evaluation of this sampler for field sampling of ICA, and other isocyanates, as well as benchmarking of this sampler in comparison to other more established methods.

By use of other sampling methods than the denuder approach, airborne ICA has been monitored in working environments. Thermally formed ICA has been monitored in metal foundries at air concentrations up to 700 $\mu\text{g m}^{-3}$ (400 ppb).^{2,31} (A conversion factor 1.76 $\mu\text{g m}^{-3} = 1$ ppb is used assuming a temperature and pressure at 25 °C and 1013 hPa, respectively). In another study ICA was detected at concentrations up to 840 $\mu\text{g m}^{-3}$ (480 ppb) during welding of district heating pipes insulated with a MDI-based PUR foam.⁶ ICA has also been detected in the breathing zone at concentrations up to 189 $\mu\text{g m}^{-3}$ (330 ppb)⁶ and 6.9 $\mu\text{g m}^{-3}$ (3.9 ppb)³² during welding on PUR-coated automotive metal sheets. In a survey performed in different Swedish PUR industries, ICA was detected during flame (up to 38 ppb) and UV (3 ppb) lamination of textiles, and PUR casting (\sim 3 ppb).²⁹ Nevertheless, the scope of occupational exposure measurements of ICA described in the literature is still scarce, and there is a need for further studies and evaluation of new methods in field.

The aim of this study was to compare the sampling efficiency of ICA using 2MP filter, impinger + filter and denuder sampling methods from controlled standard atmospheres of ICA at

different air concentrations and humidities. Another aim was to investigate the suitability of the new denuder method for measurements of ICA in workroom air in hot-work industries with potential ICA emissions.

Experimental

Chemicals and supplies

Type 1 water was provided by a Milli-Q ultrapure water purification system (Merck Millipore, Billerica, MA, USA). Cyanuric acid (98%), formic acid ($\geq 98\%$), toluene ($\geq 99.7\%$), ethyl isocyanate (EIC) (98%), phenyl isocyanate (PhI) (99%), propyl isocyanate (PIC) (99%) and 1-(2-methoxyphenyl)piperazine (2MP) were purchased from Sigma Aldrich GmbH (Steinheim, Germany), while hexamethylene diisocyanate (HDI) ($>99\%$) and urea ($\geq 99.5\%$) were purchased from Fluka Chemie GmbH (Buchs, Germany). Di-*n*-butylamine (DBA) ($\geq 99\%$), acetic anhydride (97%), ammonium acetate (98%), analytical grade methanol (MeOH), glacial acetic acid (100%) and hydrochloric acid (HCl) (37%) were purchased from Merck GmbH (Darmstadt, Germany). Sulfuric acid (H₂SO₄) (Scanpure) was purchased from ChemScan AS (Elverum, Norway). Di-*n*-butylamine-*d*₉ (DBA-*d*₉) and 2MP-*d*₃ was obtained from Ramidus AB (Lund, Sweden), while acetonitrile (ACN) (HPLC grade) and methanol (HPLC grade) were acquired from Rathburn Chemicals Ltd. (Walkerburn, Scotland). Synthetic air (99.999%), argon (Ar) (99.999%) and nitrogen (N₂) (99.999%) were obtained from YaraPraxair AS (Oslo, Norway). The calibration gas TO-14A Aromatics Mix containing a mixture of 14 volatile organic compounds (VOCs) balanced with N₂ was obtained from Restek Corp. (Bellefonte, PA, USA). The concentration of the VOCs was established by the supplier with an analytical accuracy of $\pm 10\%$.

Dynamic generation of ICA in test chamber

Dynamic generation of ICA atmospheres was performed by continuous thermal decomposition of an aqueous solution of urea to yield ICA and NH₃.³³ The atmosphere generator has been described elsewhere.¹⁸ The concentration of ICA in the generated atmospheres was varied by altering the concentration of the urea solution. Humidity was created by means of an adjustable humidifier built in-house. The temperature and humidity of the generated ICA atmospheres were continuously monitored using ChipCap-L sensor (GE Measurement & Control, Boston, Massachusetts, USA). The ChipCap-L sensor was coupled to a PicoLog data logger (Pico Technology, Cambridge, UK). The PTR-MS served as a quantitative reference for ICA as well as a monitor for the stability of the generated atmospheres. The atmosphere generator allowed parallel sampling through 12 channels. Measurement of gas flow rates was done by aid of a BIOS Drycal DC-Lite air flow calibrator (Mesa Laboratories, Inc., Colorado, US) and a Defender 510H flow meter (Mesa Laboratories, Inc.).

Personal sampler evaluation

Three different sampling methods established for isocyanate collection were evaluated by simultaneous sampling of

dynamically generated standard ICA atmospheres. Standard ICA atmospheres were created with an absolute humidity (AH) of 4 and 16 g m⁻³ and ICA atmospheres in the concentration range of approximately 5 to 640 ppb, at three different levels. The temperature in all atmospheres was 21.7 ± 0.3 °C. A total of six atmospheres were generated while performing parallel air sampling with three different air samplers ($n = 4$). The impinger + filter and the denuder sampling methods utilized DBA as derivatizing agent, while the filter method employed 2MP. All glass fibre filter (GF) materials used in this study were baked in an oven at 400 °C for three hours before use in order to remove contaminants. All sampling flow rates were measured and adjusted by the aid of a Defender 510L primary flow calibrator (Mesa Laboratories, Inc.). Initially, commercially available denuder dry samplers for isocyanates (ASSET™ EZ4-NCO, Supelco, PA, USA) were compared with freshly prepared denuders made in-house. Continuous measurements by PTR-MS were used as quantitative references for the generated ICA atmospheres.

Air sampling and sample treatment

Impinger + filter cassette, DBA. Each 30 mL impinger flask contained 15 mL 0.01 M DBA in anhydrous toluene and was backed up by a GF filter (MG160, $\varnothing = 25$ mm, pore size = 0.3 μm) (Munktell Filter AB, Falun, Sweden) placed in a polystyrene Millipore 25 mm filter cassette (Merck Millipore). Air samples were drawn at a sampling flow rate of 0.5 L min⁻¹ using Universal PCTX8 personal air sampling pumps (SKC Inc.) equipped with a low flow adapter (SKC Inc.). The air sampling time was 10 and 30 minutes. After sampling the impinger solutions and corresponding GF filters were transferred to 16 mL test tubes and sonicated for 10 minutes. The remaining sample treatment was performed as described in an earlier publication.¹⁸

Filter cassette, 2MP. The filter method is based on a method described in HSL/2007/47.³⁴ GF filters (GF/B, $\varnothing = 25$ mm, pore size = 1.0 μm) (Whatman International Ltd., Maidstone, UK) were impregnated with 400 μL 52 mM 2MP in anhydrous toluene. The toluene was allowed to evaporate for one hour. Millipore 25 mm filter cassettes were assembled together with 2MP-impregnated GF/B filters and stored in a refrigerator (4 °C) until use. Filters not immediately assembled with filter cassettes were stored in a freezer (-19 °C) until use. Air sampling was performed at a flow rate of 1.0 L min⁻¹ using SKC Universal personal air sampling pumps with sampling times of 10 and 20 minutes. Immediately after sampling the GF filters were transferred to 4 mL glass vials containing 2 mL adsorption solution consisting of 0.26 mM 2MP in anhydrous toluene. Each vial was then added 100 μL acetic anhydride and allowed to react with excess 2MP for 30 minutes. The solutions were evaporated to dryness under a stream of nitrogen. Then, 2.00 mL 1 ng μL^{-1} ICA-2MP-*d*₃ in ACN (internal standard [ISTD]) was added to all vials followed by 10 minute sonication. Finally, the solutions were filtered and transferred to 1.5 mL glass vials. Calibration solutions ($n = 6$) were prepared by spiking with 500 μL (0.04–4 ng μL^{-1}) ICA-2MP in ACN to blank filters in 2 mL adsorption solution. Otherwise, the calibration solutions were treated in the same manner as the samples. The final

calibration solutions covered the concentration range 0.01–1 ng μL^{-1} ICA-2MP.

In-house prepared denuder, DBA. Air samples were collected on freshly in-house prepared denuders impregnated with equimolar amounts (1.57 mmol, each) of DBA and acetic acid in MeOH. The denuders consisted of an annular denuder section coupled with a circular GF end filter. The denuders were prepared according to a previously reported method.²⁷ Air sampling was performed at a flow rate of 0.2 L min^{-1} using Casella Tuff™ 4 (Casella CEL Inc., Buffalo, NY, USA) personal air sampling pumps equipped with a low flow adapter (SKC Inc., Eighty Four, PA, USA). Sampling times were 10, 20 and 30 minutes, respectively. Preparation and treatment of calibration standards ($n = 8$) and samples were performed using an extraction procedure which is described in detail elsewhere,¹⁸ unless stated otherwise. Isocyanate derivatives of DBA and DBA- d_9 were prepared in-house according to a previous publication.¹⁸

Isocyanate-2MP and -DBA derivatives

2MP and 2MP- d_3 derivatives of ICA were synthesized according to a method described elsewhere.³⁵ The method was however modified for preparation of DBA and DBA- d_9 derivatives of ICA.¹⁸ Isocyanate/diisocyanate-DBA and -DBA- d_9 derivatives of MIC, EIC, PIC, PhI and HDI were synthesized according to a method presented in another publication.²⁷ Stock solutions of the derivatives were prepared by dissolution in ACN.

Storage testing of denuder samplers

Freshly prepared denuders ($n = 18$) were placed in an airtight container. The container was flushed with Ar and placed in a refrigerator (4 °C). Samples were removed ($n = 3$) for analysis 1, 8, 14, 28, 56 and 84 days after preparation. The container was flushed with Ar after every removal.

LC-MS measurements of derivatives

A LC-MS system consisting of a CapLC™ capillary gradient pump and a Micromass QuattroLC tandem quadrupole (MS/MS) (Waters Corp., Massachusetts, USA) was used for separation and quantification of isocyanate-DBA and -2MP derivatives. The instrumental conditions for the isocyanate-DBA derivatives are described elsewhere.¹⁸

Isocyanate-2MP derivatives. 1 μL sample solution in a partially filled 5 μL sample loop containing 4 μL $\text{H}_2\text{O}/\text{ACN}$ 90/10 (% v/v) focusing liquid was introduced onto a Kromasil® C_{18} column (1.0 mm I.D. \times 15 cm) (AkzoNobel, Separation Products, Bohus, Sweden) with 3.5 μm particles and pore size 100 Å, at a flow rate of 40 μL min^{-1} . The sample was eluted using a gradient which was initially held at 20% B for 2 minutes. The gradient was delivered from 20 to 95% B in 8 minutes, followed by a hold at 95% B for 7 minutes. Reconditioning of the column was done with 20% B for 7 minutes. Solvent A consisted of 10 mM ammonium acetate with pH 6.0. Solvent B consisted of ACN. Detection of the isocyanate-2MP derivatives was done in the positive electrospray mode. The capillary voltage was set at 3.7 kV. The cone and extraction cone voltages were 15 and 2 V,

respectively. The RF lens voltage was set at 0.4 V, while the multiplier voltage was 650 V. The source and desolvation gas temperatures were 110 and 300 °C, respectively. The desolvation gas flow was adjusted to 360 L h^{-1} . Multiple reaction monitoring (MRM) was performed with a dwell time of 0.3 s. Argon was used as collision gas, and the collision cell pressure was adjusted to 2.9×10^{-3} mbar. The collision energy was set to 15 eV.

PTR-MS measurements

A Compact PTR-MS (Ionicon Analytik GmbH, Innsbruck, Austria) was used as reference method for measurement of ICA air concentrations during the laboratory testing of personal samplers in various atmospheres. The instrument was operated using H_3O^+ as reagent ion, and the experimental set up is described elsewhere.¹⁸ Instrument transmission was accounted for prior to experiments using the TO-14A Aromatics Mix (Restek Corp.). Single ion monitoring (SIM) of the $[\text{M} + \text{H}]^+$ ions of ICA and ACN was performed for mass-to-charge (m/z) values 44 and 59 using reaction rates k at 2.89 and 5.36×10^{-9} $\text{cm}^3 \text{s}^{-1}$, respectively. Monitoring of the corresponding $[\text{M} + \text{H}]^+$ ion for ACN was done for supplemental purposes only. Instrument drift was accounted for by measurement of benzene (m/z 79) from the TO-14A Aromatics Mix.

Since the PTR-MS response efficiency for ICA is affected by sample air humidity,^{18,36} external calibration was required. The PTR-MS calibration for ICA is described in detail elsewhere,¹⁸ but will briefly be described here. Measurements of ICA in air were performed using PTR-MS and Fourier transform-infrared spectrometry (FT-IR) at an absolute humidity (AH) of 1.2–16.3 g m^{-3} and ICA concentration range of 27–490 ppb at ambient conditions (298 ± 2 K and 1000 ± 10 hPa). Using FT-IR as a quantitative reference method, the PTR-MS response to ICA demonstrated a linear ($R^2 > 0.999$) relation with sample air AH, independent of air concentration. The PTR-MS measurements of ICA (m/z 44) were corrected with respect to AH according to eqn (1)

$$[\text{ICA}]_{\text{AH corrected}} = \frac{[m/z 44]_{\text{ppb}}}{f_{\text{ICA}}} \quad (1)$$

where f_{ICA} (the PTR-MS response to ICA relative to the FT-IR response) = $0.2532 - 0.0073 \times \text{AH}$. Eqn (1) written in parametric form is given by

$$[\text{ICA}]_{\text{AH corrected}} = \frac{[m/z 44]_{\text{ppb}}}{0.2532 - 0.0073 \times \text{AH}} \quad (2)$$

Exposure measurements in work room atmospheres

Sampling strategy. A field survey was carried out in industries where hot-work was performed on materials coated with or containing PUR, PF or UF resins. Five different industries located in Norway were included in this survey; three auto workshops, two steel foundries, demolition of off-shore installations, metal recycling plant and railway repair workshop. The number of personal and stationary air samples collected at the

different worksites, along with their respective sampling times, is presented in Table 1. The general sampling strategy focused on task-based personal air sampling during execution of a hot-work procedure. However, for continuous and very fragmented (e.g. welding) hot-work operations spanning several hours, personal air sampling was executed continuously with a maximum sampling time of approximately 30 minutes per sampler. Additionally, stationary air sampling was performed at distances up to about 30 m from the hot-work zone. The maximum stationary air sampling time was approximately 30 minutes per sampler. A total of 23 workers participated in the survey. 164 personal and 28 stationary air samples were collected. All samples were collected using home-made denuder samplers. The air sampling flow rate was 0.2 L min⁻¹ using Casella Tuff™ 4 pumps equipped with low flow adapters.

Industry sites

Auto workshops. During auto bodywork restoration welding is performed in close proximity to paint and adhesives. The procedure for auto bodywork restoration was similar for all three workshops. Restored auto bodywork was glued and welded to the vehicle. Paint was sanded off all surfaces subject to heat from welding. An epoxy resin was generously applied to the lips of the new auto body part prior to fitting to the vehicle. The lips were spot welded to the vehicle using a spot or metal inert gas (MIG) welder, while straight edges were butt welded by MIG welding. The surface temperature of the steel sheets was measured on the nearest paint from the weld seam/spot (about 2–3 cm away) measured using a Fluke 561 infrared thermometer (Fluke Corp., Everett, WA, USA). Local exhaust ventilation was used during welding. Personal air sampling was also performed during modelled car paint removal with a pneumatic sanding tool. The sampling times were 5–38 minutes (median 24 min). A total of 8 workers participated and 19 personal air samples were collected.

Steel foundries

Foundry 1. The foundry manufactured steel casts using the sand cast technique with a UF resin as binder. Continuous day and night shift work production was carried out, with reduced load during the night shift. Air sampling was carried out during a night shift and an afternoon shift during the casting process.

During the night shift two workers performed both preparation of the melt and casting. The moulds filled during the night shift had a height of approximately 2 m, thus the personnel was standing on the mould itself during casting. The casting was done in two different sections of the plant where stationary air sampling was performed at each section. A total of three melt batches were poured during the night shift. During the afternoon shift 3 workers performed the casting exclusively. Most of the moulds filled during the afternoon shift were smaller with a height of less than 1 m. Six melts were poured during the afternoon shift, and samples were collected from five workers. Stationary air sampling was performed during the entire night shift in close proximity (less than 10 m) to the casting process. A total of 27 personal and 8 stationary air samples were collected. Personal air samples were collected outside the respirator. The sampling times for the personal and stationary air samples were 7–16 minutes (median 9 min) and 26–34 minutes (median 30 min), respectively.

Foundry 2. The foundry manufactured steel casts using the sand cast technique by use of a PF resin. Production was carried out only during the day shift. Air sampling was performed during one day shift. Two workers carried out the casting process exclusively. Personal air sampling was carried out during the casting process, except for the two last hours of the shift when uninterrupted air sampling was performed. Workers used a clear plastic visor for protection. Stationary air sampling was performed continuously throughout the whole shift at two locations in the production hall. The stationary sampling locations were approximately 10 and 30 m from the casting area. A total of 11 personal and 20 stationary air samples were collected. The sampling times for the personal and stationary air samples were 7–16 minutes (median 12 min) and 34–45 minutes (median 33 min).

Demolition; off-shore installation. The site performed demolition of a decommissioned off-shore installation. A large portion of the demolition work consisted of dissecting large steel structures by flame cutting. All structures subject to flame cutting were coated with a thick layer of PUR-paint. Flame cutting was performed during day shifts in two proximate

Table 1 Number of workers and the amount of personal and stationary air samples collected during the execution of various tasks performed in different industries/worksites. The corresponding air sampling time range (min–max) and median are presented

| Worksite | Work task | Workers <i>n</i> | Personal | | Stationary | | |
|-------------------------|-------------------------------|---------------------|------------|--|------------|--|----|
| | | | <i>n</i> | Sampling time [min] Min–max Median | <i>n</i> | Sampling time [min] Min–max Median | |
| Auto workshops | Welding | 8 | 19 | 5–38 24 | — | — | |
| Foundry 1 (UF-resin) | Casting | 5 | 27 | 7–16 9 | 8 | 26–34 | 30 |
| Foundry 2 (PF-resin) | Casting | 2 | 11 | 9–33 12 | 20 | 29–45 | 33 |
| Metal recycling plant | Metal sorting | 3 | 33 | 27–56 30 | — | — | |
| | Flame cutting | 1 | 9 | 13–40 9 | — | — | |
| Railway repair workshop | Steel softening/straightening | 3 | 12 | 10–23 16 | 3 | 28–44 | 32 |
| Demolition | Flame cutting | 3 | 65 | 14–42 30 | — | — | |
| TOTAL | | 23 | 176 | | 31 | | |

locations. One location was situated outdoor and the other was positioned inside an open-end storage building. The open end of the storage building was partly covered with a large tarpaulin. Personal air sampling was performed during two consecutive day shifts on three workers. Two samplers in parallel were used on each worker. A total of 65 personal air samples were collected. The sampling times were 14–42 minutes (median 30 min).

Scrap metal reclamation plant. The plant processed scrap metal from various sources. Scrap metal was loaded into and processed by an automated shredding and sorting installation. Metal pieces that were too large for automated processing were manually dissected mechanically or by flame cutting. One worker executed the flame cutting outdoor while personal air sampling was performed. One of the final conveyor belts delivering processed iron scrap metal required manual removal of residual non-metallic items. A ventilated booth built around this conveyor housed 3 workers that manually removed non-metallic items from the conveyor belt. The processed scrap metal on the conveyor belt was often hot and some bits were coated with residual oil and paint. Personal air sampling was carried out while the workers were inside the booth. Air sampling was performed for two consecutive day shifts on four workers. A total of 42 personal air samples were collected. The sampling times were 27–56 minutes (median 30 min).

Railway repair workshop. The workshop performed maintenance work on railway freight wagons and other train related equipment. Bent parts, such as handles and latches, occurred sometimes and required straightening. Straightening was performed by softening the part(s) using an open flame. All metal surfaces were painted. The paint on the bulk of the freight wagons was of unknown origin. Handles were usually painted with high visibility alkyd paint. Personal air sampling was carried out during heating of parts. The air sampling was performed on three non-consecutive day shifts. Stationary air sampling was performed on one day in a centre location of the workshop on three workers. A total of 12 personal and 3 stationary air samples were collected. The sampling times for the personal and stationary air samples were 10–23 minutes (median 16 min) and 28–44 minutes (median 32 min).

Results and discussion

Personal sampler evaluation

A commercially available denuder for isocyanate sampling, including ICA, has recently been launched, based on the method developed by Marand and co-workers.²⁷ This sampler is in theory an attractive choice for personal field air sampling of ICA during hot-work, due to the solvent-free design. In order to investigate the applicability of the commercially available sampler for field sampling of ICA, it was however of interest to evaluate the performance of this sampler in comparison to more established sampling methods.

Denuder background build-up. During preliminary experiments the unexposed commercial denuder (blind sample) displayed a relatively large background contribution to the

measured ICA-DBA derivative prior to sampling. In order to investigate the ICA-DBA background build-up in detail, which is an obvious limiting factor for practical use of the sampler in field, an identical sampler was prepared in-house, and the performance of freshly prepared in-house made denuder samplers was compared to the commercial samplers. The background on freshly in-house prepared denuders was about four times lower than what was found on the commercial denuders. At the end of our study, the observation of background build-up of ICA-DBA on the commercial denuder sampler was supported by a validation report from SGS, reporting an ICA background on blank samplers of 0.3 µg per sampler,³⁷ making the use of the commercial sampler questionable for ICA monitoring.

Given the unknown production date of the commercial denuder samplers it was of interest to examine the potential influence of storage conditions on the amount ICA-DBA background with time. In-house prepared denuders stored in an Ar atmosphere did not exhibit any significant background build-up (Student's *t*-test, 95% CI, $p = 0.199$) over a period of 84 days, while substantial build-up was observed under ordinary conditions (polypropylene (PP) pouches) (Fig. 1). After storage for 164 days, the highest mass determined on the denuder was equivalent to 450 ng ICA. Apart from the formerly mentioned thermal processes, ICA is known to be formed in the atmosphere by photo-oxidation of amines and amides.^{38–40} Diesel engines employing urea selective catalytic reduction (SCR) systems are also known to emit ICA during operation.⁴¹ ICA has been measured in outside ambient urban air at typical concentrations of about 50–100 ppt.^{41–43} Thus, ambient ICA is a viable source of contamination during preparation of denuder samplers when the impregnated GF material is left in a ventilation hood (1 hour) allowing the solvent (methanol) to evaporate from the impregnation solution. The exact source of the

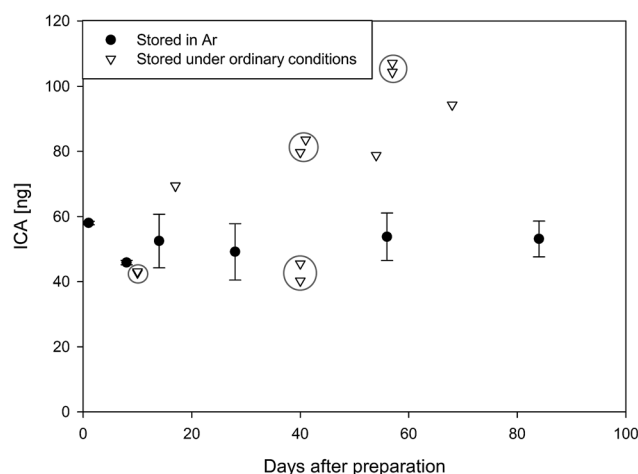


Fig. 1 Plot showing the background levels of ICA-DBA, expressed as the equivalent amount of ICA [ng], on unexposed in-house prepared denuder samplers stored in an argon atmosphere ($n = 18$) (●) (mean) and under ordinary conditions (polypropylene (PP) pouches) ($n = 11$) (▽). Circles indicate two ($n = 2$) samples from different sampler batches. Error bars indicate one standard deviation.

increasing background during storage remains unclear, but can potentially be explained in terms of diffusive sampling of ambient ICA. However, this mechanism may have limited significance as the stored denuders are capped and reported ambient ICA air concentrations are low.^{41–43} Generation of ICA through oxidation of DBA and subsequent creation of ICA-DBA is another possible mechanism, among others, that cannot be ruled out. However, the mechanisms behind the observed build-up of ICA-DBA are beyond the scope of this paper, and the study design does not allow for further investigations beyond speculations. Background build-up was also observed for MIC and EIC (results not shown). Nonetheless, it is important for the purpose of field application of the in-house prepared denuders that only freshly prepared samplers are to be used. In addition, drying of the impregnated GF material during preparation of the denuders should ideally be carried out in an inert atmosphere, as also communicated in another recent study.²⁶

Personal sampler comparison. The recovery and precision of the in-house prepared denuder with DBA, with emphasis on ICA, was compared with the DBA impinger + filter and the 2MP filter methods. Parallel air sampling ($n = 4$, each sampler) was performed from standard ICA atmospheres covering a concentration range of 5.5 to 640 ppb at three different concentrations and two different humidities (AH 4.0 and 16 g m⁻³). A total of six atmosphere experiments were done. PTR-MS served as a reference method for quantification of the ICA atmospheres. The recoveries of ICA using the three sampling methods along with the ICA air concentrations determined by PTR-MS are summarized in Table 2. Air sampling times for each sampling method during simultaneous air sampling is presented in Table 3. The P values obtained by comparing ICA recoveries achieved with the different sampling methods (Student's t -test, 95% CI) are presented in Table 4.

In-house prepared denuder method. The mean recoveries of ICA obtained using in-house prepared denuders were in the range 73–115% (mean 88%) with a precision of 8.9–12.1% RSD (Table 2). The in-house prepared denuder was not significantly affected by sample air humidity, with respect to recovered ICA.

Impinger + filter cassette method. The mean recoveries and precision of ICA obtained by impinger + filter sampling were in

the range 89–115% (mean 98%) and 2.8–9.3% RSD, respectively (Table 2). In contrast to similar studies,^{26,27} sample air humidity did not have a significant adverse effect on the sampling efficiency of ICA. This may be due to the reduced sampling flow rate of 0.5 L min⁻¹ (and not 1 L min⁻¹) in the present study,⁴⁴ which results in a lower temperature drop and less condensation of water in the impinger flask during air sampling. The chosen lower flow rate was based on another study which pointed out the somewhat higher sampling efficiency of ICA (~7%) obtained by using a lower impinger air sampling flow rate of 0.5 L min⁻¹, compared to a flow rate of 1 L min⁻¹.⁴⁴ Also, a lower flow rate would permit a more complete diffusion of isocyanate vapours to the impinger solution, thus increasing sampling efficiency. This increases the applicability of this method for ICA sampling, but the limitation regarding the use of flammable solvents remains.

Filter cassette method. The 2MP filter cassette method achieved mean recoveries and precision of ICA in the range 62–100% (mean 74%) and 2.2–27% RSD, respectively (Table 2). At low ICA air concentration (5.6 ppb) high humidity (AH 15 g m⁻³) exhibits a negative effect on the sampling precision of ICA, most likely due to interaction of water with the filter medium disturbing the derivatization process.

Sampler comparisons. Based on the blind sample background variability the method limits of detection (LOD) for the in-house prepared denuder, impinger + filter and filter cassette methods were 24, 8.9 and 9.4 ng ICA, respectively. For a 30 minute air sample this equals 2.2 ppb (in-house made denuder), 0.34 ppb (impinger + filter) and 0.18 ppb (filter cassette). The PTR-MS LOD for ICA was based on a background S/N of 2 (Karl *et al.*)⁴⁵ and calculated according to

$$\text{LOD}_{\text{ICA}} = \frac{[m/z 44]_{\text{background,ppb}} + 2 \times \text{SD}_{\text{background,ppb}}}{f_{\text{ICA}}} \quad (3)$$

where LOD_{ICA} is the PTR-MS limit of detection for ICA corrected for AH dependent response, $[m/z 44]_{\text{background,ppb}}$ is the background signal from $m/z 44$ in ppb, and $\text{SD}_{\text{background,ppb}}$ is the standard deviation of the background signal in ppb and f_{ICA} is AH dependent correction factor. Eqn (3) in numerical form is given by

Table 2 Recoveries of ICA in dynamically generated standard ICA atmospheres by air sampling using 2MP filter cassette, impinger + filter cassette and in-house prepared denuder sampling methods ($n = 4$, each) relative to PTR-MS. ICA air concentrations according to PTR-MS and the absolute humidity (AH) is presented. The temperature was 21.8 ± 0.3 °C

| AH, g m ⁻³ | PTR-MS | | 2MP filter cassette | | Impinger + filter cassette | | In-house prepared denuder | |
|-----------------------|------------|--------|---------------------|--------|----------------------------|--------|---------------------------|--------|
| | [ICA], ppb | RSD, % | % recovery | RSD, % | % recovery | RSD, % | % recovery | RSD, % |
| 4.1 | 7.3 | 35.3 | 100 | 2.4 | 115 | 4.1 | 115 ^a | 12.1 |
| 15.4 | 5.6 | 45.1 | 68.9 | 27.0 | 98.1 | 5.9 | 105 | 10.5 |
| 4.0 | 78.9 | 14.0 | 73.3 | 5.5 | 93.8 | 3.1 | 75.3 ^a | 11.6 |
| 15.7 | 63.5 | 13.0 | 62.4 | 7.2 | 88.9 | 5.9 | 76.4 | 9.5 |
| 3.9 | 518 | 6.0 | 69.6 | 2.2 | 91.0 | 2.8 | 72.9 | 8.9 |
| 15.6 | 640 | 5.0 | 71.5 | 2.7 | 99.9 | 9.3 | 80.0 | 10.2 |

^a Sample size $n = 3$.

Table 3 Air sampling times (in minutes) during simultaneous air sampling of standard ICA atmosphere using 2MP filter cassette, impinger + filter cassette and in-house prepared denuder sampling methods. ICA air concentrations according to PTR-MS and the absolute humidity (AH) is presented

| AH, g m ⁻³ | PTR-MS | | 2MP filter cassette | Impinger + filter cassette | In-house prepared denuder |
|-----------------------|------------|--------|---------------------|----------------------------|---------------------------|
| | [ICA], ppb | RSD, % | Sampling time, min | Sampling time, min | Sampling time, min |
| 4.1 | 7.3 | 35.3 | 20 | 30 | 30 |
| 15.4 | 5.6 | 45.1 | 20 | 30 | 30 |
| 4.0 | 78.9 | 14.0 | 10 | 10 | 20 |
| 15.7 | 63.5 | 13.0 | 10 | 10 | 20 |
| 3.9 | 518 | 6.0 | 10 | 10 | 10 |
| 15.6 | 640 | 5.0 | 10 | 10 | 10 |

Table 4 Student's *t*-test and the corresponding *p* value comparing the percent recovered ICA between three different sampling methods; 2MP filter (filter), impinger + filter cassette (IF) and in-house denuder (IHD) methods. The air concentration of ICA, according to PTR-MS, and absolute humidity (AH) of each atmosphere is presented^a

| AH, gm ⁻³ | [ICA], ppb | IF vs. filter | IF vs. IHD | Filter vs. IHD |
|----------------------|------------|---------------|------------|----------------|
| 4.1 | 7.3 | <0.01 | 0.96 | 0.19 |
| 15.4 | 5.6 | 0.04 | 0.15 | 0.01 |
| 4.0 | 78.9 | <0.01 | 0.06 | 0.74 |
| 15.7 | 63.5 | <0.01 | 0.04 | 0.02 |
| 3.9 | 518 | <0.01 | 0.01 | 0.39 |
| 15.6 | 640 | 0.01 | 0.02 | 0.13 |

^a *p* < 0.05: Significant difference.

$$\text{LOD}_{\text{ICA}} = \frac{[m/z \ 44]_{\text{background,ppb}} + 2 \times \text{SD}_{\text{background,ppb}}}{0.2532 - 0.0073 \times \text{AH}} \quad (4)$$

With the instrument operating conditions applied in this study the estimated PTR-MS LOD for ICA was 1.8 and 2.8 ppb in atmospheres with an AH of 4 and 15 g m⁻³, respectively.

The impinger + filter cassette method provided ICA recoveries (mean 98%) with the lowest deviation from the PTR-MS, compared to the other sampling methods in this study. At low ICA air concentration (7.3 ppb) and AH (4 g m⁻³) the impinger + filter overestimates slightly the ICA concentration (115%). However, PTR-MS quantification of ICA at the lowest air concentrations is based on extrapolation of the PTR-MS calibration for ICA using higher concentrations.¹⁸ Furthermore, at low ICA air concentrations the PTR-MS quantification is associated with relatively high instrumental uncertainty (35 and 45% RSD) (Table 2). Thus, none of the investigated sampling methods differ significantly (Student's *t*-test, 95% CI, *p* < 0.05) from the PTR-MS (Table 2) at low ICA air concentrations (5.6 and 7.3 ppb).

The 2MP filter method provided the overall lowest ICA recoveries (mean 74%) which were significantly lower (Student's *t*-test, 95% CI, *P* < 0.05) compared to the impinger + filter cassette method, in all six experiments (Table 2). At low ICA

air concentration (5.6 ppb) and high AH (15 g m⁻³) the variability of the 2MP filter method is higher (27% RSD) than the general trend (2.4–7.2% RSD). Sennbro *et al.* have previously reported equal performance of the 2MP filter cassette and impinger + filter cassette method (*r* = 0.95, regression slope = 1.1) for measurements of ICA.²⁸ However, in the present study the lower impinger + filter cassette sample air flow rate (0.5 L min⁻¹) most certainly has improved the impinger + filter sampling efficiency, which may explain the lower 2MP filter cassette/impinger + filter cassette ratios (7%).⁴⁴ Additionally, the ICA atmospheres in this study were of much lower complexity (thermally decomposed urea), resulting in a lower amount of potential interfering components in the sampling atmosphere. Finally, a larger volume of impinger solution (15 mL) was used in the present study, than in the comparative studies (10 mL),^{26,27} where a larger volume presents a larger surface area increasing sampling efficiency and possibly increasing the threshold for water to interfere with the derivatization process.

The in-house prepared denuder method achieved ICA mean recoveries in brief in the same range as the two other methods under study. The recoveries were though slightly higher than that of the 2MP filter cassette method, and with the absence of any apparent humidity effects. At higher ICA air concentrations (64–640 ppb) the in-house prepared denuder method produced ICA recoveries in the range 73–80%. At low ICA air concentrations (5.6 and 7.3 ppb) the ICA recoveries were 105 and 115%, respectively, which do not differ significantly from that obtained by the impinger + filter cassette method (Student's *t*-test, 95% CI, *P* = 0.15 and 0.96, respectively). However, the ICA atmospheres at low concentrations are relatively close to the method LOD for the in-house prepared denuder (2.2 ppb, 6 L air sample). Thus, it cannot be excluded that the ICA-DBA background on the sampler may have influenced on the measured ICA when using the in-house prepared denuder method.

In two other studies where the denuder sampler has been compared to impinger + filter sampling, the amounts of trapped ICA on the denuder samplers was reported to be higher than that of the impinger + filter samplers, by a factor of 1.14–3.70 and 1.8–2.8,^{26,27} depending on the sample air humidity. In the present study, where lower impinger sampling flow rates and larger impinger solution volumes were applied, which

contributes to improvement of the impinger + filter sampling efficiency for ICA, the difference in trapped ICA masses between the two sampler types were diminished, especially in the lower concentration region (~6 ppb). At higher ICA concentrations (64–640 ppb) the denuder was significantly lower (Student's *t*-test, 95% CI, $P < 0.05$), illustrated by factor of 0.80 (640 ppb, AH 15.6 g m^{-3}), which still is not as prominent as in the two other studies.

Based on our experimental data, the impinger + filter cassette method appears to be the most suitable method from an analytical perspective, when low sampling flow rates and increased impinger solution volumes were applied. However, this sampler is not considered optimal for personal air sampling of ICA during hot-work, due to the risk of solvent spillage and its flammability. Nevertheless, the impinger + filter cassette method is a feasible candidate for stationary air sampling where the risk of fire is low. The 2MP filter method showed evidence of negative impact of humidity (AH 15.4 g m^{-3}) on the sampling efficiency and precision of ICA at low (5.6 ppb) sample air concentration (Table 2). Thus, this sampling method has limitations for ICA sampling.¹⁷ The in-house prepared denuder method exhibits adequate ICA recoveries, but suffers from higher background signal for ICA, compared to the impinger + filter cassette and 2MP filter methods. Combined with the low (0.2 L min^{-1}) air sampling flow rate of the denuder sampler the method LOD is roughly 6 and 10 times than that of the impinger + filter cassette and 2MP filter methods, respectively. Furthermore, reagent blank values of ICA-DBA for the in-house prepared denuder method is about 11 times higher compared to the impinger + filter cassette method. This is most likely due to higher amount of derivatizing agent (10.5 times) used in the in-house prepared denuder method, and might be optimized in further studies.

In summary, the in-house prepared denuder method demonstrates ICA recoveries roughly 80 to 105% relative to the impinger + filter cassette method. The inherent fire-safe design makes the in-house prepared denuder method most suitable

among the investigated sampling methods for air sampling ICA during hot-work processes, and was thus selected for ICA sampling during hot-work in this study.

Exposure assessment of thermally degraded ICA in work room air by use of the denuder sampler

Six industrial sites where hot-work is carried out with high probability of generation of ICA were selected for field evaluation of the denuder sampler. One to eight workers, 23 in total, were recruited in each worksite, where all of them were executing hot-work operations. The denuder method allows for the determination of both isocyanates and diisocyanates. Therefore, the measurements of MIC, EIC, PIC, PhI and HDI were also included. Reported ICA air concentrations are based on a denuder method LOD of 24 ng ICA. Since the LOD for each sample varies with air sampling time, values less than the LOD are reported as such instead of numerical value of each LOD. ICA air concentrations obtained by personal and stationary air sampling at different worksites are summarized in Table 5.

Flame applications. The exposure measurements were performed during flame cutting for metal reclamation purposes on paint coated steel surfaces. Hot-work tasks involving the use of open flames resulted in highest ICA air concentrations measured during this survey. Flame cutting of decommissioned off-shore steel structures coated with several layers of PUR-based paint resulted in high peak concentrations of ICA (Table 5), with sampling times of 14 to 42 minutes. Flame cutting indoor (median 27 ppb, 2.5–210 ppb, $n = 28$) resulted in a higher median than the same task performed outdoor (median 9.0 ppb, 1.8–320 ppb, $n = 32$). However, the highest peak ICA air concentration was measured outdoor most likely due to shifting wind conditions and the need for the worker to sometimes be situated partly inside the structure (pipe) to be dissected. Outdoor flame cutting performed at a metal reclamation plant dissected various metal parts such as automotive parts, steel pipes, steel tanks and heat exchangers. Thus, both

Table 5 Median^a concentration and range (min–max)^a of ICA determined by personal and stationary denuder air sampling during the execution of various hot-work tasks at different industries/worksites and number of samples% $n > \text{LOD}$

| Worksite | Task | Personal | | | Stationary | | |
|--|--------------------------------------|--------------------|---------------|----------------|--------------------|---------------|----------------|
| | | % $n > \text{LOD}$ | Median ppb | Min–max ppb | % $n > \text{LOD}$ | Median ppb | Min–max ppb |
| Auto workshops | Welding/grinding | 0 | — | — | | | |
| Foundry 1 (UF-resin) [total] | Casting | 56 | 16 | 7.7–26 | | | |
| Night shift | | 40 | 13 | 7.7–21 | 0 | — | — |
| Afternoon shift | | 65 | 16 | 16–26 | | | |
| Foundry 2 (PF-resin) | Casting | 82 | 14 | 7.2–34 | 85 | 7.5 | 1.5–44 |
| Demolition; off-shore installations [total] | Flame cutting | 92 | 19 | 1.8–320 | | | |
| Indoor | | 100 | 27 | 2.5–205 | | | |
| Outdoor | | 84 | 9.0 | 1.8–320 | | | |
| Metal reclamation plant | Manual sorting | 48 | 6.3 | 2.5–150 | | | |
| | Flame cutting | 78 | 21 | 4.9–75 | | | |
| Railway repair workshop | Steel softening/straightening | 58 | 7.0 | 5.1–19 | 0 | — | — |

^a The median, minimum and maximum and values are obtained from the samples which are $> \text{LOD}$.

paint and oil residue was subject to thermal decomposition. Personal air sampling revealed generation of ICA (median 21 ppb, 4.9–75 ppb, $n = 7$).

ICA was also detected in personal air samples at a railway repair shop during the usage of flame for cutting and softening/straightening bent steel components indoors (median 8.9 ppb, 3.3–21 ppb, $n = 10$). MIC, EIC, PIC, PhI and HDI were detected during all flame related applications, but at much lower air concentrations than that of ICA. To the authors' knowledge, occupational measurements of ICA during flame cutting of coated steel are not yet reported in the literature.

Metal casting. The two steel foundries included in this survey at which air samples were collected used different binders (UF- and PF resin) for the manufacture of their moulds. Upon thermal breakdown, UF resins generally results in formation of ICA in large excess relative to other isocyanates.⁴⁶ Additionally, ICA is the exclusive isocyanate formed upon thermal decomposition of urea.^{47,48} Thus, the concentrations of ICA was expected to be significantly higher in Foundry 1 (UF resin) compared to Foundry 2 (PF resin). However, the personal air samples revealed similar median air concentrations and ranges of ICA in Foundry 1 (median 16 ppb, range 7.7–26 ppb, $n = 16$) and Foundry 2 (median 14 ppb, range 7.2–34 ppb, $n = 9$) (Table 3). Low concentrations (relative to ICA) of MIC, EIC and PIC were also detected in both foundries. ICA was not detected (<LOD) in the stationary samples collected at Foundry 1, probably due to ventilation. In Foundry 2 the ICA air concentrations obtained by stationary sampling (median = 7.5 ppb, range 1.5–44 ppb, $n = 17$) did not differ significantly (Student's t -test, 95% CI, $p = 0.085$) from that obtained by personal sampling, indicating an inadequate ventilation system. MIC also exhibited similar distributive behavior.

In Foundry 1 the median concentration and range of ICA was similar during the afternoon shift (median 16 ppb) and the night shift (median 13 ppb) (Table 5). This observation was in contrast to the expectation as the afternoon shift consisted of casting in several smaller moulds, compared to the night shift. Thus, more smoke close to the floor was generated. EIC and PIC was also detected, but at considerably lower concentrations than that of ICA. In general, the casters in both foundries positioned themselves as to avoid the majority of the smoke generated during and after casting.

Welding and grinding in auto workshops. Automotive panels normally have a clear PUR-based top coat, which when subjected to heat may lead to emission of ICA and other isocyanates. During welding and grinding performed on vehicle body parts in auto workshops the air concentrations of the measured components was mostly below the LOD. ICA was less than LOD in all samples. Low levels of MIC (0.06–0.43 ppb, $n = 3$) and PIC (0.036–0.14 ppb, $n = 6$) were detected during welding on the underside of a vehicle, when the placement of local ventilation was non-optimal. The temperature of the welded panels (2–3 cm from weld) reached up to 200 °C for short periods of time. One sample was acquired during low-power (no sparks) sanding of a vehicle door panel, where all measured components were below their respective LODs. The low level of isocyanate exposure is mainly attributed to proper welding technique and an overall appropriate usage of local ventilation.

Other tasks. ICA was detected in air during manual metal sorting (median 6.3 ppb, range 2.5–150 ppb, $n = 16$) at a scrap metal reclamation plant in a ventilated booth built around a conveyor belt. Occupational measurements of ICA during manual metal sorting have not been previously reported, to the authors' knowledge. The difference of ICA air concentrations between the three workers in the timeframe of each sampling period (~30 min) was typically within an order of magnitude. During one sampling period the ICA concentration range (<2.1–150 ppb) was about two orders of magnitude. Also, the workers that performed the manual sorting smoked tobacco inside the booth, which may have contributed to the measured ICA.⁵ MIC, EIC, PIC PhI and HDI were also detected at much lower air concentration than that of ICA.

Conclusions

The denuder sampler has been shown to be an attractive and user-friendly alternative for collection of airborne ICA during hot-work operations. The sampler provides sufficient collection efficiency and is unaffected by sample air humidity. However, due to the possibility of contamination from the environment it is recommended that the time between preparation of samplers and analysis does not exceed 14 days. However, there is potential for improvement of the denuder method LOD by performing preparation, storage and transport in an inert atmosphere to minimize background ICA-DBA interference. Further studies may explore the possibility of reducing the amount of derivatizing agent aiming at reducing ICA-DBA background build up, allowing also short-term (5 minute) measurements of ICA in air.

The field evaluation of the denuder sampler demonstrated that ICA is formed during hot-work in amounts that might be of relevance to workers' health. The sampler is suitable, both with regard to applicability and sensitivity, for monitoring of ICA during hot-work. The methodology is well suited for usage during hot-work eliminating the need for field extraction. The applicability of the sampler for short-term sampling related to peak exposures is limited to higher peak concentrations due the low sampling flow rates and ICA-DBA background levels influencing on the LOD. Due to the relatively high method LOD, short-term air sampling of ICA is only appropriate when high ICA air concentrations are expected.

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