Stability of isocyanates sampled in fire smokes

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Abstract

Inhalation of airborne isocyanates is associated with acute asthma attacks and inflammation in the respiratory tract as well as cancer. These highly reactive compounds are used as monomers in various applications such as foams for insulation materials and upholstery furniture and are therefore commonly found in fire smoke from insulation materials, such as rigid polyisocyanurate (PIR) foams. Consequently, there is an increasing concern regarding the potential adverse health effects they may cause during this type of exposure.

The aim of this study was to investigate the stability of generated isocyanates from aerobic pyrolysis of PIR after sampling in the derivatisation solution as well as after sample preparation to establish the optimal storage conditions and rate of degradation. Both airborne and particle-bound isocyanates were collected, using dibutylamine (DBA) as derivatisation agent in a midget impinger and impregnated filter after the impinger. The rapid degradation of the generated isocyanates after sampling emphasises the need for a prompt sample preparation and analysis, in particular for the collected mono-isocyanates, as the concentration decreased by 50% within 4-8 hours.

Key words: Isocyanates, fire, polyisocyanurate, foam, HPLC-MS/MS, fire toxicity

1. Introduction

Isocyanates are highly reactive compounds used extensively as monomers and polymers in the production of rigid polyisocyanurate (PIR) building insulation materials (Avar et al. 2012). Previous studies have shown that burning PIR foams release airborne isocyanates (Blomqvist et al. 2003; Stec and Hull 2011), indicating that human exposure may occur during fires. Isocyanate exposure, through inhalation or absorption through the skin, can cause acute asthma attacks, respiratory tract sensitisation and is also associated with cancer (Bello et al. 2007; Wisnewski et al. 1999; Lockey et al. 2015; Redlich and Karol 2002).

Due to their reactivity, isocyanates needs to be derivatised during sampling in order to stabilise them and minimize losses prior to analysis (Spanne et al. 1996; Gylestam et al. 2014). One of the most commonly used derivatisation agent nowadays is dibutylamine (DBA) (Gylestam et al. 2014; Marand et al. 2005; Karlsson et al. 2005).

Collection methods for airborne isocyanates include impingers (UK Health and Safety Executive 2014), filters or denuders (Gylestam et al. 2014), or a combination of both (UK Health and Safety Executive 2014). The main advantage of using impingers is the favourable kinetic conditions for quantitative isocyanate collection (Henneken, Vogel, and Karst 2007). However, the impinger method does not efficiently collect particles between 0.01 and 1.5 μm (Mårten Spanne, Grzybowski, and Bohgard 1999) leading to potential losses in adsorbed isocyanates on airborne particles. Therefore in-line impregnated filters after the impinger are often used for the collection of isocyanates absorbed on particle matter (Karlsson et al. 2000; BS ISO 17734-1:2013 2013; Health and Safety Executive HSE 2014; Creely et al. 2006).

Yet, fire smoke could contain compounds capable of interfering with isocyanate analysis, either by reacting with the them or causing matrix effects during analysis (Woolley et al., 1975; Blomqvist et al. 2003). There is currently a very limited amount of studies for the stability of isocyanates generated in fires after sampling. We present an investigation to establish the optimal storage conditions and rate of degradation of isocyanates generated from the aerobic pyrolysis at 400 °C of rigid PIR insulation foam at 400 °C, collected by impinger-filter sampling and analysed by high-performance liquid

chromatography coupled to a tandem mass spectrometer (HPLC-MS/MS). The temperature of 400°C
in the furnace is assumed to represent oxidative pyrolysis (British Standard Institute Standards
Publication 2013), and is relatively close to the depolymerisation temperature of PIR foam (Allan,
Daly, and Liggat 2014). It can therefore be assumed that this temperature will generate high
concentrations of isocyanates during pyrolysis compared to higher temperatures, where the monomers
will decompose further.

2. Materials and methods

2.1 Chemicals

Acetonitrile (HPLC grade, 99.9%) and toluene (HPLC grade, 99.9%) was purchased from Fischer
Scientific (Loughborough, UK). Mobile phase A was prepared using ultrapure water obtained from a
Millipore Milli-Q Gradient A10 system (Millipore, Bedford, MA, USA). Formic acid ($\geq$95%),
dibutylamine (DBA) ($\geq$99.5%) and non-deuterated as well as deuterated labelled (d_9- or d_{18}- labelled)
isocyanate standard mixtures, see Online Supplementary Material, were purchased from Sigma-
Aldrich (Steinheim, Germany).

2.2 Insulation materials

The insulation material used was rigid polyisocyanurate foam (PIR) at 33 kg m^{-3}. The sample used
was commercially available and purchased at local vendors, with an estimated organic content of
100%.

2.3 Sample generation and collection

The NFX 70-100 static tube furnace (Figure 1) is a bench-scale furnace in which the sample is
introduced to the furnace and thermally decomposed.
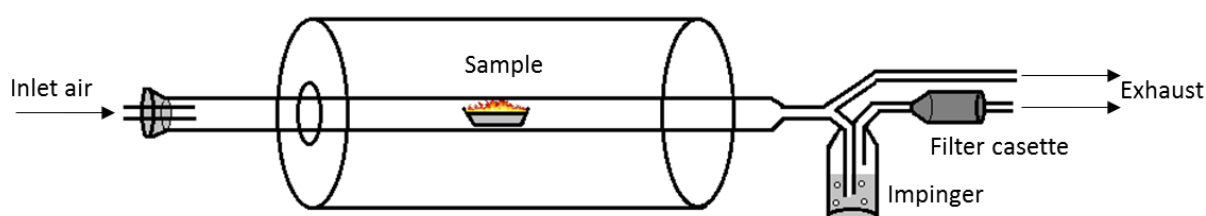
Figure 1. Schematic figure of the NFX 70-100 static tube furnace set-up used in this study.

Immediately prior to the sampling, the glass fibre filter (25 mm, Whatman Grade GF/C, Sigma-Aldrich) mounted behind a midget impinger, was impregnated by the derivatisation solution (0.01 M DBA in toluene) at an air flow of 1 L min^{-1} for 4 minutes. The midget impinger was put in an ice bath throughout the experiment. After that, the insulation foam (0.25 g) was introduced into the middle of the NFX 70-100 tube furnace set at 400°C. No ignition for any samples was observed. The samples were aerobically pyrolysed in an air flow of 2 L min^{-1}, and a subset of the effluent, 1 L min^{-1}, was collected for ten minutes after sample introduction. Blank samples were collected before and after sample runs.

2.4 Isocyanate stability optimisation

Nine different time intervals (0, 1, 2, 4, 8, 24, 48, 120 and 240 h) after sample collection were analysed and duplicate samples were stored at either room temperature or in a refrigerator (6-8°C). The stability of the isocyanates after the vaporisation step was also investigated at four different time intervals (0, 24, 120 and 240 h). The samples were stored at 8°C between the different HPLC-MS/MS analyses and analysed in triplicates.

2.5 Sample preparation

After isocyanate sampling, both the impinger solution and filter were transferred to a 25 mL glass vial. The vials were ultra-sonicated for 15 min, after which the solution was diluted 1:100 or 1:1000 *v:v* with toluene and 0.5 mL of internal standard (ISTD) solution (500 ng mL^{-1}) was added. The samples were evaporated to dryness by a gentle flow of air, and the residue was dissolved in 0.5 mL acetonitrile and transferred to an HPLC vial for analysis. For details on HPLC-MS/MS analysis as well as method validation, see Online Supplementary Material. For details on the MS/MS and validation parameters, Table 1 in the Online Supplementary Material.

3. Results and discussion

3.1 Isocyanate stability after sampling

The stability of the sampled isocyanates (total mass charge yield approximately 23 mg g^{-1} for each sample)-were investigated at two storage temperatures, room temperature or refrigerator (6-8°C), either in the sampling solution or after the preparation, i.e. the vaporisation of the toluene and exchange for acetonitrile. Regardless of storage conditions a rapid and pronounced degradation of the four identified isocyanates, Isocyanic acid (ICA), Methyl isocyanate (MIC), Phenyl isocyanate (PHI) and Methylene bisphenyl diisocyanate (MDI) prior to the sample preparation was found (Figure 1a-d). This could be due to the presence of water, amines and amino-isocyanates as well as partially polymerised polyurethanes present in the fire smoke, all of which could speed up the degradation of isocyanates (Blomqvist et al. 2003; Woolley, Fardell, and Buckland 1975). For example, primary aliphatic amines have up to five times faster reaction rate with isocyanates than secondary amines such as the derivatisation reagent DBA (Herrington and Hock 1998). Additionally, other compounds generated in fires, such as water and alcohols can potentially also speed up the rate of degradation of the analysed isocyanates.

The concentration of ICA, MIC and PHI decreased by approximately 50% within a few hours at both storage conditions before sample preparation (Figure 2a-c). The highest losses occurred in the time interval within four hours for ICA and between 4-8 hours for MIC for both storage conditions prior to the sample preparation (Figure 2a-b). For PHI the highest loss occurred within two hours at room temperature and between 4-8 hours for samples stored at 8°C before sample preparation. The most stable derivatised isocyanate was MDI, for which the concentration decreased with approximately around 50% after 48 hours of storage. All in all, our results emphasise the importance of a rapid sample preparation prior to analysis.

All isocyanates were more stable in solution after sample preparation (Figure 2a-d). This could be due to the removal of some of the volatile amines, amino-isocyanates, alcohols and water present in the derivatisation solution during the vaporisation step of the sample preparation. However, the use of corresponding deuterated internal standard (ISTD) for all target isocyanates, compensates for the

degradation after sample preparation as the rate of degradation of the deuterated DBA-isocyanate ISTD occurs at the same rate as the non-deuterated (Figure 2a-d). The results from this study underline the need to use ISTDs in order to accurately quantify isocyanates sampled from fire smoke.
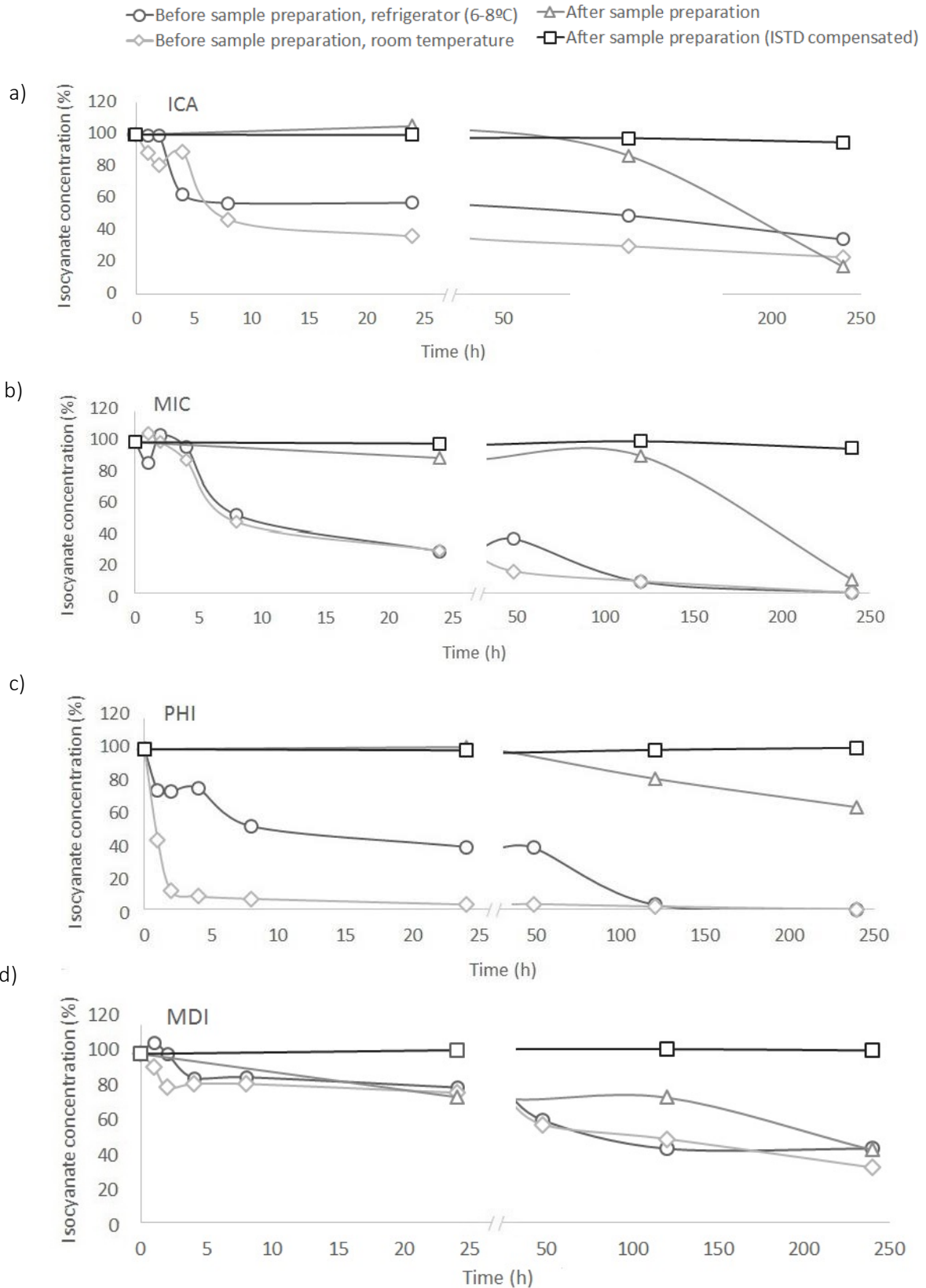
Figure 2. Isocyanate stability of a) MIC, b) EIC, c) PHI and d) MDI from aerobically pyrolysed rigid polyisocyanurate (PIR) insulation foam in the NFX 70-100 tube furnace at 400°C. Samples were collected using a fritted impinger with 15 mL derivatisation solution kept in an ice bath followed by a filter. The time for sample preparation after sampling is indicated in hours. Note that the x-axis is broken for clarification.

4. Conclusion

A rapid degradation of isocyanate-DBA urea derivatives after sample collection but before the sample preparation was found, most likely due to reaction with other volatiles and semi-volatiles present in the fire smoke. This emphasises the necessity for immediate sample preparation after collection.

Moreover, the loss of isocyanates, due to degradation of the isocyanate-DBA derivative, is less pronounced after sample preparation. This is most likely due to a removal of volatile compounds which are driving the degradation process during the vaporisation step of the sample preparation. However, the addition of deuterated ISTD compensates for this loss as these standards will degrade at the same rate as the target compounds. The use of ISTDs is therefore essential for the correctness of the quantification of highly reactive compounds such as isocyanates.

Conflict of interest

The authors reports of no conflict of interest.

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