

# **MDI and TDI: Safety, Health and the Environment.**

**A Source Book and Practical Guide**

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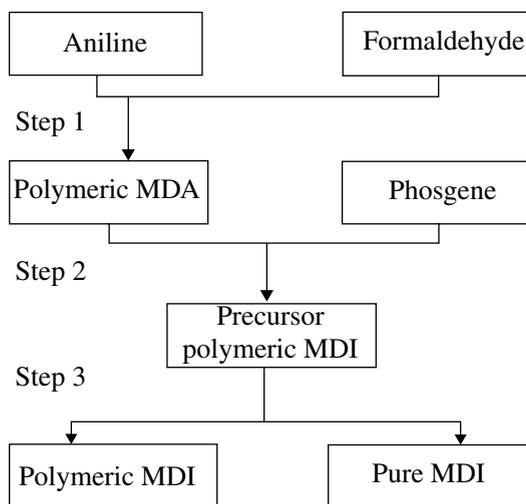
## 5 Supporting sciences

### 5.1 Chemistry of manufacture of MDI and TDI

MDI and TDI are produced in continuous processes on enclosed plants, with capacities of the order 100 000 to 150 000 tonne/year. The plants are often sited in petrochemical complexes so that the diisocyanate precursors can be manufactured on site and linked in to the diisocyanate production process. In spite of the complexities of manufacture, which is proprietary information, the basic reaction paths are relatively simple and are described below. Further information can be obtained from reviews by Twitchett (1974), Gum *et al.* (1992), Oertel (1993) and HMIP (1995).

#### Manufacture of MDI

The key steps are given below:



Pure MDI consists of a minimum of 95 % of 4,4'-MDI. The term *monomeric MDI* is sometimes used for 4,4'-MDI, but can also include the other diisocyanate isomers 2,4'-MDI and 2,2'-MDI.

#### **Step 1: condensation of aniline and aqueous formaldehyde**

When aniline is reacted with formaldehyde in aqueous acid, a mixture of methylenediphenyl diamines (methylenedianilines) and higher oligomers is

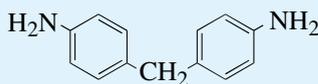
produced. This mixture is often known as *polymeric MDA*. The composition of the reaction product depends on the ratios of the starting materials and on the reaction conditions.

### Polymeric MDA: typical constituents

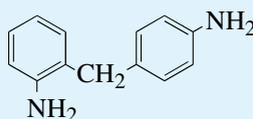
The box below shows some of the major constituents having aromatic amino ( $-\text{NH}_2$ ) functional groups. Molecules of increasing functionality from functionality two, are produced in ever decreasing amounts. Here, the term *functionality* describes the number of amino groups in a given molecule: a functionality of two means that there are two amino groups in the molecule.

#### Examples of constituents of polymeric MDA, of functionality 2, 3 and 4

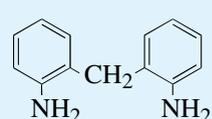
Functionality 2: diamino components



4,4'-methylenediphenyl  
diamine

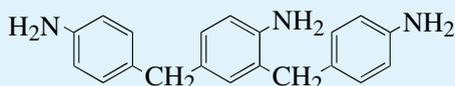


2,4'-methylenediphenyl  
diamine

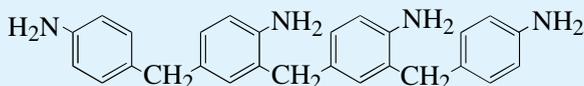


2,2'-methylenediphenyl  
diamine

Functionality 3: major triamino component

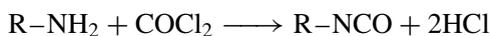


Functionality 4: major tetraamino component



### Step 2: phosgenation of polymeric MDA in a solvent

Each of the aromatic amino groups of polymeric MDA is converted into an aromatic isocyanate group by phosgenation in a solvent such as monochlorobenzene.

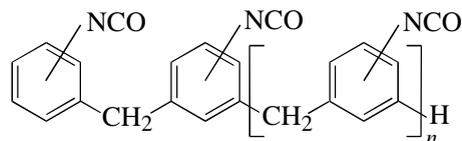


The hydrogen chloride and solvent are removed from the reaction mix by distillation and are reused. The remaining reaction product is polymeric MDI, comprising a mixture of 2-, 3-, 4- and higher-ring polyisocyanates and a number of minor constituents, some present in the parts per million range. These minor constituents do not usually contribute directly to

polyurethane polymer formation, but may influence the chemical reactivity of the polyisocyanates.

### Polymeric MDI: typical constituents

As indicated above, polymeric MDI is a mixture containing monomeric MDIs and higher molecular weight polyisocyanates and is not a conventional polymer of high molecular weight, as the name implies. More strictly, it could be best described as a homologous series or a mixture of chemical homologues. To the main components of polymeric MDI can be ascribed the following structure:

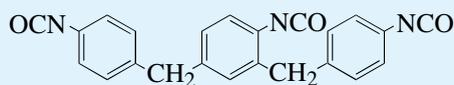


### Examples of constituents of polymeric MDI, of functionality 2, 3 and 4

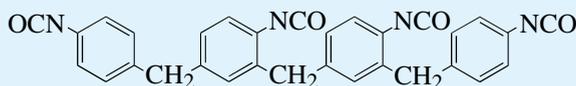
Functionality 2: diisocyanato components



Functionality 3: major triisocyanato component



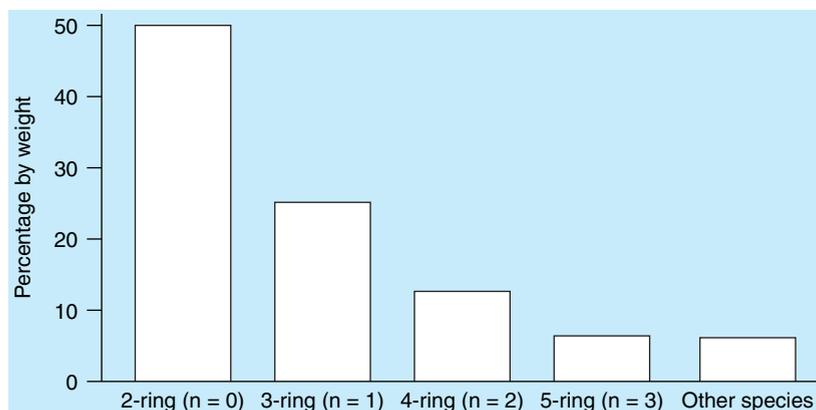
Functionality 4: major tetraisocyanato component



The predominant chain structures arising from the precursor polymeric MDA are those in the resulting polymeric MDI. The methylene chain links are *meta* to each other on the benzene rings. The NCO groups are in the 2- or 4-positions relative to the methylene chain linkages.

Polymeric MDIs from different manufacturers are similar, but vary in the proportions of the di- and multi-ring species. Typically, polymeric MDI contains 50% of 2-ring isomers, 25% of 3-ring isomers, 12% of 4-ring isomers, and 6% of 5-ring isomers (Figure 5.1.1). Polymeric MDI contains

approximately 45 to 55 % of 4,4'-MDI. Manufacturers ensure that a given grade of polymeric MDI meets a defined technical specification, and gives consistent applicational properties and reproducible properties in the polymers made from it.



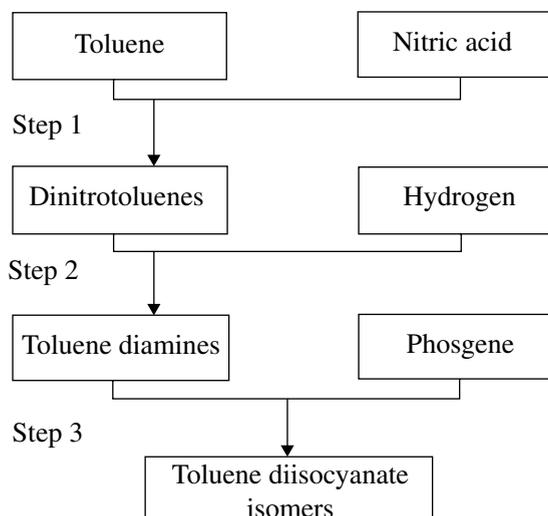
**Figure 5.1.1** The functionality distribution of a typical polymeric MDI

### Step 3: isolation of pure MDI

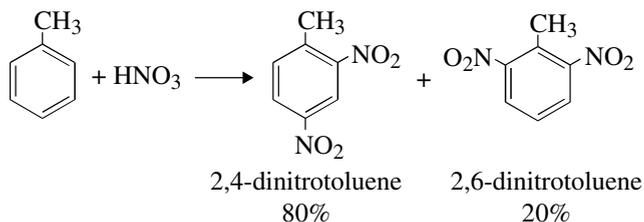
Pure MDI is isolated from precursor polymeric MDI by either distillation or crystallization. Commercial pure MDI is usually 95 % minimum 4,4'-MDI, with a small amount of the 2,4'-isomer. The precursor polymeric MDI is so formulated that, after removal of some of the pure MDI, the residual polymeric MDI can be used as such or can be blended with further polymeric MDI prior to use.

### Manufacture of TDI

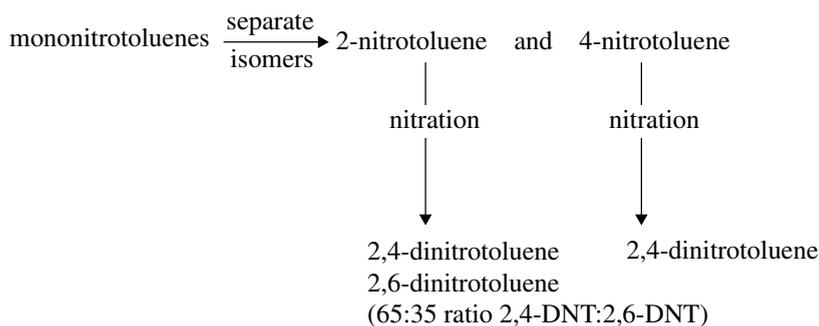
TDI is manufactured by a continuous process. The key manufacturing steps are given below:



### Step 1: dinitration of toluene



The dinitration of toluene is a two-stage process. In the first stage, a mixture of 2- and 4-nitrotoluene isomers is formed. When this mono-nitration mixture is further nitrated, usually in a continuous process, an 80/20 mixture of the 2,4- and 2,6-dinitro isomers is produced. This is the basis for 80/20 TDI. The mononitrotoluene isomers may, however, be separated if required. If only 4-nitrotoluene is used in the second nitration step, 2,4-dinitrotoluene is produced. This is the basis for 2,4-TDI. If the 2-nitrotoluene is further nitrated, a 65/35 mixture of 2,4- and 2,6-dinitrotoluene isomers is formed; this is the basis for 65/35 TDI:

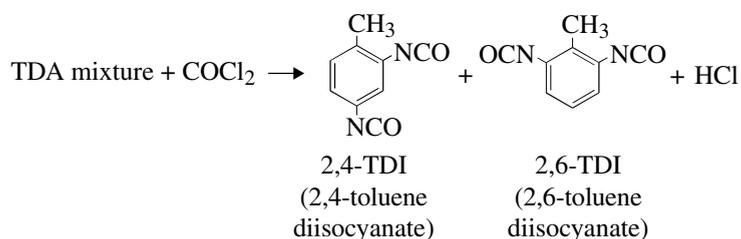


### Step 2: hydrogenation of nitro groups

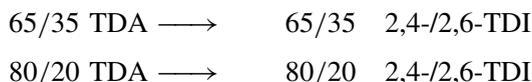
The above 80/20 or 65/35 dinitrotoluene isomer mixture is catalytically hydrogenated to the corresponding toluene diamine isomer mixture. Unwanted isomers (2,3-TDA and 2,5-TDA) are removed by distillation.

### Step 3: phosgenation in a solvent

The aromatic amino groups are converted to isocyanato groups by phosgenation in a solvent such as dichlorobenzene:



The solvent and hydrochloric acid are distilled from the mixture and re-used.

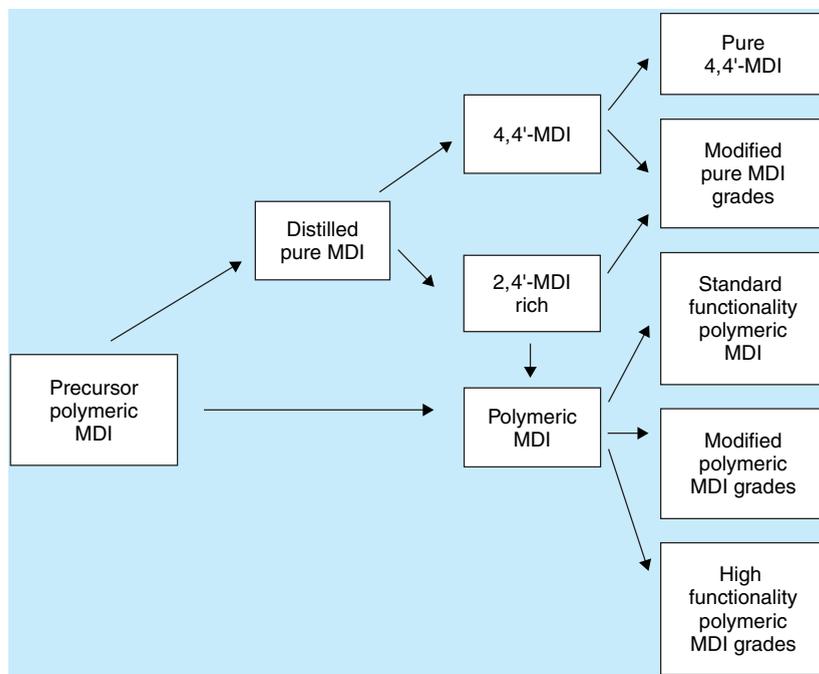


The TDI production process is highly efficient and produces material of approximately 99% purity.

### Modified MDI and TDI

MDI and TDI may be modified to give chemical products having different chemical or handling properties, and giving new effects in the polymers produced from them. This further processing may be carried out on the original manufacturing site or on other sites, notably at systems houses (also known as converters or formulators) which are enterprises in which chemical properties of the components of polyurethanes are formulated to fulfill the needs of specific applications. Few of the formulation details involved in producing the diverse range of modified diisocyanates are in the public domain.

Pure MDI, polymeric MDI, or TDI can be converted to form modified products which are often termed *variants* and *prepolymers*. The reactions lead to a range of modified materials having differences in important properties such as functionality, isocyanate content and viscosity. Figure 5.1.2 illustrates some of the manufacturing pathways to different types of MDI.



**Figure 5.1.2** Some routes to grades of pure MDI and polymeric MDI

These modified materials have improved handling properties and allow more precise control of the nature of the final polymer produced in the polyurethane

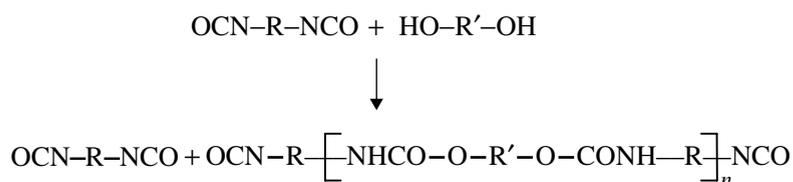
reaction. Chemical modification of MDI and TDI always produces products with lower isocyanate contents than the MDI or TDI from which they were derived. It is not possible to predict the resulting viscosity or functionality without a detailed knowledge of the chemistry and raw materials used to make the product. The examples in Table 5.1.1 give an indication of the changes in viscosity of products made by modifying MDI, and the average functionalities that can be achieved over a range of isocyanate content. The manufacturers of the products should always be consulted if there is any doubt about the identity or properties of modified MDIs or TDIs since trade names are often very similar to one another.

**Table 5.1.1** Range of properties of some types of MDI.

MDI type	NCO content %	Viscosity at 25 °C mPas	Average functionality
Typical polymeric MDI	30.7	230	2.70
Modified MDI (A)	30.6	130	2.49
Modified MDI (B)	24.3	170	2.21
Modified MDI (C)	22.0	1300	2.70

### **MDI and TDI prepolymers**

The term *prepolymer* is usually reserved for isocyanato-terminated reaction products of a di- or poly-isocyanate with a stoichiometric deficiency of a hydroxyl-terminated polyol. The polyols can be simple low molecular weight diols or triols; higher molecular weight hydroxyl-terminated polyethers or polyesters are also used.

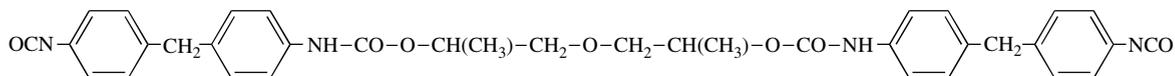


Prepolymers can have widely varying amounts of excess unreacted di- or poly-isocyanate. Some TDI prepolymers are further processed to reduce the residual TDI to very low levels.

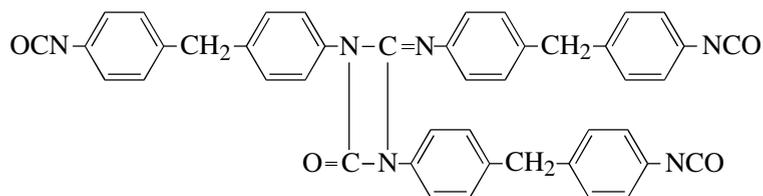
### **Pure MDI variants**

Pure MDI is used to produce certain polyurethanes having properties not otherwise attainable using polymeric MDI, for example, elastomers having extremely high levels of abrasion resistance. However, pure MDI is difficult to handle because it is a solid at factory temperatures and because it tends to dimerize. Two ways in which pure MDI can be modified to produce MDI variants of lower melting points and resistance to dimerization are given below. These variants comprise mixtures of MDI reaction products and unreacted pure MDI:

- Reaction of some of the isocyanato groups with an aliphatic diol (or a mixture of diols) to give, for example:



- Partial uretonimine-modification of 4,4'-MDI (See Part 5.3, *Chemical reactions of MDI and TDI*). Use has been made of this reaction to modify 4,4'-MDI to give liquid commercial products.



uretonimine of 4,4'-MDI

Polyurethanes produced using the above variants have the characteristic properties attributable to the use of pure MDI, rather than polymeric MDI.

#### **4,4'-MDI/2,4'-MDI mixtures**

The melting point of pure MDI (95 % minimum 4,4'-MDI) can be reduced from 40 °C to about 25 °C by adding 2,4'-MDI to obtain a eutectic mix of composition of 60 % 2,4'-MDI and 40 % 4,4'-MDI (Golov *et al.*, 1971).

## Reading

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### **Further reading**

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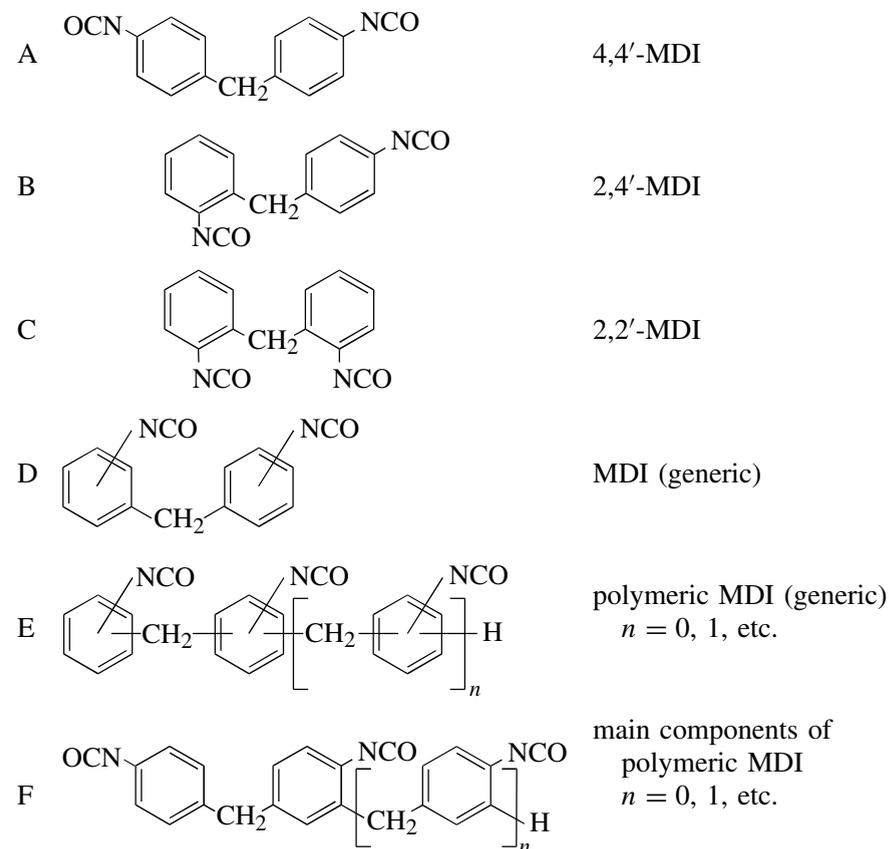
Ulrich, H. (1996). *Chemistry and Technology of Isocyanates*, Wiley, Chichester (ISBN 0-471-96371-2).

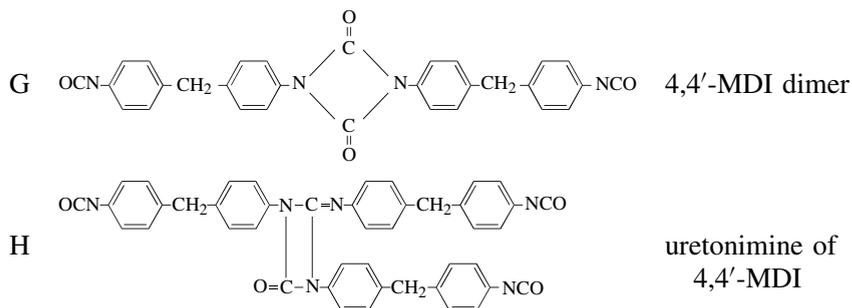
## 5.2 Structure and nomenclature

This text gives chemical structures and attributes to them the names found in the scientific and technical literature. Various systems of nomenclature, as well as nonsystematic names, are used to describe the types of MDI and TDI. Two systems are widely used to define chemicals within regulatory, legal and academic spheres: those of the Chemical Abstracts Service (CAS)<sup>TM</sup> Registry and those of the International Union of Pure and Applied Chemistry (IUPAC). The names of MDI and TDI as designated by both of these systems are included in this text. Also included are names which may be used in texts where complex nomenclature could cause confusion, and a list of synonyms found in the literature.

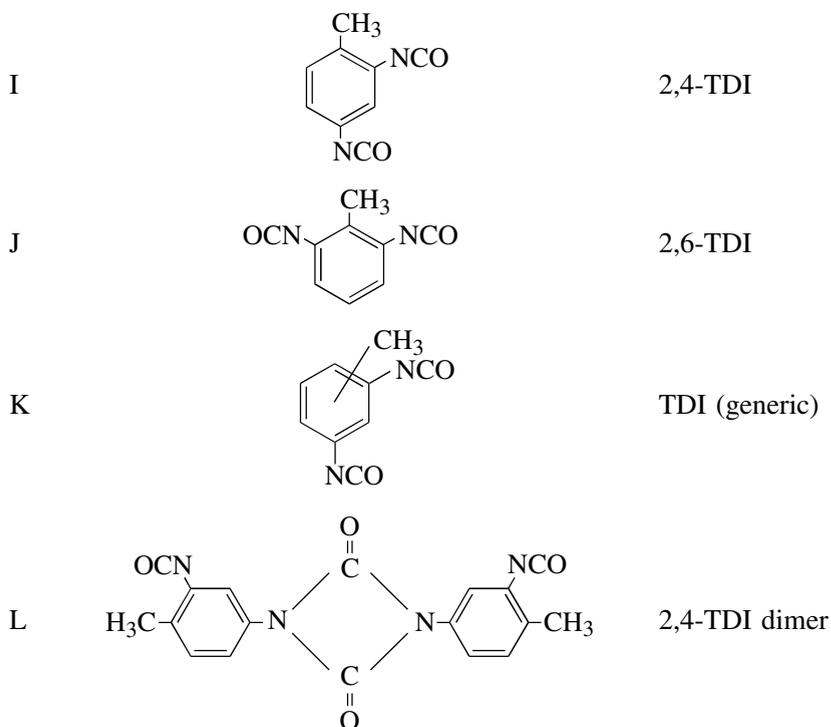
### Structures

#### Structures of MDI species





### Structures of TDI species



### CAS Registry numbers and preferred names

CAS Registry numbers are used to identify both pure chemicals of defined structure (including isomer mixtures) and reaction products of undefined structures. Table 5.2.1 gives CAS numbers and preferred names for MDI species, preceded by a reference to the structure if illustrated above. It should be noted that the list of species is not comprehensive.

In Table 5.2.2 are given CAS numbers and preferred names for TDI species, preceded by a reference to the structure if illustrated above. It should be noted that the list of species is not comprehensive. These names are as cited by the CAS Registry. However, the *isocyanatomethyl* component present in some of the preferred names suggests the presence of a  $-\text{CH}_2\text{NCO}$  group, which is not the case.

**Table 5.2.1 CAS Registry numbers and preferred names for MDI species.**

Structure	CAS number	CAS preferred name	Description
A	101-68-8	benzene, 1,1'-methylenebis[4-isocyanato-	4,4'-MDI
B	5873-54-1	benzene, 1-isocyanato-2-[(4-isocyanatophenyl)methyl]-	2,4'-MDI
C	2536-05-2	benzene, 1,1'-methylenebis[2-isocyanato-	2,2'-MDI
D	26447-40-5	benzene, 1,1'-methylenebis[isocyanato-	MDI (generic)
E	9016-87-9	isocyanic acid, polymethylenepolyphenylene ester	polymeric MDI (generic)
F	25686-28-6	benzene, 1,1'-methylenebis[4-isocyanato-, homopolymer	main components of polymeric MDI
G	17589-24-1	1,3-diazetidone-2,4-dione, 1,3-bis[4-[(4-isocyanatophenyl)methyl]phenyl]-	4,4'-MDI dimer
H	31107-36-5	1,3-diazetidone-2-one, 1,3-bis[4-[(4-isocyanatophenyl)methyl]phenyl]-4-[[4-[(4-isocyanatophenyl)methyl]phenyl]imino]-	uretonimine of 4,4'-MDI
-	39310-05-9	benzene, 1,1'-methylenebis[isocyanato-, homopolymer	generic polymeric MDI

**Table 5.2.2 CAS Registry numbers and preferred names for TDI species.**

Structure	CAS number	CAS preferred name	Description
I	584-84-9	benzene, 2,4-diisocyanato-1-methyl-	2,4-TDI
J	91-08-7	benzene, 1,3-diisocyanato-2-methyl-	2,6-TDI
K	26471-62-5	benzene, 1,3-diisocyanatomethyl- <sup>a</sup>	TDI (generic)
L	3320-33-0	1,3-diazetidone-2,4-dione, 1,3-bis(3-isocyanato-4-methylphenyl)-	2,4-TDI dimer
-	1321-38-6	benzene, diisocyanatomethyl-	totally unspecified TDI
-	9017-01-0	benzene, 1,3-diisocyanatomethyl-, homopolymer	generic TDI polymer
-	9019-85-6	benzene, 1,3-diisocyanatomethyl-, trimer	generic TDI trimer derived from CAS 26471-62-5
-	26006-20-2	benzene, 2,4-diisocyanato-1-methyl-, homopolymer	2,4-TDI polymer

<sup>a</sup>The US Environmental Protection Agency has stated that the generic TDI description, *benzene, 1,3-diisocyanatomethyl-*, CAS number 26471-62-5, should be used for all mixtures of 2,4-TDI and 2,6-TDI.

In Table 5.2.3 is given a short list of selected products obtained by reaction of MDI or TDI with defined diols. A search of the CAS Registry would be needed for the numbers of other specific reaction products.

## IUPAC names

The IUPAC has devised a formal system of nomenclature which does not include a system of assigning unique numbers as does the CAS Registry

**Table 5.2.3 CAS Registry numbers for some MDI and TDI reaction products.**

Number	Chemical name
52747-01-0	benzene, 1,1'-methylenebis[4-isocyanato-, polymer with [(1-methyl-1,2-ethanediyl) bis(oxy)] bis[propanol] <i>MDI-tripropylene glycol copolymer</i>
28853-59-0	1,2-propanediol, polymer with 1,1'-methylenebis[4-isocyanatobenzene] <i>MDI-propylene glycol copolymer</i>
59942-19-7	2-propanol, 1,1'-oxybis-, polymer with 1,3-diisocyanatomethylbenzene <i>TDI-dipropylene glycol copolymer</i>
71342-83-1	ethanol, 2,2'-oxybis, reaction products with TDI <i>TDI-diethylene glycol copolymer</i>

**Table 5.2.4 IUPAC names for MDI species.**

Structure	Abbreviation	IUPAC name
A	4,4'-MDI	1-isocyanato-4-(4-isocyanatobenzyl)benzene
B	2,4'-MDI	1-isocyanato-2-(4-isocyanatobenzyl)benzene
C	2,2'-MDI	1-isocyanato-2-(2-isocyanatobenzyl)benzene
F	polymeric MDI	no name, because it is a mixture

**Table 5.2.5 IUPAC names for TDI species.**

Structure	Abbreviation	IUPAC name
I	2,4-TDI	2,4-diisocyanato-1-methylbenzene
J	2,6-TDI	1,3-diisocyanato-2-methylbenzene
K	generic TDI	no name, because it is a mixture

Service. The IUPAC system does not extend to *mixtures* of chemicals as these cannot be defined by a specific structure. In the case of MDI and TDI, IUPAC names are used almost exclusively in academic literature. Tables 5.2.4 and 5.2.5 contain the IUPAC names for MDI and TDI.

### Convenient names for MDI and TDI

In this book, the editors have adopted the terms shown in Tables 5.2.6 and 5.2.7 for general use, where it is not demanded or desirable that a specific system be used. The names are compatible with the acronyms MDI and TDI.

The term *toluene* as part of the chemical names listed in Table 5.2.7 is used widely. However, it is incorrect, in that this use does not fit into any comprehensive system of nomenclature. Following the example of *methane*,

**Table 5.2.6 MDI nomenclature.**

Type	Abbreviation	Chemical name
Generic	MDI	methylenediphenyl diisocyanate
Pure	monomeric MDI pure MDI	almost 100 % 4,4'-MDI
Isomers	2,2'-MDI	2,2'-methylenediphenyl diisocyanate
	2,4'-MDI	2,4'-methylenediphenyl diisocyanate
	4,4'-MDI	4,4'-methylenediphenyl diisocyanate
Polymeric	PMDI	a mixture of 4,4'-methylenediphenyl diisocyanate (ca 50 %) and related
	polymeric MDI	higher molecular weight species

**Table 5.2.7 TDI nomenclature.**

Type	Abbreviation	Chemical name
Generic	TDI	toluene diisocyanate
Isomers	2,4-TDI	2,4-toluene diisocyanate
	2,6-TDI	2,6-toluene diisocyanate
Mixtures	80/20 TDI	a mixture of 80 % 2,4-toluene diisocyanate and 20 % 2,6-toluene diisocyanate
	65/35 TDI	a mixture of 65 % 2,4-toluene diisocyanate and 35 % 2,6-toluene diisocyanate

*methyl* and *methylene*, TDI could be referred to as *toluylene* diisocyanate: *toluylene* may be used throughout the table in place of *toluene*. However, anomalously and contrary to the above sequence, the mono-isocyanate from toluene is always called *tolyl* isocyanate.

## Synonyms

In Table 5.2.8 are collected the diversity of names of MDI and TDI species which have been found in the literature. The terms *methylene diisocyanate*, *MIC*, *4,4'-bis(carbonylamino)-diphenylmethane* and *phenol, 2,4'-methylene diisocyanate* have been used incorrectly for MDI. The term *2,4-bis(carbonylamino) toluene* has been used incorrectly for 2,4-TDI.

## Commercial product names

MDI and TDI are sold under a variety of names, which appear on labels and in company literature. Different types of MDI or TDI from a single manufacturer can vary in composition and physical properties, such as viscosity. These different grades are usually denoted by additional code numbers or letters. It is, therefore, important to refer to the manufacturers' material safety data sheets for detailed information on product identity and properties.

Table 5.2.8 Synonyms for MDI and TDI.

MDI	TDI
<b>4,4'-MDI</b> <ul style="list-style-type: none"> <li>• MDI</li> <li>• MMDI</li> <li>• pure MDI</li> <li>• monomeric MDI</li> <li>• bis-(<i>p</i>-isocyanatophenyl)methane</li> <li>• bis(4-isocyanatophenyl)methane</li> <li>• di-(4-isocyanatophenyl)methane</li> <li>• diphenylmethane-4,4'-diisocyanate</li> <li>• isocyanic acid, methylenedi-<i>p</i>-phenylene ester</li> <li>• methylenebis(<i>p</i>-phenyl isocyanate)</li> <li>• methylenebis(<i>p</i>-phenylene isocyanate)</li> <li>• methylenebis(4-isocyanatobenzene)</li> <li>• methylenebis(4-phenyl isocyanate)</li> <li>• methylenebis(4-phenylene isocyanate)</li> <li>• methylene-<i>p</i>-phenylene diisocyanate</li> <li>• methylenedi-<i>p</i>-phenylene isocyanate</li> <li>• <i>p,p'</i>-diphenylmethane diisocyanate</li> <li>• 4,4'-diisocyanatodiphenylmethane</li> <li>• 4,4'-diphenylmethane diisocyanate</li> <li>• 4,4'-methylenebis(phenyl isocyanate)</li> <li>• 4,4'-methylenedi-<i>p</i>-phenylene diisocyanate</li> <li>• 4,4'-methylenediphenyl diisocyanate</li> <li>• 4,4'-methylenediphenylene isocyanate</li> </ul>	<b>2,4-TDI</b> <ul style="list-style-type: none"> <li>• 2,4-diisocyanatotoluene</li> <li>• 2,4-diisocyanato-1-methylbenzene</li> <li>• isocyanic acid, 4-methyl-<i>m</i>-phenylene ester</li> <li>• 2,4-toluene diisocyanate</li> <li>• toluene 2,4-diisocyanate</li> <li>• 2,4-tolylene diisocyanate</li> <li>• tolylene 2,4-diisocyanate</li> <li>• 2,4-toluylene diisocyanate</li> <li>• toluylene 2,4-diisocyanate</li> <li>• 4-methyl-<i>m</i>-phenylene isocyanate</li> </ul>
<b>2,4'-MDI</b> <ul style="list-style-type: none"> <li>• 2,4'-diisocyanatodiphenylmethane</li> <li>• 2,4'-diphenylmethane diisocyanate</li> <li>• 1-isocyanato-2-[(4-isocyanatophenyl)methyl] benzene</li> </ul>	<b>2,6-TDI</b> <ul style="list-style-type: none"> <li>• 2,6-diisocyanato-1-methylbenzene</li> <li>• 2,6-diisocyanatotoluene</li> <li>• isocyanic acid, 2-methyl-<i>m</i>-phenylene ester</li> <li>• 2,6-toluene diisocyanate</li> <li>• toluene 2,6-diisocyanate</li> <li>• 2,6-tolylene diisocyanate</li> <li>• tolylene 2,6-diisocyanate</li> <li>• 2,6-toluylene diisocyanate</li> <li>• toluylene 2,6-diisocyanate</li> <li>• 2-methyl-<i>m</i>-phenylene isocyanate</li> </ul>
<b>2,2'-MDI</b> <ul style="list-style-type: none"> <li>• 2,2'-diisocyanatodiphenylmethane</li> <li>• 2,2'-diphenylmethane diisocyanate</li> </ul>	<b>Mixed isomers</b> <ul style="list-style-type: none"> <li>• TDI</li> <li>• toluene diisocyanate</li> <li>• diisocyanatotoluene</li> <li>• isocyanic acid, methyl-<i>m</i>-phenylene ester</li> </ul>
<b>Non isomer specific MDI</b> <ul style="list-style-type: none"> <li>• diisocyanatodiphenylmethane</li> <li>• methylenediphenylene diisocyanate</li> <li>• diphenylmethane diisocyanate</li> <li>• diphenyl methane diisocyanate</li> <li>• di-(isocyanato phenyl)methane</li> <li>• methylenebis(phenylisocyanate)</li> </ul>	<b>Non isomer specific TDI</b> <ul style="list-style-type: none"> <li>• TDI</li> </ul>
<b>Polymeric MDI</b> <ul style="list-style-type: none"> <li>• technical MDI</li> <li>• crude MDI</li> <li>• polymethylene polyphenyl isocyanate</li> <li>• polymeric diphenylmethane diisocyanate</li> <li>• oligomeric MDI</li> </ul>	

## Further reading

CMA and SPI (1993). *Instruction Manual. Nomenclature for Diisocyanates: TDI, MDI and Derivatives*, Chemical Manufacturers Association and Society of the Plastics Industry, Inc., Washington and New York.

## 5.3 Chemical reactions of MDI and TDI

Isocyanates are molecules capable of a wide variety of chemical reactions. They react readily with nucleophiles, due to the positive charge on the carbon atom in the double bond sequence, as shown in the resonance structures:



Active hydrogen compounds, such as water, alcohols, amines and carboxylic acids, add across the N=C double bond to form derivatives of carbamic acid:



Nucleophilic reactions are the basis of polyurethane manufacture. Typically, diisocyanates are reacted with molecules containing two or more hydroxyl or amino groups, resulting in polymeric products. Nucleophilic reactions of isocyanates can be catalyzed by tertiary amines and by a wide variety of metal salts.

MDI and TDI undergo self-reactions involving the reaction of two or more isocyanato groups to produce dimers (from two isocyanato groups), isocyanurates (from three isocyanato groups) and carbodiimides (from two isocyanato groups). Dimers slowly form spontaneously at normal ambient temperatures, eventually resulting in the separation of solids.

Steric hindrance influences the rate of reaction of the isocyanate group. Thus, in 2,4-TDI the isocyanate group in the 4-position reacts more rapidly than that in the 2-position which is adjacent to the methyl group, and 2,6-TDI is less reactive than 2,4-TDI (Bailey *et al.*, 1956; Brock, 1959). One consequence of this is that the TDI vapour emitted during the manufacture of flexible polyurethane foam will be enriched with 2,6-TDI, so any analytical methods used for industrial hygiene purposes will need to quantitate mixtures containing both isomers.

Many reactions involved in the manufacture of polyurethanes are multiphase in their initial stages and it is impossible to predict the precise chemical structures that result. Catalysts and surfactants are also frequently included in polyurethane reaction mixtures and these additives have important effects on processibility and on the properties of the resulting polyurethane.

In common with other organic chemicals both MDI and TDI are subject to free radical reactions. This is particularly important in the atmosphere, and results in their complete degradation. This topic is discussed more fully in *Part 4, The environment*.

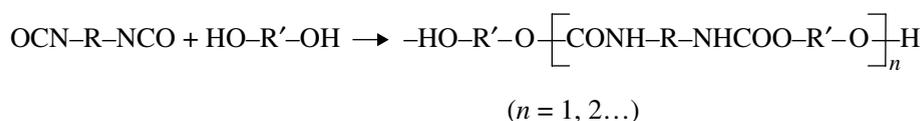
## Reaction with –OH groups

### Alcohols

The reaction of an isocyanate with an alcohol gives a carbamic ester (a urethane) with the evolution of heat. This reaction forms the basis of the manufacture of polyurethanes and is catalysed by a variety of substances.



The reaction between a diisocyanate and a diol will thus produce a polyurethane addition polymer:



The heats of reaction of primary and secondary butyl alcohols reacting with phenyl isocyanate, the three tolyl isocyanates and 2,4-TDI, have been measured and found to be in the range 77.3 to 104.9 kJ/mol isocyanate (Lovering and Laidler, 1962).

Branching, and eventually crosslinking, of the polymer will occur when either or both of the reactants has a functionality greater than two.

Fully cured polyurethanes are completely stable at ambient temperatures. However, the urethane-forming reaction can be reversed to a very limited extent at elevated temperatures, for example above 200 °C (Rosenberg, 1984). Certain mechanical operations such as the grinding of fully cured polyurethanes may generate sufficiently high local temperatures to liberate traces of diisocyanate. Urethanes made from phenols are thermally much more labile than those from aliphatic alcohols, and this reversibility has been used to make polyurethane enamels in which the diisocyanate used to cure the enamel is liberated only during stoving.

### Water

MDI and TDI react with water to give polymeric ureas. This reaction is discussed in greater detail in *Part 4, The environment* in the context of environmental impact. The reaction of an isocyanate with water gives a carbamic acid, which is unstable and readily breaks down into the corresponding amine and carbon dioxide. The amine then reacts readily with any isocyanate still available to yield a substituted urea:



*Further discussion of mechanisms of urea formation*  
Shkapenko *et al.* (1960),  
Aleksandrova *et al.* (1967),  
Malwitz (1994).

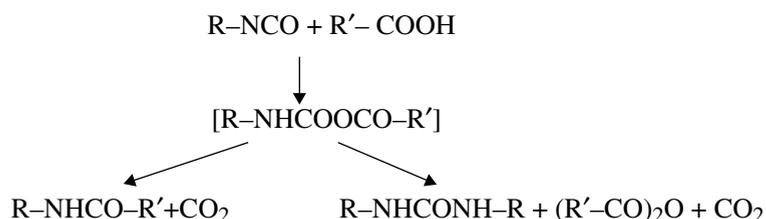
Though the above equations adequately represent the key products formed from the reaction of an isocyanate with water, the actual reactions may not be so straightforward. It has been postulated (Naegeli *et al.*, 1938) that a carbamic acid may react with available isocyanate to form a carbamic anhydride, which subsequently decomposes to give a substituted urea and carbon dioxide.



It has been suggested that MDI may form a hydrate in the presence of water (Gude'hn, 1985), but a simpler explanation seems to be that MDI particles can become coated with plaques of polyurea (Mann, 1987).

### Carboxylic acids

Isocyanates react with carboxylic acids to form initially the unstable mixed anhydrides. Depending on reaction conditions and the nature of the starting materials, the mixed anhydride decomposes either to the amide or to the carboxylic acid anhydride plus a substituted urea.



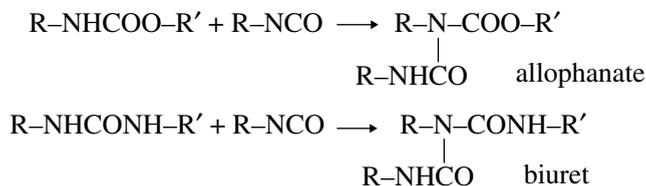
### Reaction with -NH groups

#### Amines, carbamates and ureas

Both primary and secondary amines react readily with isocyanates to form substituted ureas:



The reaction of MDI and TDI with diamines leads to the formation of polyureas, a reaction used to modify the physical characteristics of the polyurethane product, for example by crosslinking or chain extending. At higher temperatures isocyanates further react with the NH group present in carbamates and ureas to form allophanates and biurets, respectively:



The formation of allophanates and biurets leads to branching and crosslinking in polyurethanes.

### Reaction with -SH groups

Mercaptans and thiophenols react with isocyanates to produce thiocarbamates (thiourethanes).



The rates of reaction of thiols with isocyanates are highly dependent upon the reaction environment. Under conditions in which a nonionized SH group is present, the reaction rates are slower than those of the corresponding reactions with alcohols. However, when the thiol group is present as an ionized S<sup>-</sup> group, for example in a polarizing solvent or in the presence of a base, the reaction rates with isocyanates are greatly increased. Indeed, under these conditions, isocyanates may react preferentially with thiols even in the presence of alcohols (Smith and Friedrich, 1959).

### Reaction with biological molecules

Clearly the reaction of MDI and TDI with biological molecules is important in understanding the mechanisms by which these diisocyanates affect living systems. Biological molecules have many groups reactive to isocyanates. Hydroxyl groups are found in water, carbohydrates, and proteins. Aliphatic amino groups are present in proteins, as are carboxylic acids and thiol groups. Thiols are also widely available in body fluids and tissues as the tripeptide glutathione. This variety of reactive groups can lead to theoretical possibilities for competitive reactions in most biological situations. The extent to which a particular reaction takes place, if at all, depends on a number of parameters:

- the physical form of the diisocyanate (vapour, aerosol or liquid);
- the mode of exposure of the diisocyanate (inhalation, ingestion, or by skin contact, with or without a solvent);
- the concentration of the diisocyanate at the reaction site;
- the biological availability of the reactive molecules at the application site; biological systems contain substances and structures which can significantly affect reaction pathways;
- the prevailing biological pH.

Because of the many possible reactants and the inherent reactivity of MDI and TDI, no diisocyanate survives unchanged when it encounters a biological system. The MDI or TDI reaction products are eliminated from such systems by metabolic processes. Some investigators have studied urinary metabolites following diisocyanate administration. When these are subject to strong acid hydrolysis aromatic amines are liberated, permitting chemical analysis. This, of course, does not necessarily imply that the free aromatic amines are present at any stage *in vivo*.

Most of the experimental work *in vitro* and *in vivo* has been conducted with TDI. In the vapour state, TDI reacts efficiently *in vitro* at pH 7.4 with the serum protein albumin over a wide concentration range. This reaction with the protein competes successfully with the hydrolysis of TDI to the diamine. It is believed that the epithelial cells and the subepithelial supporting structure are the primary airway reaction targets *in vivo*, giving rise to high molecular weight protein reaction products of about 70 kDa (Kennedy, 1990). It is not yet understood which reactive groups are targetted on protein molecules, though terminal primary amino and possibly sulphhydryl groups may be involved. This is still an area of research activity. It is believed that the reaction products of glutathione with diisocyanates are labile, enabling transfer reactions of diisocyanate residues to other biological reactive groups to take place (Day

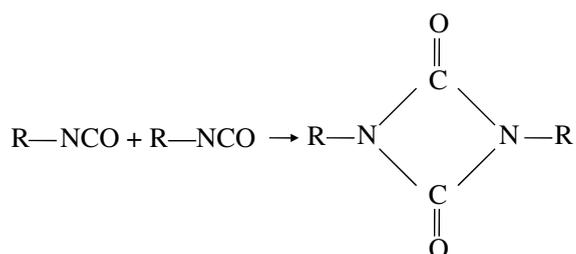
*et al.*, 1997; Lange *et al.*, 1999). The availability of such a mechanism may explain how diisocyanate residues migrate across some membrane boundaries and are found, for example, attached to blood proteins. Such adducts would then be eliminated by normal metabolic processes.

In contrast to the inhalation administration of TDI, oral application of TDI does seem to result in the production of some TDA from hydrolysis in the acidic aqueous medium of gastric secretions (Timchalk *et al.*, 1994). The respective amines can also be produced from MDI and TDI when the diisocyanates are administered in certain polar organic solvents (see below), and this can lead to erroneous conclusions in studies.

## Self-reactions

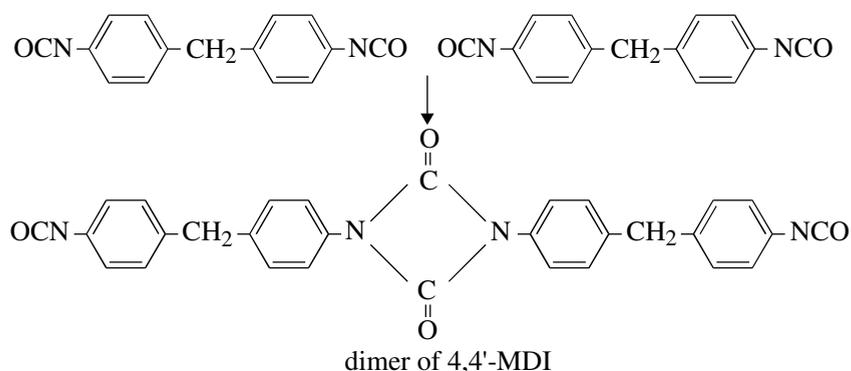
### Dimerization

An example of a [2+2] cycloaddition reaction occurs when an aromatic isocyanate reacts with itself to produce a dimer, which is also known as a uretidinedione (uretidione).



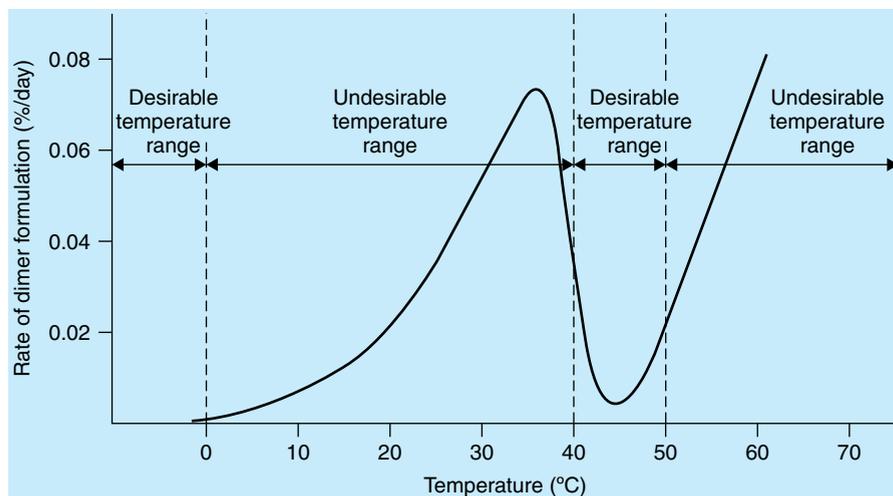
This dimerization reaction is exothermic and usually requires catalysis by phosphines or pyridine.

Pure MDI (melting point about 40 °C, 104 °F) dimerizes slowly at room temperature, without a catalyst, even though in the solid state:



The presence of dimer (uretidinedione) in excessive quantities may adversely affect the physical properties of polyurethanes prepared from the MDI. It is therefore normal to store pure MDI as a solid below 0 °C or as a liquid in the range 40 to 45 °C to minimize the rate of dimerization. In the liquid state, where the molecules of 4,4'-MDI are not so closely aligned as in the solid

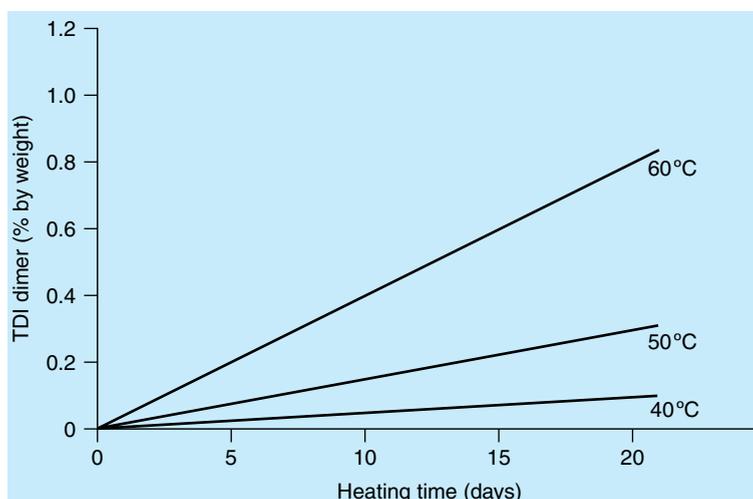
state (Wilson *et al.*, 1983), the rate of dimerization is slower except at higher temperatures above about 55 °C (Figure 5.3.1).



**Figure 5.3.1** Rate of dimerization of MDI with temperature. Based on data supplied by BASF Polyurethane (1992)

It is also important to melt pure MDI as quickly as possible prior to use. However, to minimize dimer formation, excessively high temperatures should be avoided. The preferred techniques are discussed in *Part 2, The workplace: storage and use of MDI and TDI*.

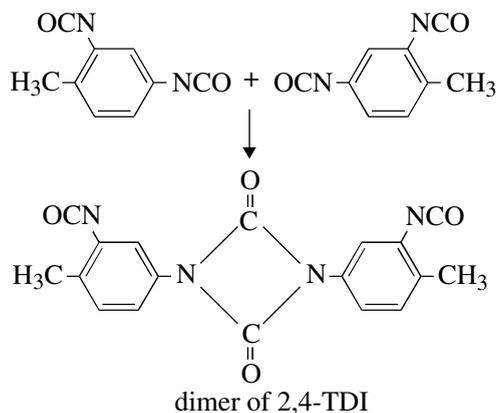
The rate of dimerization of a diisocyanate is greatly reduced by the presence of an *ortho* substituent and no dimer of 2,6-TDI is formed under normal storage conditions. The isomer 2,4-TDI dimerizes slowly (Figure 5.3.2) in the liquid



**Figure 5.3.2** TDI dimer formation over time at various temperatures. Based on information supplied by ARCO Chemical (1998)

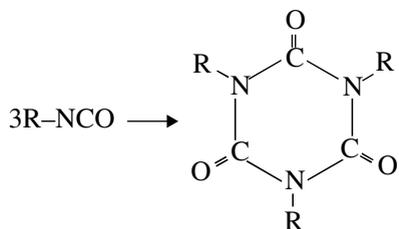
state and prolonged storage may result in some separation of solid. At about 40 °C the rate of dimerization of 2,4-TDI is approximately 0.005 % per day.

The solubility of TDI dimer in 2,4-TDI is approximately 1 % at 20 to 30 °C, 1.3 % at 40 °C and 2.2 % at 50 °C.



### Trimerization

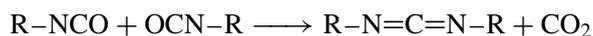
Heating isocyanates leads to trimerization with the formation of very stable cyclic isocyanurates. The rate of reaction is markedly increased by using basic catalysts.



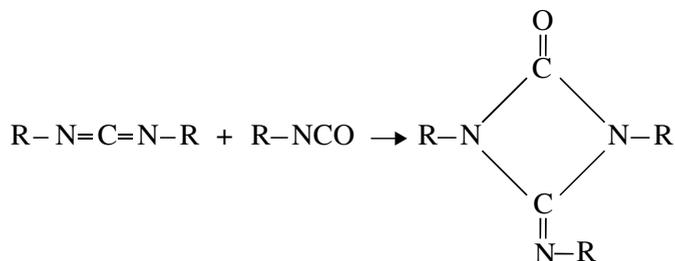
Thus, by this means of modification, TDI can form a reactive derivative containing three isocyanato groups which allows the introduction of chain branching and crosslinking. In addition, the thermal stability of the isocyanurate ring can confer fire resistance on polyurethanes into which it is incorporated. This modification is often used in the manufacture of modified rigid polyurethane foams from polymeric MDI. The trimerization reaction is carried out at the same time as polyurethane formation during the foaming process by the use of suitable catalysts.

### Other self-reactions

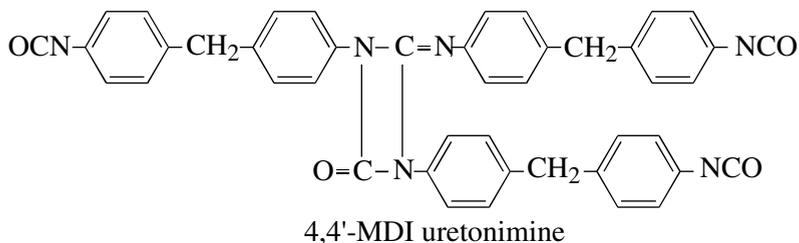
Isocyanato groups can also react with themselves to produce carbodiimides and carbon dioxide. This reaction takes place only at high temperatures unless catalysed.



Carbodiimides can react further with other isocyanato groups to give uretonimines:



An important application of the above chemistry is the partial modification of pure MDI to give a liquid product containing some 4,4'-MDI uretonimine.



## Catalysts

Isocyanate reactions are subject to catalysis by a number of substances, among which alkalis, tertiary aliphatic amines and metal salts are particularly important in commercial polyurethane systems. It is, therefore, very important that neither MDI nor TDI is contaminated with catalysts during storage, as the diisocyanates may deteriorate. Copper and zinc, which are often found in chemical processing equipment, should not be allowed to come into contact with diisocyanates since they can form chemical complexes with amine catalysts and hence act as inhibitors. Further information on these topics can be found in Saunders and Frisch (1962) and Oertel (1993).

The insolubility of both MDI and TDI in water has led investigators to dissolve the diisocyanates in water-miscible, polar organic solvents in toxicology studies. Dimethylsulphoxide (DMSO) has frequently been used. However, traces of water in DMSO cause both MDI and TDI to hydrolyse very rapidly at room temperature to give the respective diamines and polyureas (Seel *et al.*, 1999). The results of any experiment using DMSO as a solvent for diisocyanates must be treated with the greatest caution, since the test substance in contact with the biological medium is likely to be significantly reacted with water and to contain a much reduced amount of diisocyanate after a few minutes have elapsed. Most importantly, the reaction products will probably contain some aromatic amine.

In DMSO for example, 70 % of the MDI in a 0.5 % solution was reacted over 20 min in the presence of 0.04 % water (Gahlmann *et al.*, 1993). In contrast, solutions of MDI in the less polar solvent ethyleneglycoldimethylether were

*Isocyanate reactions in dimethylformamide and dimethylsulphoxide*

Barnard *et al.* (1972), Joel *et al.* (1992), Gahlmann *et al.* (1993), Seel *et al.* (1999).

stable for several hours even in the presence of approximately an equimolar proportion of water (Herbold *et al.*, 1998). Dimethylformamide also accelerates the rates of reaction of isocyanates with water, though its effect is less pronounced than those of DMSO.

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## 5.4 Physical and fire properties

This text includes the physical and fire properties of the main MDI and TDI isomers and mixtures only, as these materials have generally been seen as representative species, and have been used in most of the significant toxicological and environmental studies. The physical properties of these diisocyanates influence their toxicological and environmental effects, and all aspects of their transport, storage, handling and use. Details of the implications of these properties are dealt with in depth in the relevant parts of the book. There are numerous types of modified MDIs and TDIs. The physical properties of these, such as melting points, vapour pressures and viscosities, may differ very significantly from those of the parent molecules. The differences will be

particularly significant in the case of solvent-based MDI and TDI products, notably as regards fire properties.

Various test methods have been used over the years to determine physical properties and these have been defined by standards organizations such as the American Society for Testing and Materials (ASTM) and the Deutsches Institut für Normung (DIN). More recently, regulatory bodies have prepared guideline test methods based in many cases on existing national standards and on scientific consensus methods. In certain cases new test methods have had to be formulated.

*Organization for Economic Co-operation and Development (OECD). Guidelines for the Testing of Chemicals.*

OECD Test Guidelines are accepted as standard methods for safety testing, and provide the common basis for the international acceptance of test data.

The OECD guidelines for testing of chemicals (OECD, 1993) and the European Commission Directive on the classification, packaging and labelling of dangerous substances, annex on test methods (CEC, 1984), deal especially with those physical and physico-chemical properties which are important for hazard assessment and modelling. Values for the physical properties of MDI and TDI which have been determined using these guideline methods have been given prominence in this text.

These guideline methods may be supported by further testing, such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC records the heat flow into or from a test sample relative to an inert reference material as the two samples are scanned through a prescribed temperature sequence. Processes such as melting, boiling or decomposition are clearly indicated as marked deviations in the smooth heat flow–temperature chart. TGA is a test which records weight changes occurring during a controlled heating programme. Weight changes have significance in their own right, and can also be used to help interpret DSC data.

Values quoted in the literature for the physical properties of MDI and TDI varied considerably. Therefore, the International Isocyanate Institute Inc. (III) undertook a study (Kelly *et al.*, 1997) to determine a range of basic properties, using guideline methods. The study results have been given prominence in this text. However, earlier work, or that done under different conditions, has been included where there is sufficient information in the literature to give an indication of the test method and the material used. Test results vary slightly according to the exact nature of the material being studied.

## **MDI**

Pure MDI is a waxy solid, white to pale yellow in colour, and all handling and usage procedures have to be adapted to the fact that this material is not liquid at most ambient temperatures. Polymeric MDI is an oily brown translucent liquid throughout the ambient temperature range and has a characteristic earthy, musty odour. Smell should never be used as a warning of possible exposure to MDI, as the odour threshold is above typical workplace exposure limits. The threshold has been reported as 400 ppb (Woolrich, 1982) but this level will vary with the individual. This quoted level is considerably higher than the vapour concentration at 20 °C.

A summary of the physical properties of MDI is given in Table 5.4.1.

## **Spectra**

Spectra are given in Figures 5.4.1 to 5.4.3.

**Table 5.4.1 Summary of MDI physical properties.**

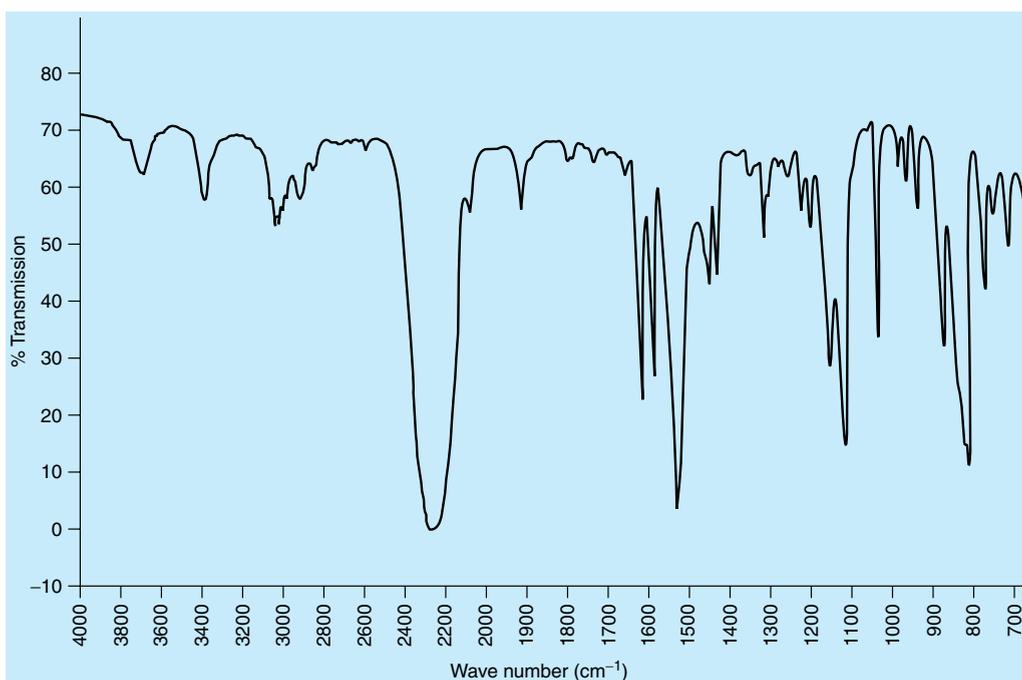
Property		4,4'-MDI	Polymeric MDI
Molecular weight		250.3	<sup>a</sup>
Melting point	°C	40	5
Boiling point	°C	>300	>300
Relative density	at 20 °C	1.325	1.238
Density	g/cm <sup>3</sup>	1.182 at 50 °C	–
Viscosity	mPa s	4.7 to 5.0 at 50 °C	100 to 250 at 25 °C
Vapour pressure	Pa	$6.2 \times 10^{-4}$ at 20 °C	$3.1 \times 10^{-4}$ at 20 °C <sup>b</sup>
Saturated vapour concentration	µg/m <sup>3</sup>	64 at 20 °C	32 at 20 °C
Autoignition temperature	°C	>601	>600
Flash point	°C	211	208
Explosivity		Not explosive <sup>c</sup>	Not explosive
Refractive index		1.5906 <sup>50d</sup>	–
Partition coefficient		see Part 4, The environment	

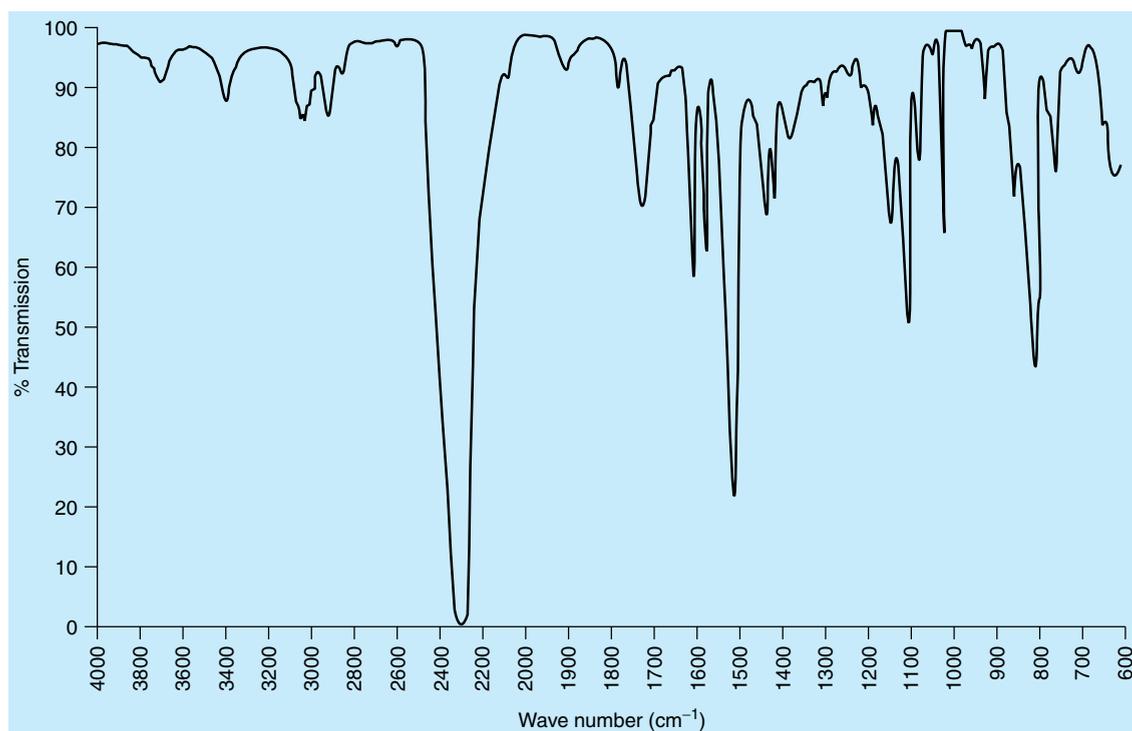
<sup>a</sup>Polymeric MDIs are proprietary mixtures, so no unique molecular weight can be cited. The composition depends upon the production source. However, an indication of the molecular weight of a notional composition can be calculated. If the simplified chemical formula given in Figure 5.1.1 is used, and values of  $n$  ranging from  $n = 0$  to  $n = 12$  are used, then the notional average molecular weight of the mixture is 380.

<sup>b</sup>Assuming PMDI contains 50 % by weight of 4,4'-MDI.

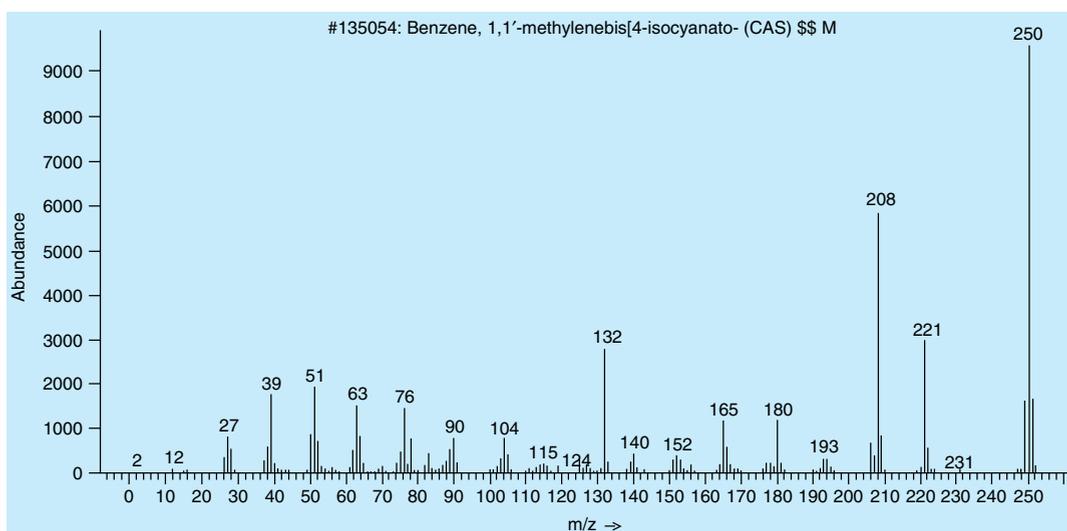
<sup>c</sup>MDI dust has not been tested for explosivity.

<sup>d</sup>See Chadwick and Cleveland (1981).

**Figure 5.4.1 Infrared spectrum of 4,4'-MDI**



**Figure 5.4.2** Infrared spectrum of polymeric MDI



**Figure 5.4.3** Mass spectrum of 4,4'-MDI. Reproduced by courtesy of John Wiley & Sons, Ltd

### **Melting and freezing ranges of MDI**

The melting ranges of 2,4'-MDI and 4,4'-MDI (Table 5.4.2) were determined as 34 to 38 °C and as 39 to 43 °C, respectively (Kelly *et al.*, 1997) using the capillary method (OECD Test Guideline 102 and EC Method A1). The value for 4,4'-MDI was supported by information from differential scanning

Composition of MDI samples used in the III study (Kelly *et al.*, 1997)  
 4,4'-MDI >99.5 % MDI content of which  
 99.6 % 4,4'-MDI  
 0.4 % 2,4'-MDI.  
 2,4'-MDI >99 % purity.  
 PMDI containing 50.2 % 4,4'-MDI.

**Table 5.4.2 Melting and freezing points of MDI.**

2,4'-MDI		4,4'-MDI		PMDI	
Melting point	36 °C	Melting point	40 °C	Freezing point	5 °C

**Table 5.4.3 Boiling points of MDI.**

Method used	4,4'-MDI	PMDI
Siwoloboff	>300 °C at 1013 hPa	>300 °C at 1011 hPa
DSC	364 °C	>358 °C

calorimetry on the same material, which showed the melting point to be 40 °C (see Figure 5.4.4). A crystallizing point apparatus was used in this study to determine the freezing point of a sample of polymeric MDI containing 50 % 4,4'-MDI. However, the freezing point of polymeric MDI varies with the composition of the material.

The melting points of 4,4'-MDI/2,4'-MDI mixtures have been measured. The fusion diagram showed a eutectic point at 25 °C for the mixture of 40 % 4,4'-MDI and 60 % 2,4'-MDI (Golov *et al.*, 1971).

#### Melting points of 4,4'-MDI and 2,4'-MDI

The melting point of a substance depends upon its purity, the method used for determination, and the interpretation of the information from that method. III studies of the melting point of '4,4'-MDI' (99.6 % 4,4'-MDI / 0.4 % 2,4'-MDI) have given a value of 40 °C (DSC method) and a range of 39 to 43 °C (capillary method). Since it is not unusual for a single value to be sought, we have chosen 40 °C as a reasonable value to cite. Historically, melting point values in the range 38 to 39.5 °C have been cited for 4,4'-MDI in the technical literature. Since no information on the purities of the samples or on the methods used has been found, the authors have not cited these earlier values. Similarly, a value of 36 °C has been chosen for the melting point of 2,4'-MDI.

#### Boiling range

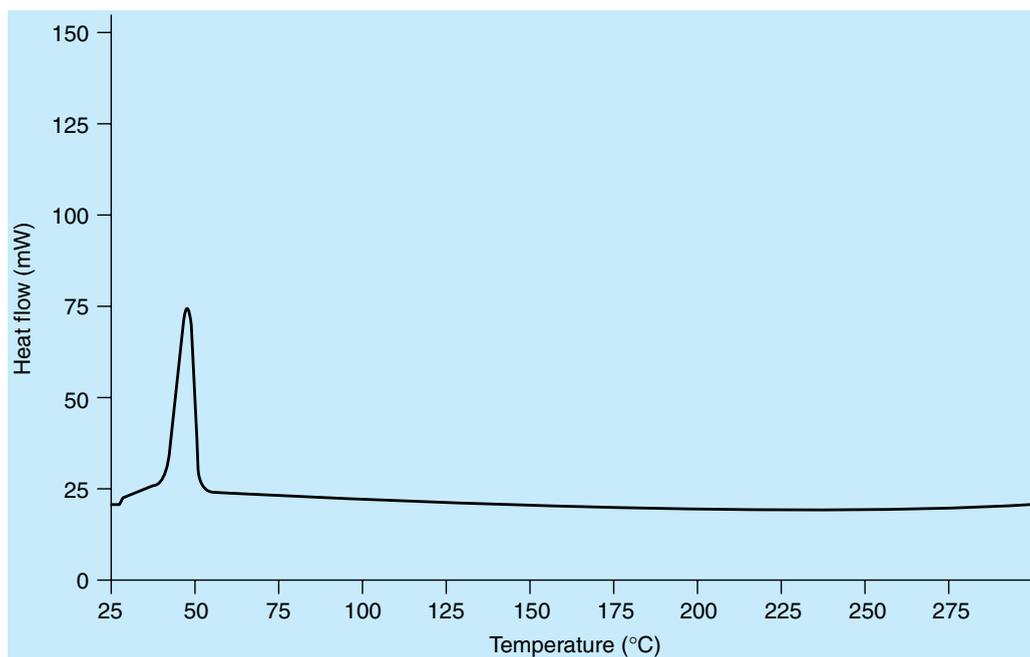
The Siwoloboff method (OECD Test Guideline 103 and EC Method A2) was used in the III study (Kelly *et al.*, 1997) to determine the boiling point of 4,4'-MDI, see Table 5.4.3. Differential scanning calorimetry supported the result. Both the Siwoloboff method and DSC showed that there was no boiling of polymeric MDI up to 300 °C.

#### Decomposition of MDI

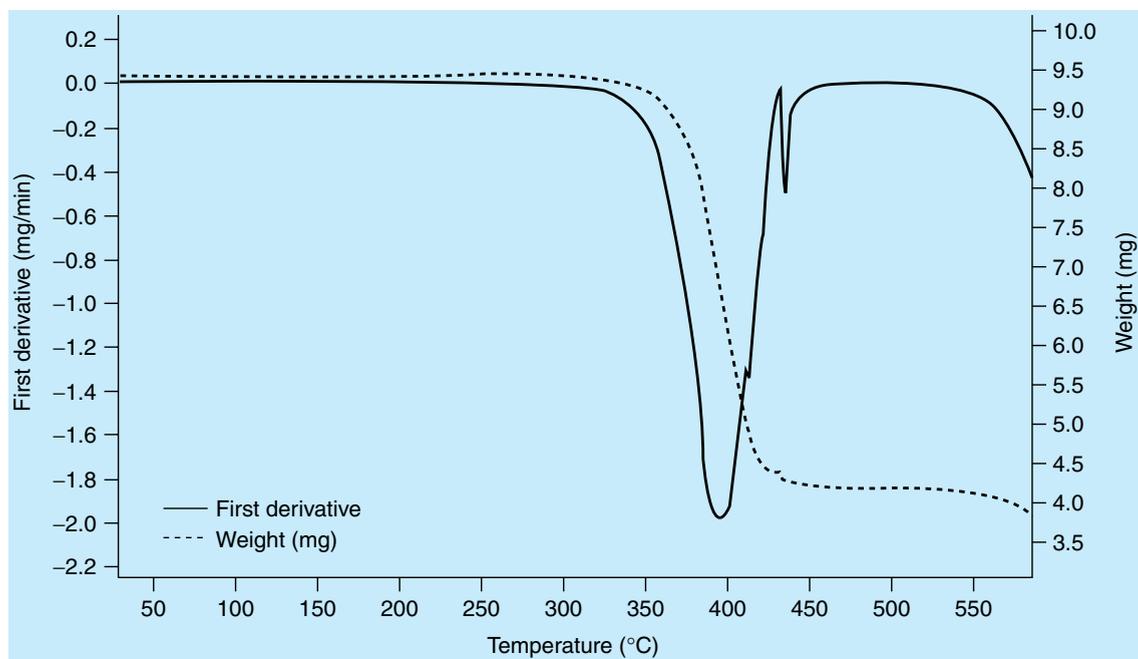
Decomposition of MDI is reported to occur at high temperatures. Kalos (1988), in a study of the thermal decomposition chemistry of 4,4'-MDI, found exothermic degradation starting at 246 °C, but the III study (Kelly *et al.*, 1997) did not note any exothermic decomposition of this material (see Figure 5.4.4). However, the study did show mild exothermic decomposition of 2,4'-MDI at around 338 °C and polymeric MDI also showed mild exothermic decomposition starting at 354 °C (see Figure 5.4.8).

#### Differential scanning calorimetry and thermogravimetric analysis

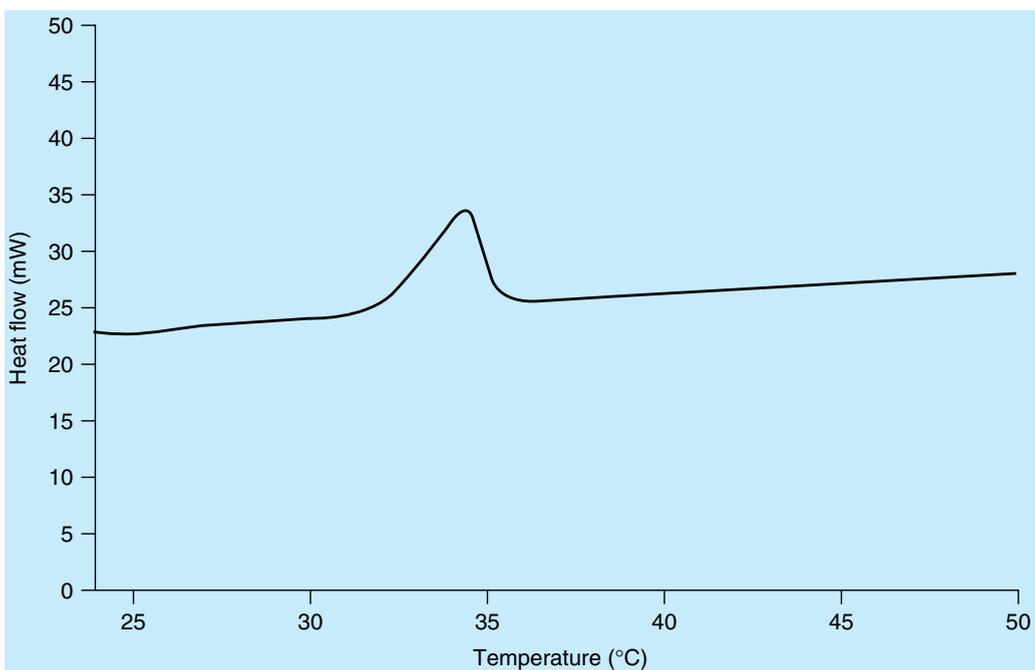
These tests were carried out as part of the III study (Kelly *et al.*, 1997) (Figures 5.4.4 to 5.4.9).



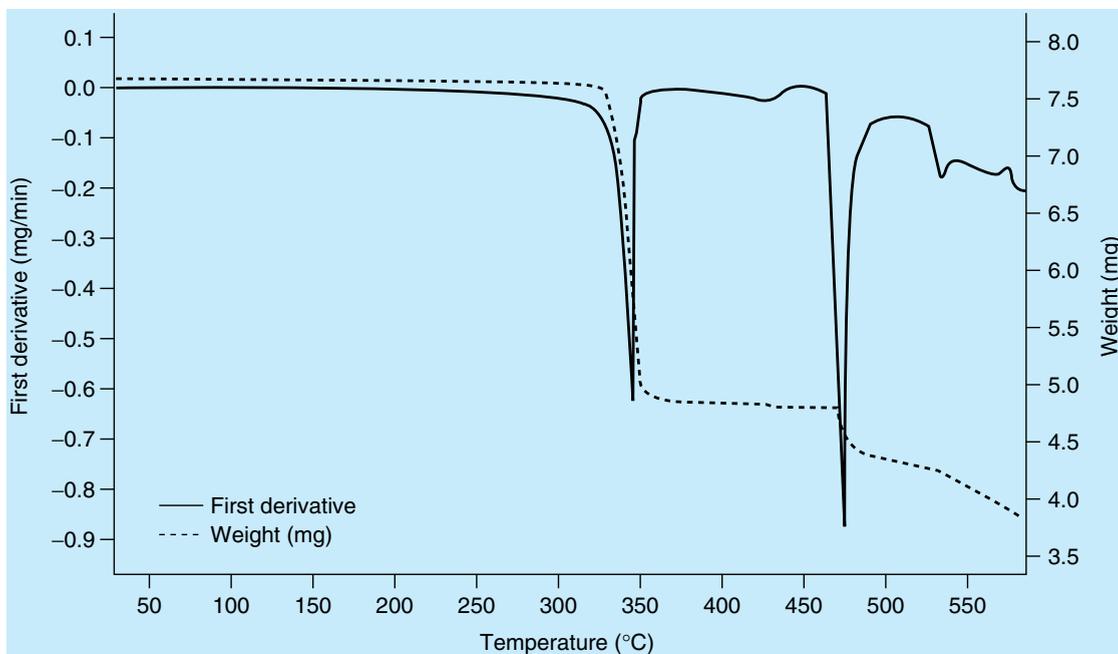
**Figure 5.4.4** Differential scanning calorimetry of 4,4'-MDI



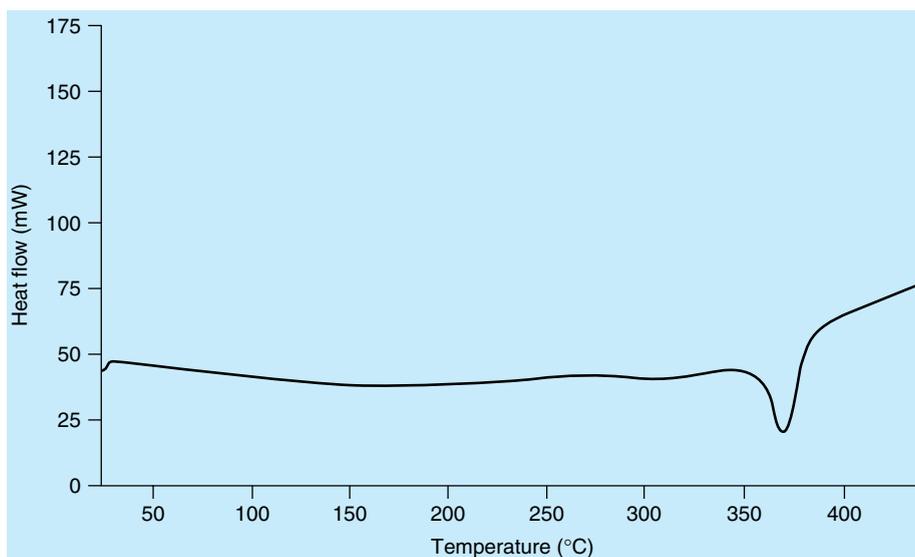
**Figure 5.4.5** Thermogravimetric analysis of 4,4'-MDI



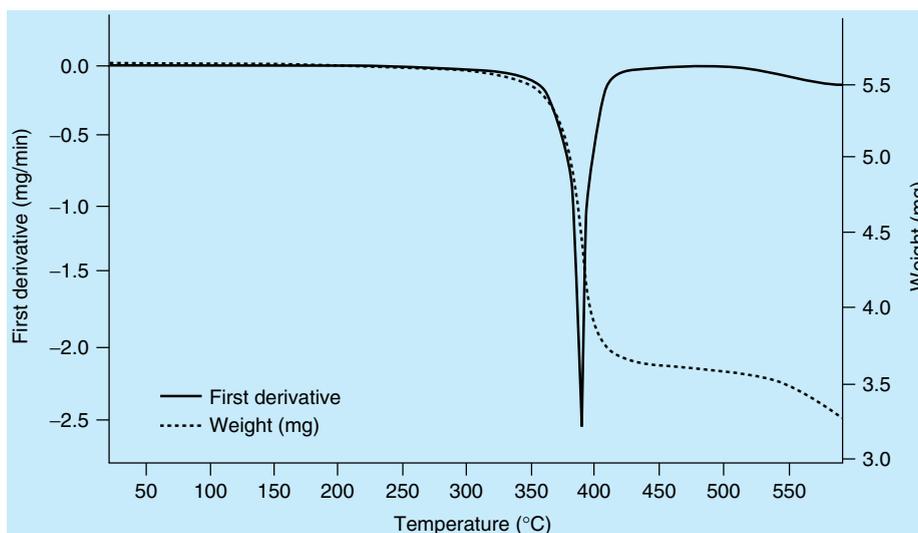
**Figure 5.4.6** Differential scanning calorimetry of 2,4'-MDI



**Figure 5.4.7** Thermogravimetric analysis of 2,4'-MDI



**Figure 5.4.8** Differential scanning calorimetry of polymeric MDI



**Figure 5.4.9** Thermogravimetric analysis of polymeric MDI

### Density

The relative density of a solid or liquid is the ratio between the mass of a volume of the substance, determined at 20 °C, and the mass of the same volume of water, determined at 4 °C. The relative density,  $D_4^{20}$ , is dimensionless.

The relative density,  $D_4^{20}$ , of solid 4,4'-MDI, measured using a gas comparison pycnometer (OECD Test Guideline 109 and EC method A3), was determined as 1.325 (Kelly *et al.*, 1997), see Table 5.4.4. This value is slightly above generally accepted density figures, but it is known that the gas comparison pycnometer may give higher values, as small cavities in the material can be accessed by this method. The density of the same sample of 4,4'-MDI was measured, using a pycnometer, as a liquid at 50 °C, giving a value of 1.182 g/cm<sup>3</sup>. The relative density of polymeric MDI was determined as 1.238 in the same study, using a density meter.

**Table 5.4.4 Density of MDI.**

	4,4'-MDI	PMDI
Relative density at 20 °C	1.325	1.238
Density at 50 °C g/cm <sup>3</sup>	1.182	–

### **Viscosity**

Values in the range 4.7 to 5.0 mPa s at 50 °C are generally quoted for the viscosity of 4,4'-MDI in its liquid state. These values are usually taken from the trade literature, and are unsupported by details of determination methods and conditions.

Viscosities of the various compositions of polymeric MDI are product specific, but are generally in the range 100 to 250 mPa s at 25 °C, although some products may have much higher values.

### **Solubilities**

MDI is hydrophobic, almost insoluble in water and, being more dense than water, will sink beneath it. Any MDI which dissolves reacts rapidly with the water. These characteristics have prevented the solubility of MDI being determined under equilibrium conditions.

MDI is soluble in nonaqueous solvents such as aromatic hydrocarbons, nitrobenzene, acetone, ethers and esters. For experimental work, such as toxicological studies, MDI has been dissolved in dimethylsulphoxide, but it has been shown (Gahlmann *et al.*, 1993) that MDI reacts rapidly with any water present in the dimethylsulphoxide to yield a variety of products. In this situation the dimethylsulphoxide acts as a catalyst for the diisocyanate–water reaction. The implications of this reaction in toxicological testing are discussed in *Part 3, Health*. Dimethylformamide has also been used as a solvent for MDI, and MDI has been found to react with any water present in the dimethylformamide to give urea derivatives (Tsumura and Inoue, 1980).

### **Vapour pressure**

In Table 5.4.5 are listed the results of those studies on MDI for which a method is given, and in which there are no obvious errors. Values at 20 °C, extrapolated where necessary, are quoted for comparison. For the high-temperature study such extrapolation is likely to lead to error, so a value at 150 °C is quoted for comparison with that of TDI (Table 5.4.14).

In the assessment of the relative merits of the above studies, it is important to understand the difficulties inherent in the measurements, particularly at ambient temperatures. The vapour pressure of MDI at ambient temperatures is extremely low, and is below the satisfactory range of most static methods. Further, MDI may contain trace impurities of significantly higher volatility; also it will react with traces of water to produce carbon dioxide. Consequently, static procedures, where the pressure of vapour in equilibrium with liquid is measured, can seriously overestimate the vapour pressure, unless adequate precautions are taken.

**Table 5.4.5 MDI: experimental values of vapour pressure.**

Material	Method	Temperature range °C	Vapour pressure		Study	Reference
			20 °C Pa	150 °C Pa		
2,4'-MDI	Static	24 to 41	0.0014		Shell	Kelly <i>et al.</i> (1997)
4,4'-MDI	Effusion	38 to 85	0.0007		Dow	Chakrabarti (1989)
	Gas saturation	20 to 70	0.0005		Bayer	Brochhagen and Schal (1986)
	Effusion <sup>a</sup>	65 to 89	0.0008		Upjohn	de Kruif and Zandvoort, (undated) (ca 1981)
	Static <sup>a</sup>	160 to 210		45	Upjohn	de Kruif and Zandvoort, (undated) (ca 1981)
PMDI (ca 50 % 4,4'-MDI)	Effusion	15 to 73	0.0003		Dow	Chakrabarti (1989)
	Static	23 to 56	0.0009		Shell	Kelly <i>et al.</i> (1997)

<sup>a</sup>These references do not include experimental data.

#### Vapour pressure over 4,4'-MDI

The Chakrabarti data are probably the most reliable for MDI. However, all the data for 4,4'-MDI in the table are well represented by the Antoine equation of best-fit:

$$\text{Log}_{10} P = 10.25 - 2961/(t + 200)$$

where the vapour pressure ( $P$ ) is in pascals (Pa) and the temperature ( $t$ ) is in °C.

The vapour pressures calculated from the above best-fit equation are given in Table 5.4.6. Also included in the table are the saturated vapour concentrations at the corresponding temperatures, as calculated from the vapour pressures using the conventional equation of state.

#### Vapour pressure over polymeric MDI

For polymeric MDI, the experimental data, mainly from the Chakrabarti study, show a reasonably linear correlation of vapour pressure with the weight proportion of monomeric MDI in the sample. There is also evidence, from the de Kruif study, that the vapour above polymeric MDI is composed predominantly of 4,4'-MDI. Therefore, in the absence of volatile impurities, the vapour above polymeric MDI is essentially monomeric MDI, at a pressure roughly proportional to its concentration in the sample. This allows notional values of the vapour pressure of polymeric MDI to be estimated. Whilst the concentration of 4,4'-MDI in polymeric MDI varies according to the proprietary product, the concentration is normally about 50 %. Hence, to an approximation, values of polymeric MDI vapour pressure can be assumed to be about half those of 4,4'-MDI. Such notional values are given in Table 5.4.7.

#### Vapour pressure over solid 4,4'-MDI

The calculated values in Table 5.4.6 relate to the pressures of vapour above liquid, which will be higher than those above the solid. The ratio of these

**Table 5.4.6 4,4'-MDI: best fit values of vapour pressures and saturated vapour concentrations.**

Temperature °C	Vapour pressure Pa	Saturated vapour concentration $\mu\text{g}/\text{m}^3\text{a}$
-10	$4.6 \times 10^{-6}$	0.5
-5	$1.2 \times 10^{-5}$	1.3
0	$2.8 \times 10^{-5}$	3.1
5	$6.4 \times 10^{-5}$	7.0
10	$1.4 \times 10^{-4}$	15
15	$3.0 \times 10^{-4}$	31
20	$6.2 \times 10^{-4}$	64
25	$1.2 \times 10^{-3}$	120
30	$2.4 \times 10^{-3}$	240
35	$4.5 \times 10^{-3}$	440
40	$8.2 \times 10^{-3}$	790
50	$2.5 \times 10^{-2}$	$2.4 \times 10^3$
100	2.4	$2.0 \times 10^5$
150	62	$4.5 \times 10^6$
200	700	$4.5 \times 10^7$

These calculated values relate to the pressures of vapour above liquid 4,4'-MDI, which will be higher than those above the solid. The values can probably be used without appreciable error for 2,4'-MDI.

<sup>a</sup>TDI values in Table 5.4.14 are expressed as  $\text{mg}/\text{m}^3$  units.

**Table 5.4.7 Polymeric MDI: best fit values of vapour pressures and saturated vapour concentrations calculated from 4,4'-MDI.**

Temperature °C	Vapour pressure Pa	Saturated vapour concentration $\mu\text{g}/\text{m}^3\text{a}$
-10	$2.3 \times 10^{-6}$	0.3
-5	$6 \times 10^{-6}$	0.7
0	$1.4 \times 10^{-5}$	1.6
5	$3.3 \times 10^{-5}$	3.5
10	$7 \times 10^{-5}$	7.5
15	$1.5 \times 10^{-4}$	16
20	$3.1 \times 10^{-4}$	32
25	$6 \times 10^{-4}$	60
30	$1.2 \times 10^{-3}$	120
35	$2.3 \times 10^{-3}$	220
40	$4.1 \times 10^{-3}$	400
50	$1.3 \times 10^{-2}$	$1.2 \times 10^3$
100	1.2	$1.0 \times 10^5$
150	31	$2.3 \times 10^6$
200	350	$2.3 \times 10^7$

<sup>a</sup>TDI values in Table 5.4.14 are expressed as  $\text{mg}/\text{m}^3$  units.

pressures can be predicted from the melting point of the substance. For 4,4'-MDI, melting point 40 °C, the pressure above the solid is calculated to be 63 % of the notional (extrapolated) value above liquid at 20 °C, and 80 % at 30 °C. The difference is unlikely to be significant, considering the very low pressures involved.

### Fire properties

Fire properties of MDI are given in Table 5.4.8.

**Table 5.4.8 Fire properties of MDI.**

Property		4,4'-MDI	Polymeric MDI
Autoignition temperature	°C	>601	>600
Flash point (Pensky–Martens closed cup)	°C	211	208
Explosivity		Not explosive <sup>a</sup>	Not explosive

<sup>a</sup>MDI dust has not been tested for explosivity.

### Autoignition

Using the EC method A15, the III study (Kelly *et al.*, 1997) found no auto-ignition of 4,4'-MDI up to a temperature of 601 °C. Similarly, no autoignition of polymeric MDI was found up to 600 °C.

### Flash point

4,4'-MDI was found to have a flash point of 211 °C, using the Pensky–Martens closed cup apparatus (EC method A9) (Kelly *et al.*, 1997). In the same study, the flash point of polymeric MDI was determined as 208 °C.

### Explosivity

Differential scanning calorimetry and thermogravimetric analysis of 4,4'-MDI and polymeric MDI (see Figures 5.4.4 to 5.4.9) show no indications of explosivity, the polymeric MDI sample used in the III study (Kelly *et al.*, 1997) showing only a mildly exothermic decomposition. These DSC and TGA data, combined with the similarity in the composition of MDI to TDI which showed no explosivity in the EC method A14 test, led the researchers to indicate that it is reasonable to conclude that MDI is not explosive in the sense of the A14 test.

The fire behaviour is discussed in *Part 5.5, Fire behaviour of MDI and TDI*.

### TDI

Ranging from colourless to pale yellow, all forms of TDI have a characteristic pungent odour. The reported odour threshold is significantly above typical workplace exposure limits and therefore odour must never be used as a criterion for exposure. For further details of odour threshold, see *Part 2, Key theme 2: Protecting health*.

A summary of the physical properties of TDI is given in Table 5.4.9.

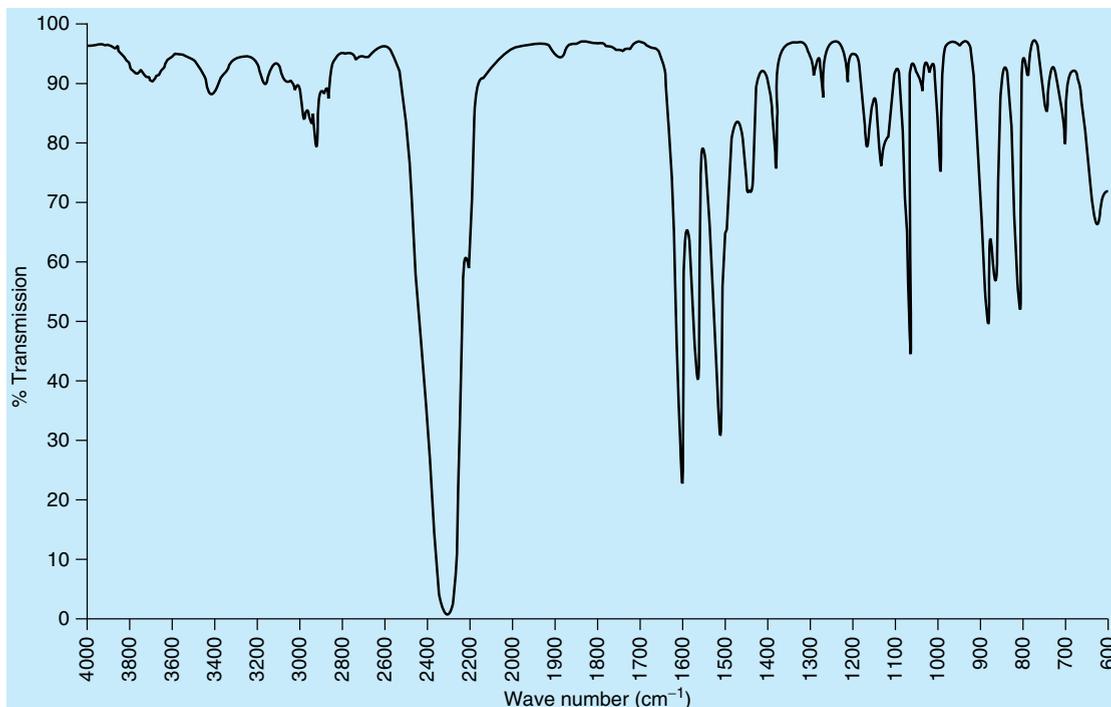
### Spectra

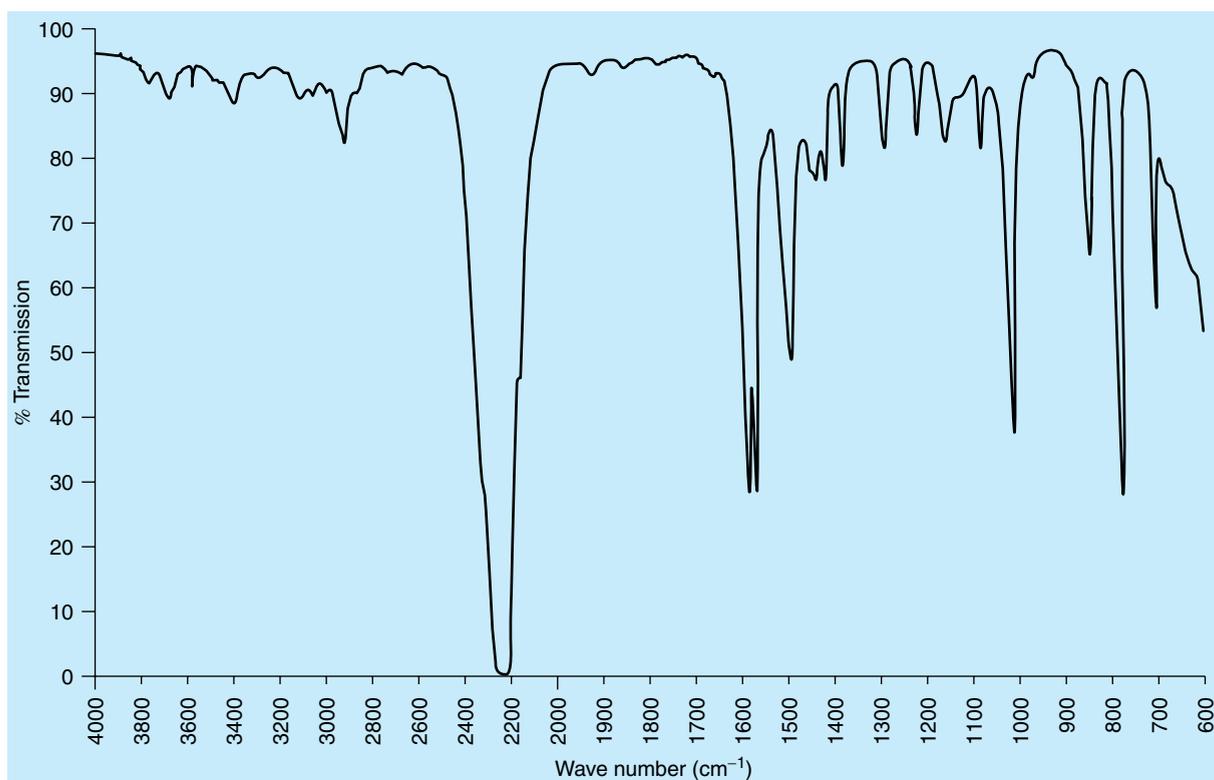
Spectra for TDI are given in Figures 5.4.10 to 5.4.13.

**Table 5.4.9 Summary of TDI physical properties.**

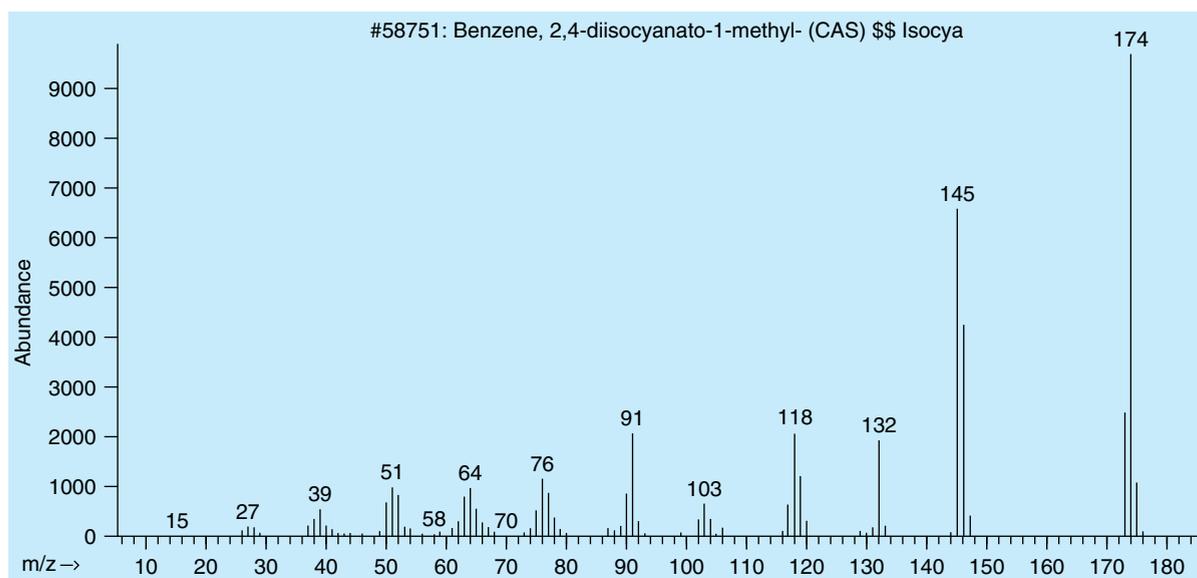
Property	2,4-TDI	2,6-TDI	80/20 TDI	65/35 TDI
Molecular weight	174.2	174.2	174.2	174.2
Melting point °C	21	10.5	9.5 to 10	4
Boiling range °C	252 to 254	247 to 249	252 to 254	253 to 255
Relative density	1.214 at 25 °C	1.226 at 20 °C	1.220 at 20 °C	1.222 at 20 °C
Viscosity mPa s	ca 3 at 25 °C	–	ca 3 at 25 °C	ca 3 at 25 °C
Vapour pressure Pa	1.4 at 20 °C	1.4 at 20 °C	1.4 at 20 °C	1.4 at 20 °C
Saturated vapour concentration mg/m <sup>3</sup>	100 at 20 °C	100 at 20 °C	100 at 20 °C	100 at 20 °C
Autoignition temperature °C	–	–	>595	>598
Flash point °C	–	–	132.4	128.3
Explosivity	Not explosive	Not explosive	Not explosive	Not explosive
Refractive index	–	1.5654 <sup>a</sup> at 25 °C	1.5666 <sup>a</sup> at 25 °C	1.5663 <sup>a</sup> at 25 °C
Partition coefficient	See Part 4, The environment			
Thermodynamics	See Further reading			

<sup>a</sup>See Chadwick and Cleveland (1981).

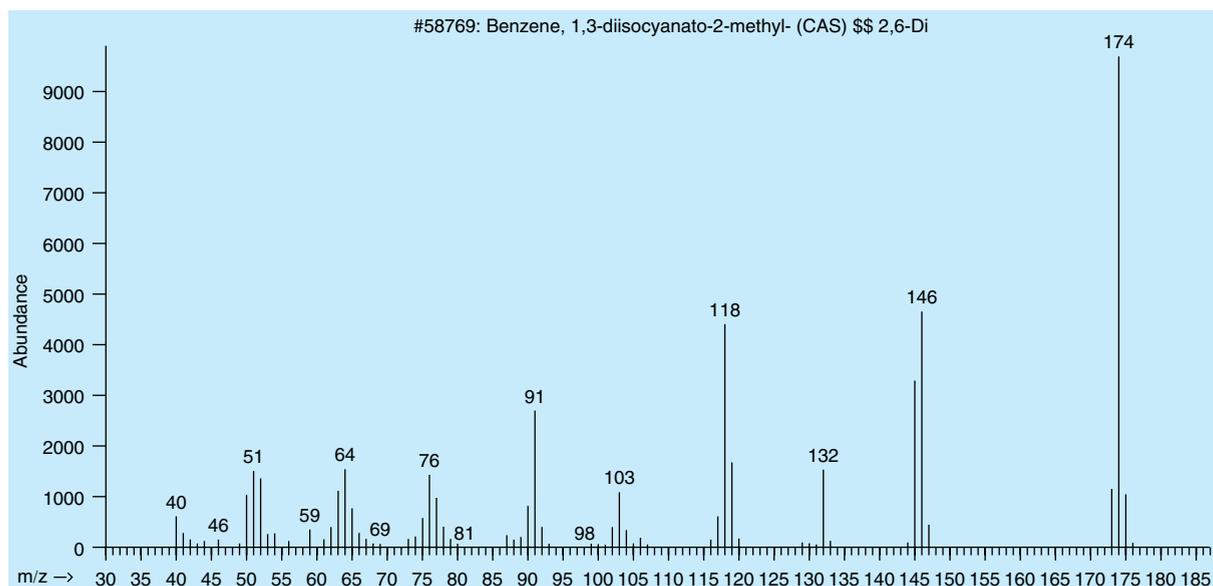
**Figure 5.4.10 Infrared spectrum of 2,4-TDI**



**Figure 5.4.11** Infrared spectrum of 2,6-TDI



**Figure 5.4.12** Mass spectrum of 2,4-TDI. Reproduced by courtesy of John Wiley & Sons, Ltd



**Figure 5.4.13** Mass spectrum of 2,6-TDI. Reproduced by courtesy of John Wiley & Sons, Ltd

### Melting and freezing ranges of TDI

A study (Kelly *et al.*, 1997) of the physical properties of TDI determined the melting point of the single isomers, 2,4-TDI and 2,6-TDI, using a crystallizing point apparatus (OECD Test Guideline 102 and EC Method A1).

Composition of TDI samples used in the III study (Kelly *et al.*, 1997)

2,4-TDI	99.9 % purity
2,6-TDI	97.0 % purity
80/20 TDI	99.8 % purity
of which	80.2 % 2,4-TDI
	19.8 % 2,6-TDI
65/35 TDI	99.8 % purity
of which	67.5 % 2,4-TDI
	32.5 % 2,6-TDI

The 2,4-TDI sample gave a melting point of 21 °C (Table 5.4.10), and this value is supported by the results of differential scanning calorimetry (Figure 5.4.14). The melting point of 2,6-TDI was determined as 10.5 °C. Melting point determinations on isomer mixtures in the same study gave the values of 4.0 °C for 65/35 TDI and the range 9.5 to 10 °C for 80/20 TDI. For a note on the isomer ratio around the freezing point, see the text on TDI isomer ratios below.

**Table 5.4.10** Melting and freezing ranges of TDI species.

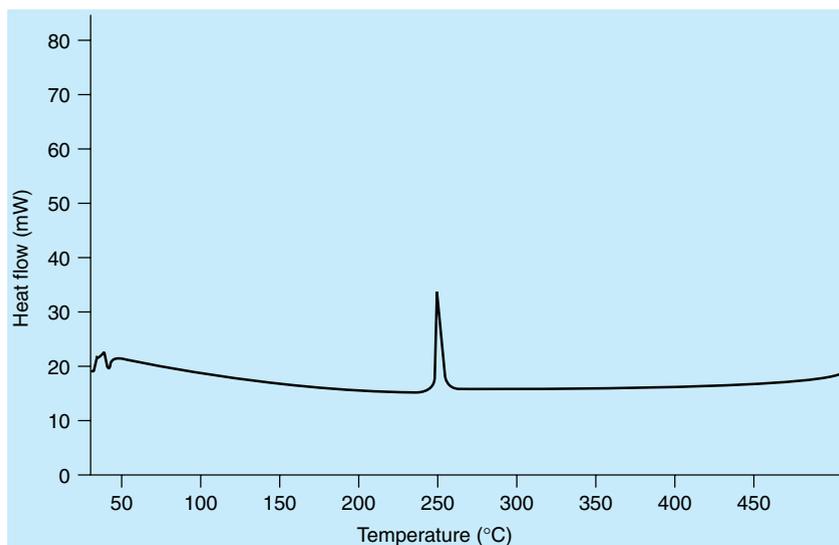
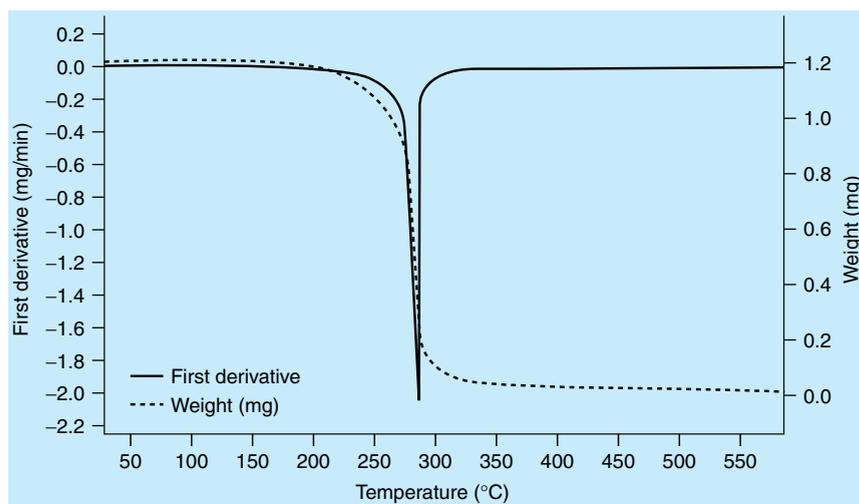
2,4-TDI	2,6-TDI	80/20 TDI	65/35 TDI
21 °C	10.5 °C	9.5 °C to 10 °C	4 °C

### Boiling range

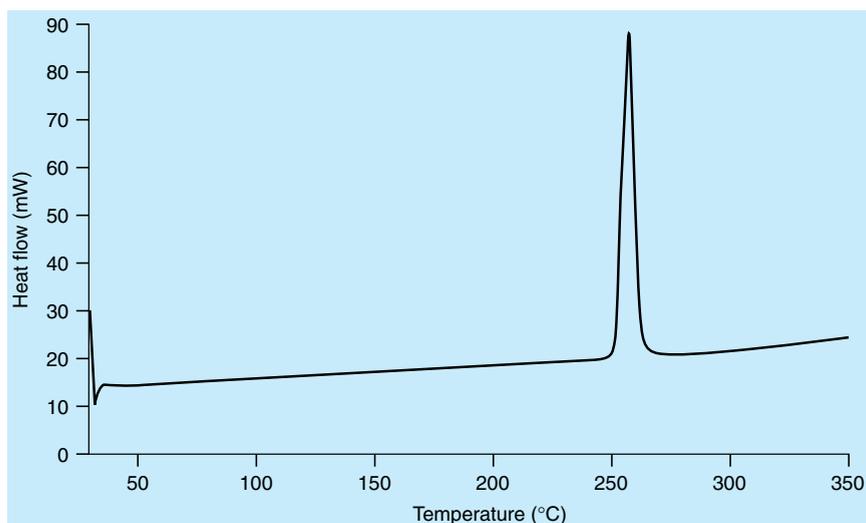
The boiling ranges of 2,4-TDI and 2,6-TDI were determined in the III study (Kelly *et al.*, 1997) using the Siwoloboff method (OECD Test Guideline 103 and EC Method A2) (Table 5.4.11). Differential scanning calorimetry of the same materials gave similar values. Mixtures of isomers had boiling ranges similar to those of the single isomers. No decomposition of TDI was noted in this study.

**Table 5.4.11** Boiling ranges of TDI species.

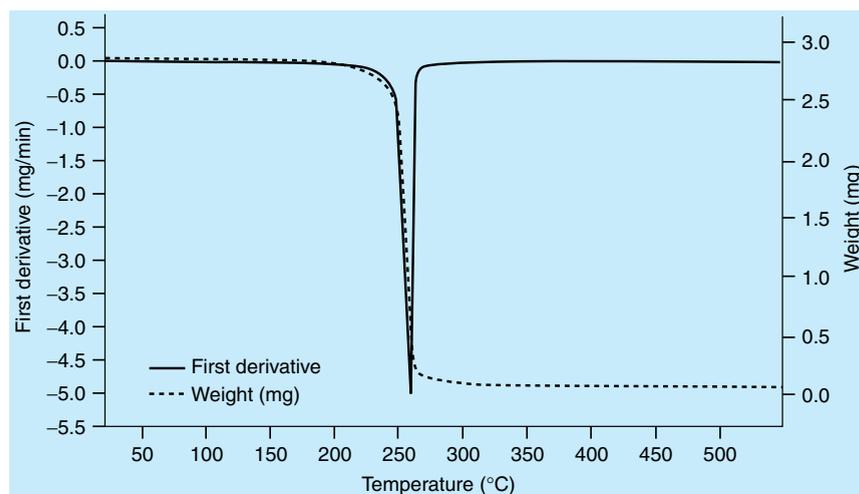
Method used	2,4-TDI	2,6-TDI	80/20 TDI	65/35 TDI
Siwoloboff	252 to 254 °C at 1011 hPa	247 to 249 °C at 992 hPa	252 to 254 °C at 1013 hPa	253 to 255 °C at 1013 hPa
DSC	249 °C	244 °C	253 °C	249 °C

**Figure 5.4.14** Differential scanning calorimetry of 2,4-TDI**Figure 5.4.15** Thermogravimetric analysis of 2,4-TDI**Differential scanning calorimetry and thermogravimetric analysis**

These tests were carried out as part of the III study (Kelly *et al.*, 1997) (Figures 5.4.14 to 5.4.17).



**Figure 5.4.16** Differential scanning calorimetry of 80/20 TDI



**Figure 5.4.17** Thermogravimetric analysis of 80/20 TDI

### Density

The relative densities,  $D_4^{20}$ , of 2,6-TDI, 80/20 TDI and 65/35 TDI were measured using the oscillating density meter method according to OECD Test Guideline 109 and EC Method A3 (Kelly *et al.*, 1997) (Table 5.4.12). The relative density of 2,4-TDI was measured at 25 °C instead of 20 °C at which it is a solid (mp 21 °C).

**Table 5.4.12** Density of TDI.

	2,4-TDI	2,6-TDI	80/20 TDI	65/35 TDI
Relative density	1.214 at 25 °C	1.226 at 20 °C	1.220 at 20 °C	1.222 at 20 °C

### Viscosity

References in the literature, such as Woods (1990), to the viscosity of 2,4-TDI and to isomer mixtures give values around 3 mPa s at 25 °C.

### Solubilities

TDI is hydrophobic, is almost insoluble in water and, as it is more dense than water, will form a layer under any water present. Any TDI which does dissolve reacts rapidly with the water. These characteristics have prevented the determination of the solubility of TDI under equilibrium conditions.

TDI is soluble in many organic solvents, such as diethyl ether, carbon tetrachloride, benzene, chlorobenzene and kerosene, as well as in olive oil and corn oil, which have been used in toxicological studies. The stability of TDI in corn oil has been investigated (Ashby, 1988) and reaction with TDI was found. Dimethylsulphoxide has been used as a solvent for TDI in experimental studies. However, it has been shown (Gahlmann *et al.*, 1993) that 2,4-TDI reacts rapidly with any water present in the dimethylsulphoxide, with the dimethylsulphoxide itself acting as a catalyst for the hydrolysis. The implications of this in toxicological studies are discussed in *Part 3, Health*.

### Vapour pressure

In Table 5.4.13 are listed the results of those studies on TDI for which a method is given, and in which there are no obvious errors. Values at 20 °C or 150 °C (extrapolated where necessary), dependent upon the temperature range of the measurement, are quoted for comparison.

**Table 5.4.13** TDI: experimental values of vapour pressure.

Material	Method	Temperature range °C	Vapour pressure		Reference
			20 °C Pa	150 °C Pa	
2,4-TDI	Gas saturation	20 to 40	1.4		Frensdorff and Adams (1975)
	Static	50 to 86	2.1		Kelly <i>et al.</i> (1997)
	Static	103 to 170		4600	Frensdorff and Adams (1975) Cole (1958)
	Static	150 to 250		4700	Daubert and Hutchinson (1990)
	Static <sup>a</sup>	120 to 190		4200	Molard (1964–1965)
	Static	135 to 181		4300	Pelloux (1994)
2,6-TDI	Effusion	–9 to 18	1.4		Bayer (1996)
	Static <sup>a</sup>	100 to 180		4900	Cole (1958)
	Static	140 to 250		5200	Daubert and Hutchinson (1990)
	Static <sup>a</sup>	120 to 190		4500	Molard (1964–1965)
80/20 TDI	Effusion	–9 to 18	0.8		Bayer (1996)
	Gas saturation	20	1.2		Wu <i>et al.</i> (1996)
65/35 TDI	Static	134 to 163		4300	Pelloux (1994)

<sup>a</sup>These references do not include experimental data.

When the relative merits of these studies are being assessed, the difficulties inherent in the measurements, particularly at ambient temperatures, must be understood. The ambient vapour pressure of TDI is low, and falls inconveniently around the upper limit of most flow methods and the lower limit of most static methods. In addition, TDI can contain trace impurities having significantly higher volatility: it will also react readily with traces of water to produce carbon dioxide. Consequently, static procedures, where the pressure of vapour in equilibrium with liquid is measured, can seriously overestimate the vapour pressure unless adequate precautions are taken.

The data of Frensdorff and Adams, and of Cole, for TDI are probably the most reliable. However, all the data for 2,4-TDI in the table are well represented by the Antoine equation of best-fit:

$$\text{Log}_{10} P = 9.66 - 2120/(t + 203)$$

where the vapour pressure ( $P$ ) is in pascals (Pa) and the temperature ( $t$ ) is in °C.

The vapour pressures calculated from the above best-fit equation are given in Table 5.4.14. Also included in the table are the saturated vapour concentrations at the corresponding temperatures, as calculated from the vapour pressures using the conventional equation of state.

**Table 5.4.14 2,4-TDI: best-fit values of vapour pressure and saturated vapour concentrations.**

Temperature °C	Vapour pressure Pa	Saturated vapour concentration mg/m <sup>3a</sup>
-10	0.047	3.7
-5	0.090	7.0
0	0.16	13
5	0.29	22
10	0.51	38
15	0.86	63
20	1.4	100
25	2.3	160
30	3.6	250
35	5.7	380
40	8.6	580
50	19	1.2 × 10 <sup>3</sup>
100	460	2.6 × 10 <sup>4</sup>
150	4500	2.3 × 10 <sup>5</sup>
200	25 000	1.1 × 10 <sup>6</sup>

These values can also be used for 2,6-TDI and mixtures of 2,4- and 2,6-TDI, without appreciable error.

<sup>a</sup>MDI values in Tables 5.4.6 and 5.4.7 are expressed as µg/m<sup>3</sup> units.

#### **Vapour pressure of 2,6-TDI and its mixtures with 2,4-TDI**

The vapour pressures of 2,6-TDI and its mixtures with 2,4-TDI appear to be very similar to those of 2,4-TDI, and predicted values for the latter can be used without appreciable error.

### **TDI isomer ratio**

Commercial TDI is predominantly an 80 % 2,4-TDI and 20 % 2,6-TDI mixture; a mixture of 65 % 2,4-TDI and 35 % 2,6-TDI is also available. However, under certain conditions, this isomer ratio can change. For example, when the temperature of an isomer mixture was raised from below its freezing point, the eutectic point was reported to be 40 % 2,4-isomer and 60 % 2,6-isomer (Dombrow, 1965). A partial melt composition will therefore have a different isomer ratio from that expected.

The 2,4-isomer is more reactive than the 2,6-isomer, due to steric factors (see *Part 5.3, Chemistry of MDI and TDI*), and air sampling in foam plants showed a large increase in the amount of airborne 2,6-TDI relative to the 2,4-isomer when compared with the ratio of isomers in the starting material (see Table 2.19).

### **Fire properties**

Fire properties of TDI are given in Table 5.4.15.

**Table 5.4.15 Fire properties of TDI.**

	80/20 TDI	65/35 TDI
Autoignition temperature °C	>595	>598
Flash point °C	132.4	128.3
Pensky–Martens closed cup		
Explosivity	Not explosive	Not explosive

### **Autoignition**

In the III study (Kelly *et al.*, 1997) using EC method A15, no autoignition of 80/20 TDI was found up to 595 °C, or up to 598 °C in the case of 65/35 TDI. The value for 80/20 TDI supports previous results: >850 °C using ASTM E–659 (ICI, 1987) and >665 °C using DIN 51795 (Mann, 1987).

### **Flash point**

The flash points of the isomeric mixtures of TDI are 132.4 °C (80/20 TDI) and 128.3 °C (65/35 TDI) as determined using the Pensky–Martens closed cup apparatus, EC method A9 (Kelly *et al.*, 1997). Commonly quoted values in the literature for the flash point of 2,4-TDI are around 132 °C, but these are without full details of test method and material.

### **Explosivity**

The data from differential scanning calorimetry and thermogravimetric analysis of 80/20 TDI (see Figures 5.4.16 and 5.4.17) show no significant thermal event apart from the boiling process. The same sample exhibited no explosive properties under the influence of shock or heat, using the EC method A14 (Kelly *et al.*, 1997). These results have been taken as an indication that other forms of TDI and MDI are also unlikely to show explosive properties.

The fire behaviour is discussed in *Part 5.6, Fire behaviour of MDI and TDI*.

#### *Explosivity testing*

The explosivity of a material is determined by a specific test (EC A14), which, in the case of a liquid, examines its sensitivity to heat (the Koenen test) and sensitivity to shock (the Fall Hammer test). These tests are only called into use when an indication of thermal instability has resulted from the study by differential scanning calorimetry and thermogravimetric analysis.

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### Further reading

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## 5.5 Fire behaviour of MDI and TDI

The determination and values of the fire and explosive properties of MDI and TDI are given in *Part 5.4, Physical and fire properties*.

The properties relevant to fire behaviour are:

- high flash points;
- high autoignition points;
- no explosive tendency.

Property	80/20 TDI	Polymeric MDI
Flash point °C	132	208
Autoignition point °C	>595	>600
Explosivity	Not explosive	Not explosive

These values were determined in a study by Ill (*Kelly et al.*, 1997)

MDI and TDI have been used commercially for over 50 years, with consumption growing more or less regularly to the present annual manufacturing level approaching 3.5 million tonnes. Despite the movement, storage and usage of large quantities of product during that time, a global literature search has failed to identify reports in which MDI or TDI has been highlighted as contributing in a significant way to any accidental fire occurrences. Searches have also been made of the records of transportation accidents involving MDI and TDI. Sources investigated have included national hazard statistic compilations, industry records and individual manufacturer company reports. Some 50 incidents involving MDI and 300 incidents involving TDI have been listed, with quantities of released material ranging from a few kilos from a drum, to 40 tonnes from a dockside land pipeline. None of the reports of the incidents indicated that any burning of the released diisocyanate occurred. Whatever inferences may be drawn from the absence of data suggestive of flammability, it does mean that structured laboratory fire test data provide the sole basis for assessing and describing the combustion behaviour of these products. Therefore this text can deal only with the behaviour of MDI and TDI in test fires.

Marlair *et al.* (1993) noted that MDI and TDI, being materials with well-known toxicological hazards, have strict handling procedures defined for them. Such careful handling, demanded as a result of the toxicological considerations, undoubtedly gives benefit in the avoidance of other unexpected hazard circumstances such as fire outbreaks.

### Test methodology

As indicated above, a normal empirical approach to understanding the fire characteristics of a material, by collating its recorded behaviour in a variety

of fire occurrences, is precluded in the case of MDI and TDI. The only data available come from tests which have gained prominence in the developing field of fire science. These tests have been applied by the diisocyanate manufacturers, either jointly through the International Isocyanate Institute Inc. (III), in conjunction with testing institutes such as the Institut National de l'Environnement Industriel et des Risques (INERIS), France, or individually by manufacturers.

In the field of fire testing, until comparatively recently, many tests had addressed a single fire property of the given material, for example, ignitability or flame propagation. Tests were structured to categorize the material simply as pass or fail. More than 700 standardized fire tests of this kind have been recorded (ISO, 1993d) and many of them are still in use to demonstrate the conformity of a product to regulatory requirements, for quality control, or for pre-selection purposes for applications such as construction. However, the use of such tests allowed the ranking of materials according to increasing levels of risk, often on the basis of a limited number of parameters.

Data from small-scale tests are difficult to extrapolate to real fire scenarios and require accurate predictive models. The derivation of adequate models constitutes a challenge to fire scientists, due to the complexity of fire phenomena. The use of large-scale test results, which are more realistic, still requires caution, given the variety of real fire scenarios which may be encountered in industrial and other situations. Real fires evolve with time from ignition to final decay, and these phases are impossible to reflect adequately in a single test.

Since the accident in Seveso, Italy, in 1976, when an explosion at the Icmeso pesticide plant released noxious chemicals into the atmosphere (Marshall, 1987), the European Union (EU) has been seeking regulatory ways to reduce such accidents in industry. The Directive on the major accident hazards of certain industrial activities (often referred to as the *Seveso Directive*) and the Directive on industrial pollution prevention and control (IPPC) has stimulated, among others, programmes of research into the understanding of fire hazard.

Recognizing that, in Europe, major chemical industry facilities may be in close proximity to areas of high population density, the EU started its Major Technical Hazards programme in 1987. This included STEP (Science and Technology for Environmental Protection) and in 1989 the MISTRAL (Fire Modelling Simulating Transfers and Risks to the Environment) programme was started. MISTRAL has the stated aim of *supplying the manager of potentially hazardous plants with tools to prevent or mitigate fire consequences* (CEC, 1995). A later phase, MISTRAL 2, was established to define the severity of a fire using the four parameters of (1) ignitability, (2) rate of pyrolysis, (3) combustion kinetics and (4) toxic and corrosive product formation. Part of this project was the development of tests to determine the parameters in the most cost-effective manner. Another part was concerned with the processing of data from the tests in a modelling exercise to predict full-scale fire and environmental hazards. A review (Cole and Wicks, 1993) indicated that full-scale fire hazards could not at that time be predicted accurately from small-scale tests, and this appears still to be the case.

*References on EU directives on major accident hazards and on IPPC*

Council Directive on major accident hazards of certain industrial activities (CEC, 1982) and its amendments (CEC, 1987; CEC, 1988; CEC, 1992).

Council Directive concerning integrated pollution prevention and control (CEC, 1996).

*References on measurement of fire parameters*

Tewarson (1980, 1994, 1995), Babrauskas (1991), Janssens (1995).

*ISO Documents*

Documents issued by ISO Committee TC92 (ISO, 1989, 1990, 1993a, 1993b, 1993c, 1993d, 1994) provide a comprehensive view regarding the appropriate use of fire tests and their results for the actual fire hazard assessment.

*References on smoke and toxic gas production*

Jin (1978), Östman and Tsantaridis (1991), Busmann *et al.* (1992), ISO (1993c).

## **Advances in test methodology**

New approaches to assessing the fire characteristics of materials have taken place, predominantly over the last decade. These approaches recognize that the whole fire course needs to be considered, from ignition, through fire growth, sustained plateau and final die-down. In particular, calorimetry has been a basis for the development of a new generation of fire tests. The technique is now acknowledged by most fire science and engineering specialists as a fundamental element in exercises to define fire properties and related fire hazards. Efficient measuring techniques have emerged to determine the most important parameters, such as the mass loss rate of a burning material and the related effective heat and combustion gas release rates.

Results obtained by the use of such tests still have technical and applicational limitations, which are due to apparatus design features and to testing protocols, and to the number of fire scenarios which may be necessary to reflect a real situation. These concepts have been developed and reviewed in a series of Guideline Technical Reports issued by the International Standards Organization (ISO).

Smoke is produced in almost all fires and can be a major hazard to life for two main reasons:

- Obscuration of light. This increases the difficulties of personnel in making their escape from the fire zone. Although optical density measurements are used to record obscuration levels, their interpretation is very difficult due to their variation with test conditions, particularly with the degree of aeration and rate of fire propagation. It is found that the results from different tests are rarely comparable.
- Toxic gas production. Similar difficulties occur in the interpretation of data from toxic gas production.

Any useful assessment of risk requires the simultaneous considerations of the probability of the occurrence happening, the relevance of the test scenario being used and the suitability of the measuring system operated. Particularly helpful notes on this topic can be found in the referenced publications (see marginal note). In the experimental work described later the reader will find data recorded to show more emphasis on toxic gas production than on smoke.

## **Fire tests on MDI and TDI**

To obtain data on the fire characteristics of MDI and TDI in the most effective way, large-scale fire tests at two facilities, and favoured laboratory-scale tests, have been used.

The large-scale tests were

- a series of pool fires in the INERIS fire gallery, using 7 to 150 kg samples in pools of 0.25 to 2.0 m<sup>2</sup> surface area.
- a series of tests at the Bayer AG fire test facility, in which closed drums containing diisocyanate (10 to 250 kg) were exposed to severe external fire conditions. The drums were either metal or polyethylene.

The laboratory-scale tests used the

- Tewarson apparatus (10 to 30 g samples);

- Cone Calorimeter (30 g samples).

Testing was concentrated upon the two main commercial products, 80/20 TDI and polymeric MDI. Other types of MDI- or TDI-based products (prepolymers, variants and materials with other isomer ratios) cannot be assumed to behave in fire in exactly the same way as the 80/20 TDI and polymeric MDI products which have been tested. Solvent grades of any of the MDI or TDI products can be expected to deviate significantly from the behaviour shown by the nonsolvent grade materials assessed.

### **Pool fire tests at INERIS**

Pool fire tests on large quantities of MDI and TDI have been carried out in the INERIS gallery. This gallery (Figures 5.5.1 and 5.5.2) was originally designed for studying fire risk in coal mines, and later proved valuable in studying fires in road and rail traffic tunnels and inside warehouses and other industrial premises. It was designed on the basis of the understanding of pool fire tests and the configuration is based on the technical approach for pool fires suggested by Emori and Saito (1983).

*References on pool fire tests*  
Blinov and Khudyakov (1957, 1958), Hall (1973), Babrauskas (1983).

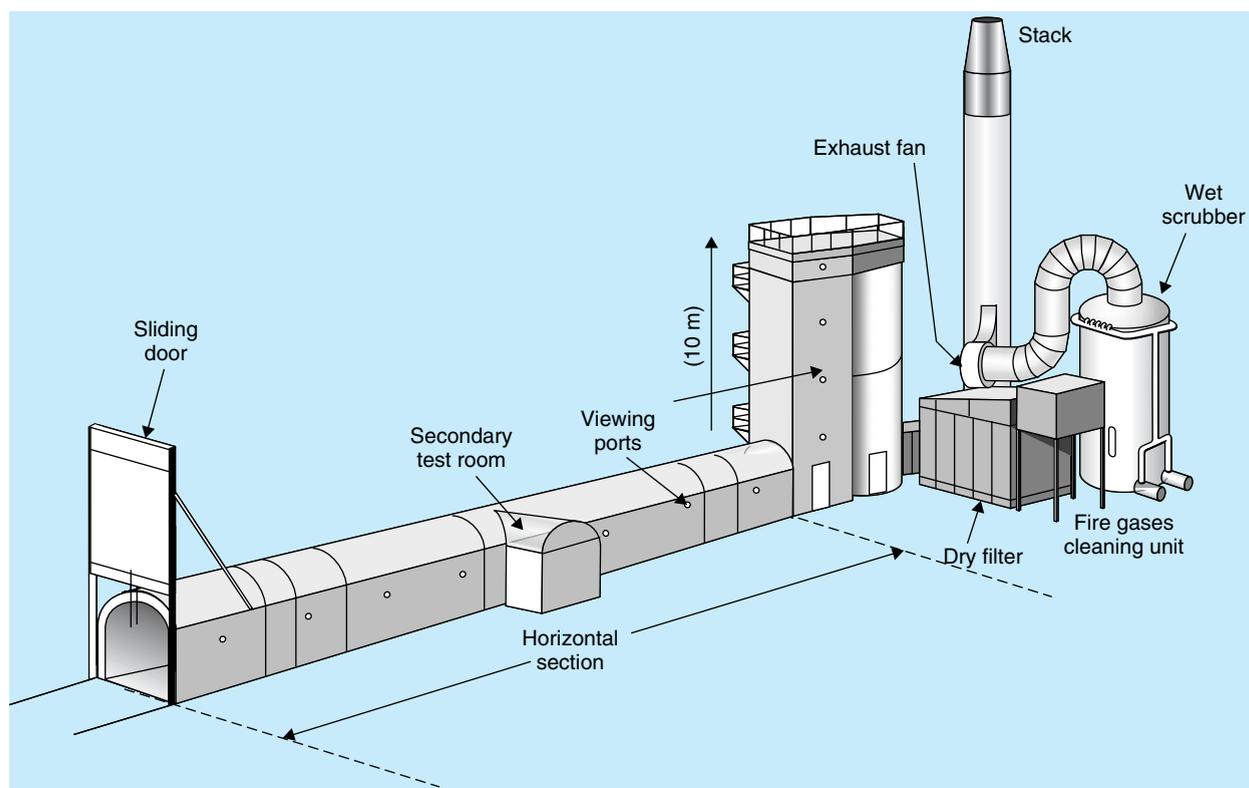


**Figure 5.5.1** INERIS test gallery, general view

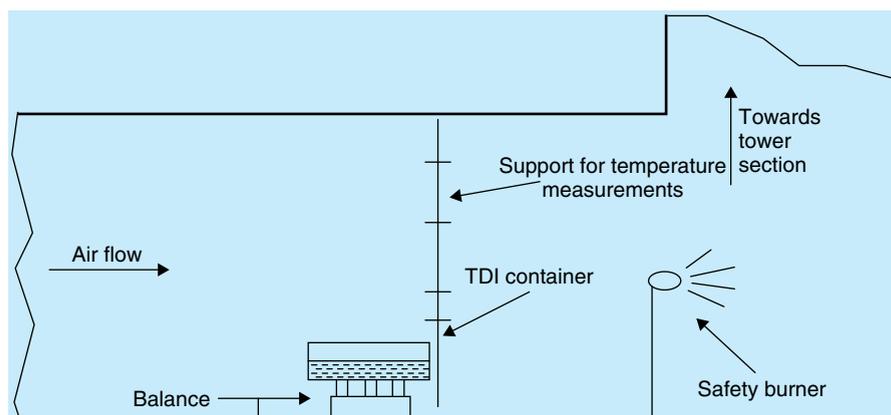
The unit is composed of

- a horizontal section (wind tunnel), nearly 50 m long and of 10 m<sup>2</sup> cross-section;
- a vertical tower, 10 m high, at the top of which are ports for sampling the gases and for heat release rate measurements;
- a vertical column transporting the fire gases plus entrained air to the gas cleaning unit;
- a gas cleaning unit, dry dust filter and a wet scrubber;
- an exhaust fan and stack.

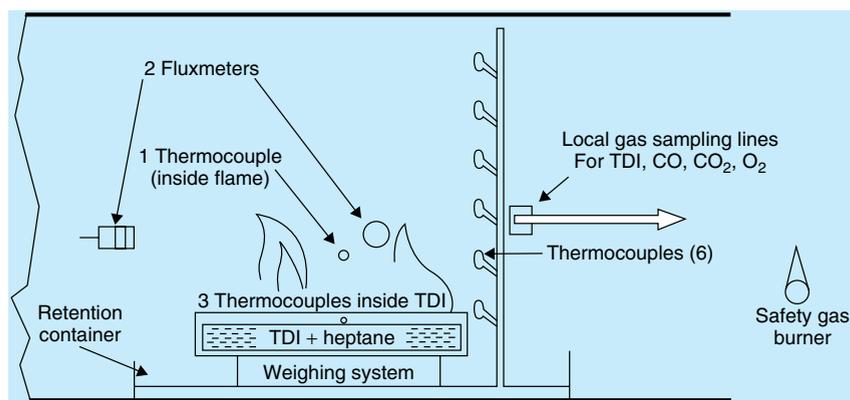
Details of the tunnel and the mounting of the sample holder and measuring devices are shown in Figures 5.5.1 to 5.5.4.



**Figure 5.5.2** INERIS test gallery, layout. Reproduced, with permission, from *The behaviour of commercially important di-isocyanates in fire conditions. Part 1: Toluene di-isocyanate (TDI)*. Marlair, Prager and Sand, 1993. © John Wiley & Sons, Ltd



**Figure 5.5.3** Sample position in test gallery. Reproduced, with permission, from *The behaviour of commercially important di-isocyanates in fire conditions. Part 1: Toluene di-isocyanate (TDI)*. Marlair, Prager and Sand, 1993. © John Wiley & Sons, Ltd



**Figure 5.5.4** Instrumentation and gas sampling in test gallery. Reproduced, with permission, from *The behaviour of commercially important di-isocyanates in fire conditions. Part 1: Toluene di-isocyanate (TDI)*. Marlair, Prager and Sand, 1993. © John Wiley & Sons, Ltd

In accordance with the general classification of fires proposed in ISO TR9122-4 (ISO, 1993b), these experiments on the large scale in the INERIS fire test gallery were based on fully developed, flaming, well-ventilated conditions for TDI and flaming and nonflaming, well-ventilated fire conditions for MDI. These are thus fuel-controlled fire scenarios, representative of situations likely to occur, for example, after structures collapse, as often happens in a major accident.

The combustion characteristics of the materials were assessed under conditions of controlled ventilation. Instrumentation was provided to monitor and record the course of the fire, its severity in terms of burning rate and heat release profile, and fire gas analysis. Provisions existed for gas emissions to be scrubbed and the effluent waters to be collected and analysed to give a further check on the environmental hazards posed by the gases emerging from the tunnel.

The MDI and TDI pool fire studies were carried out under the auspices of III and, latterly, within the MISTRAL 2 project in the EU. Both diisocyanates were ignited with some difficulty and then burned in a self-sustaining manner. In order to achieve ignition, the surface temperature of the diisocyanates had to be raised using either radiant heat or the application of burning heptane to the surface. TDI maintained a classic equilibrium, leaving no residues, whilst polymeric MDI showed a short classic burn (3 to 5 min) before char production became increasingly dominant, finally subduing the fire and leaving a considerable mass of residue. Both diisocyanates produced considerable smoke when they burned, even in well ventilated conditions. This is a common characteristic of aromatic organic compounds.

Results of these tests are summarized in Tables 5.5.1 to 5.5.4.

Figures 5.5.5 to 5.5.8 are directly recorded plots from the 1.5 m<sup>2</sup> TDI pool fire. They refer respectively to the parameters heat flux (Figure 5.5.5), mass loss (Figure 5.5.6), heat release rate (Figure 5.5.7) and rate of combustion (Figure 5.5.8), assessed continuously through the course of the fire. In all cases the graphs clearly illustrate the classical equilibrium burning state during the main period of the test (7 to 35 min), with growth and die-down regions on either side bringing the total fire period to 50 min. These curves give rise to the values for these properties recorded in column 3 of Table 5.5.2.

*References to INERIS studies on pool fires of MDI and TDI*

Cwiklinski and Marlair (1994a, 1994b),  
Marlair (1994).

**Table 5.5.1 TDI: INERIS pool test conditions.**

Test parameter	Unit	1	2	3	4
Quantity of TDI	kg	25	75	120	155
Pool area	m <sup>2</sup>	0.25	1.0	1.5	2.0
Air flow rate <sup>a</sup>	m <sup>3</sup> /h	10 470	9930	9859	9650
Propane flow to safety burner	m <sup>3</sup> /h	1.45	1.44	–	–
Total propane used	m <sup>3</sup>	2.03	1.24	–	–
Atmospheric conditions					
External temperature	°C	10.5	9.0	–	14
External pressure	mmHg	770	747	–	760
External humidity	%	72.3	82	–	–

<sup>a</sup>Corrected to 0 °C and 760 mmHg pressure.

**Table 5.5.2 TDI: INERIS pool test results.**

Test parameter	Unit	1	2	3	4 <sup>a</sup>
Burning rate	kg/m <sup>2</sup> /min	1.38	2.06	2.35	2.05
Burning duration	min	75	46	40	5
Maximum temperature	°C				
over pool surface		700	800	800	900
above burning zone		60	160	–	240
effluent gases at mixing point <sup>b</sup>		35	90	110	150
Heat release rate	kW	122	560	1100	1250
Heat flux	kW/m <sup>2</sup>	488	560	730	625
Heat flux (close to fire)					
lateral	kW/m <sup>2</sup>	1.15 to 20	5 to 6	–	10
downstream	kW/m <sup>2</sup>	7.9	15	17	7.5
Gas concentrations					(upstream)
CO <sub>2</sub> (total)	% (v/v)	0.25	1.05	–	ca 2.0
CO	ppm (v/v)	70 to 80	350	–	500 to 800
Visibility estimated from optical density measurements	m	2 to 3	1	100 % opacity	100 % opacity

<sup>a</sup>Test 4. This run ceased to give meaningful data after 5 min due to equipment failure. However, it had reached its equilibrium burning rate.

<sup>b</sup>The mixing point was at the top of the tower (height approx. 10 m).

**Table 5.5.3 PMDI: INERIS pool test conditions.**

Test parameter	Unit	Pilot run	1	2 <sup>a</sup>
Quantity of PMDI	kg	7	35.5	35
Pool area	m <sup>2</sup>	0.25	1.0	2.25
Air flow rate <sup>b</sup>	m <sup>3</sup> /h	10 590	10 590	33 000
Propane flow to safety burner rate	m <sup>3</sup> /h	1.124	1.124	–
total propane use	m <sup>3</sup>	–	1.124 (60 min)	1.84 (35 min)
to igniter (1.5 min)	litre	56 (3.5 min)	24	380
Atmospheric conditions				
External temperature	°C	–	11	12
External pressure	mmHg	–	769	744

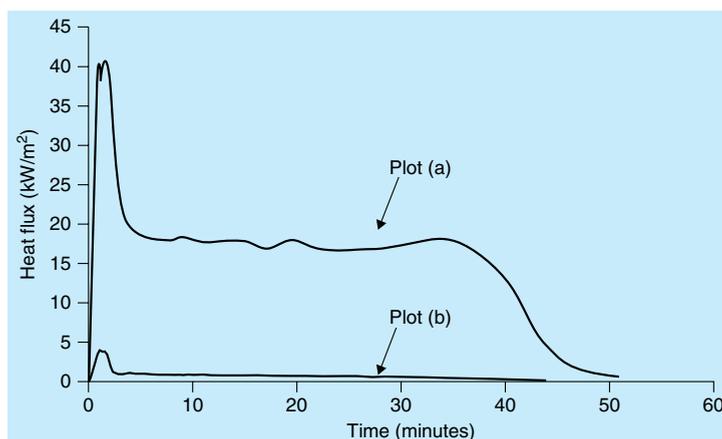
<sup>a</sup>This INERIS test was not part of the III study.

<sup>b</sup>Corrected to 0 °C and 760 mmHg pressure.

**Table 5.5.4 PMDI: INERIS pool test results.**

Test parameter	Unit	Pilot run	1	2 <sup>a</sup>
Quantity of PMDI	kg	7	35.5	35
Burning duration				
normal pool fire	min	3.5 to 6	1.5 to 6	–
transitional	min	6 to 20	6 to 12	–
impeded carbonization/smouldering	min		12 to 90	–
First char appearance	min	5.00	3.5	–
Steady state (max. rate) behaviour				
duration	min	–	3.5 to 6	–
burning rate	kg/m <sup>2</sup> /min	0.16 to 0.2	0.9	–
heat release rate	kW	–	280	–
heat flux (close to fire)				
lateral	kW/m <sup>2</sup>	–	1.0	–
downstream	kW/m <sup>2</sup>	–	2.0	–
Gas concentrations (max.) at the tower				
CO <sub>2</sub> total	% (v/v)	0.13	0.6	0.48
CO	ppm (v/v)	72	275	248
CO <sub>2</sub> /CO local		17	17 to 25	19
at tower		–	21 to 26	19
Visibility estimated from optical density measurements	m	–	1	1
Residue	kg	5.5	29.5	25.8
% of original charge		80	83	74

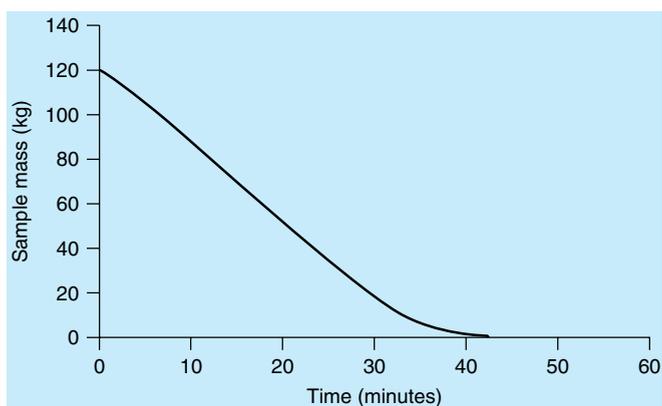
<sup>a</sup>This INERIS test was not part of the III study.



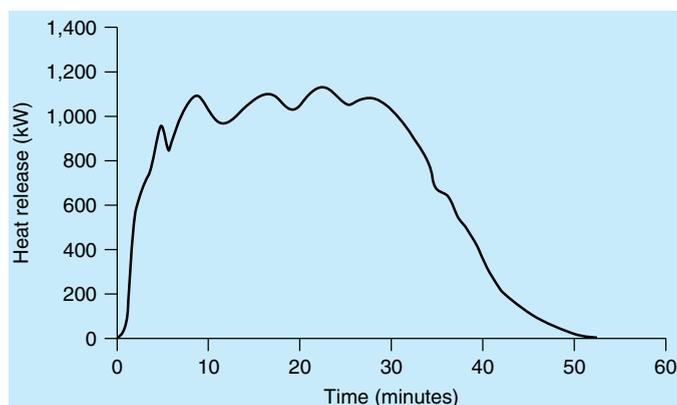
**Figure 5.5.5 TDI pool fire: heat flux with time. Plot (a): 72 cm from surface of pool. Plot (b): 7 m from surface of pool**

### **Drumstock and pool fire tests at Bayer**

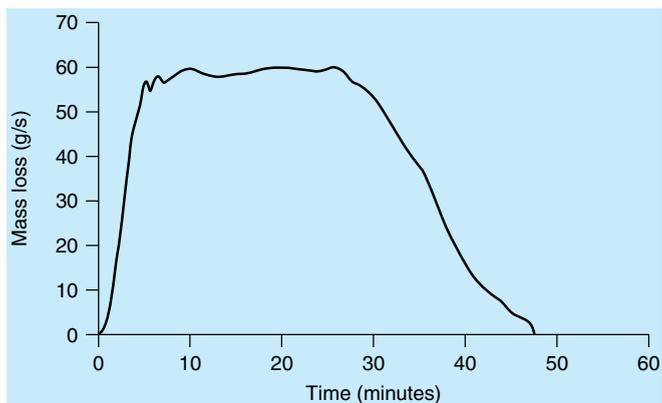
This text describes experiments carried out by Bayer AG, Germany (Klebert *et al.*, 1988). The tests, designed to predict the behaviour of polymeric MDI and TDI drumstock when engulfed in fire, involved standard drums of the appropriate diisocyanate, from 10 to 250 kg, which were placed in a variety of situations, singly or in pairs, in retaining trays. The drums were subjected



**Figure 5.5.6** TDI pool fire: mass loss with time



**Figure 5.5.7** TDI pool fire: heat release rate with time



**Figure 5.5.8** TDI pool fire: combustion rate with time

to either burning fuel oil in the retaining tray or burning wooden cribs placed beneath the trays (Figure 5.5.9). Steel drums containing TDI, and both steel and plastic polyethylene drums containing MDI, were assessed, and showed markedly different behaviour. Plastic drums were penetrated quickly by a

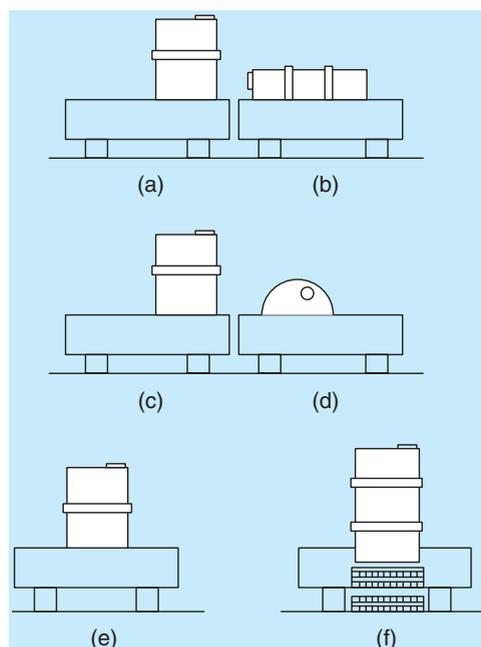
developing fire: they released their contents simply and without vigour, and the situation changed to one of a pool fire. Metal drums, however, offered resistance to the enveloping flames for some time, before becoming distorted as the internal pressures in the drum increased. This was followed by failure of the drums at their weakest points and spillage of the contents, gas evolution and torch-like flame emissions (torching), often with considerable violence and drum movement. Tables 5.5.5 and 5.5.6 record the events noted for TDI tests and Tables 5.5.7 to 5.5.9 those for polymeric MDI. Sampling of the gases evolved (Figure 5.5.10) was imprecise. The results of gas concentration measurements indicated that the burning behaviour was similar to that of the INERIS pool fires. Indeed, some pool fires of a type similar to the INERIS gallery tests were included in the drumstock programme. Results are reproduced in Tables 5.5.10 and 5.5.11.

**Table 5.5.5 TDI drums: performance.**

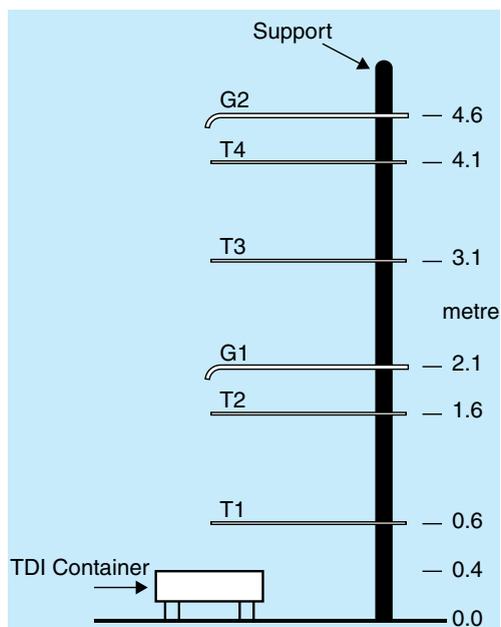
Test parameter	Unit	1	2	3	3	4	4	5
Drum positions (Figure 5.5.9)		e	e	a	b	c	d	e
Quantity of TDI	kg	10	60	60	60	30	30	250
Fuel oil	l	40	30	10	10	10	10	80
Container deformation	min	3	5	5	–	5	5	7
Contents								
Gas release	min	3	8	4	4	2	–	37
Liquid	min	–	18	–	11	2	–	39
Burning liquid	min	–	18	–	–	–	–	–
Drum closure blown out	min	–	–	28	–	–	2	–
'Torching' burst out	min	–	–	–	6	–	3	44
Burning first observed	min	4	8	28	6	6	3	39
Max. flame length	m							
Vertical		>5	–	–	3	–	4	Fireball
Angled		–	–	–	4	–	4	–
Torch		–	–	–	3	–	3	4 to 5
HCN	ppm (v/v)	–	–	–	>10	–	–	–
Drum explosion		no	no	yes	no	yes	no	no

**Table 5.5.6 TDI drums: gas analysis.**

Test parameter	Unit	1	2	3	3	4	4	5
Drum positions (Figure 5.5.9)				a	b	c	d	
Time of test	min	–	7	25	26	–	18	30
CO <sub>2</sub> (max)	% (v/v)	–	2.1	3.6	2.3	–	11	7
CO (max)	% (v/v)	–	0.16	0.95	0.16	–	>1	2.8
O <sub>2</sub> (min)	% (v/v)	–	16.0	17.5	18.8	–	5	13.0
CO <sub>2</sub> /CO		–	13	4	14	–	<11	3
HCN	ppm (v/v)	–	–	–	>10	–	–	–
					at 78 min			



**Figure 5.5.9** Drum tests: positions of drums. Reproduced, with permission, from *The behaviour of commercially important di-isocyanates in fire conditions. Part 1: Toluene di-isocyanate (TDI)*. Marlair, Prager and Sand, 1993. © John Wiley & Sons, Ltd



**Figure 5.5.10** Drum tests: monitoring points. Reproduced, with permission, from *The behaviour of commercially important di-isocyanates in fire conditions. Part 1: Toluene di-isocyanate (TDI)*. Marlair, Prager and Sand, 1993. © John Wiley & Sons, Ltd

**Table 5.5.7 PMDI drums: performance in outdoor tests.**

Test parameter	Unit	1	2	3	4	5	5
Drum positions (Figure 5.5.9)		f	e	e	e	a	b
Quantity of PMDI	kg	1 × 10	1 × 30	1 × 30	1 × 60	30	30
Fuel oil	l	–	5(+5) <sup>a</sup>	20	30	10	10
Wood crib	kg	2 × 10	–	–	–	–	–
Container rupture	min	32	17	4	3	–	–
Contents release							
Gas	min	32	17	5	5	2	5
Liquid	min	–	–	6	–	–	21
Burning liquid	min	–	–	12	14	–	11
Drum closure blown out	min	–	19	–	–	28	–
Torching burst out	min	–	–	5	4	–	3
Burning first observed	min	–	17	4	4	3	3
Max. flame length	m						
Horizontal		–	–	5 to 6	–	–	–
Vertical		>5	2	4	5 to 6	0.3	3
Angled		–	3 to 4	4	4 to 5	0.2	–
Torch		–	–	1	2	–	1 to 2
Drum explosion		no	no	no	no	no	no
Foaming reaction		–	yes	yes	yes	yes	yes

<sup>a</sup>A further 5 l of fuel oil was added during the course of the test.

**Table 5.5.8 PMDI drums: gas analysis in outdoor tests.**

Test parameter	Unit	1	2	2	2	3	3	3	4	4	4	5
Time of test	min	–	4	18	29	6	10	12	2	9	14	6.5
CO <sub>2</sub> (max.)	% (v/v)	–	0.7	1.0	0.01	1.6	2.2	1.5	2.0	2.8	2.7	0.3
CO (max.)	% (v/v)	–	–	–	0.12	0.08	0.14	0.49	0.07	0.27	0.40	–
O <sub>2</sub> (min.)	% (v/v)	–	19.8	18.5	–	17.0	16.3	17.3	16.0	14.5	15.5	20.5
CO <sub>2</sub> /CO		–	–	–	0.1	20	16	3.1	29	10	6.8	–
HCN	ppm (v/v)	2.5 to 3.0	–	–	–	–	–	–	–	–	–	–

**Table 5.5.9 PMDI drums performance in indoor tests.**

Test parameter	Unit	1	2
Quantity of PMDI	kg	15	10
Pool area	m <sup>2</sup>	0.25	0.25
Drum material		Steel	Polyethylene
Drum position (see Figure 5.5.9)		e	e
Fuel oil	l	10	7.5
First release of contents	min	4	0.25
Burning first observed	min	4	0.5
Torching burst out	min	7	–
Drum lid forced off	min	10	–
Max. flame length	m	3	2.5
Drum explosion		No	No
Foaming reaction		Yes	Yes

**Table 5.5.10 TDI: pool fire results.**

Test parameter	Unit	1	2	3	4	5	6	7	8
Quantity of TDI	kg	1.0	9.0	14.7	2.63	2.43	9.5	20.5	14.9
Pool area	m <sup>2</sup>	0.04	1.0	0.25	0.25	0.25	0.25	0.50	1.0
Fire source									
Wood crib	kg	10	10	–	–	–	–	–	–
Fuel oil	kg	–	–	4.3	3.1	3.1	11	9	5
First TDI ignition	min	–	–	7	4	8	3	4.0	3
Flame height maximum	m	3.0	3.0	3.0	2.0	2.5	2.0	2.5	3.0
Rate of combustion									
sample + fuel oil	kg/min	–	–	0.8	0.6	0.6	0.8	1.8	3.4
HCN ( Draeger tube)	ppm (v/v)	2	8	10	2	2	10	–	–
Residue	kg	0	0	0	0	0	0	0	0

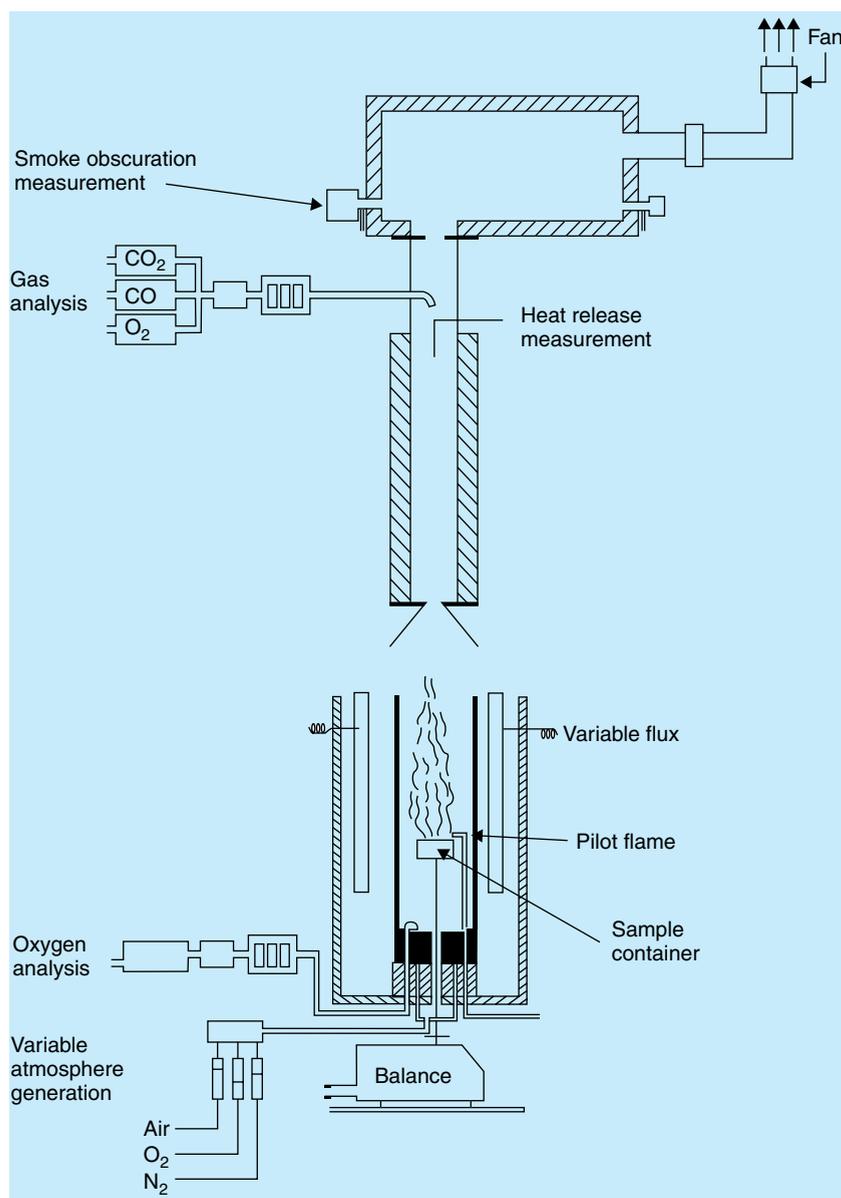
**Table 5.5.11 PMDI: pool fire results.**

Test parameter	Unit	
Quantity of PMDI	kg	1
Pool area	m <sup>2</sup>	0.041
Fire source: wood crib	kg	10
Flame height maximum	m	2.5 at 7 min
HCN	ppm (v/v)	2.5 to 3.0
Foamed residue		Yes

### **Small-scale predictive tests**

The Tewarson apparatus was developed by the Factory Mutual Research Corporation, US, under commission by the US National Bureau of Standards. The aim was to provide a method for measuring the fundamental flammability parameters of materials (Tewarson, 1977). It is suitable for liquids and solids, and was utilized in the late 1970s by Rhône-Poulenc Industries to assess the combustion characteristics of a range of diisocyanates. A gas collection and analysis unit, as shown in Figure 5.5.11, was positioned vertically above the combustion unit. A test comprised charging approximately 10 g of liquid into the aluminium specimen dish on a scale pan, holding it in a steady gas flow of defined composition, and measuring the ease of ignition of the test liquid from a pilot flame, the energy released, and the production of smoke and toxic gas. Tests were repeated under increasing levels of heat flux (0 to 30 kW/m<sup>2</sup>) at two oxygen levels. Throughout each test continuous measurements were made of mass loss, chimney temperatures, oxygen usage, and concentrations of carbon dioxide and carbon monoxide. Periodic samples of gas were taken and analyzed quantitatively for hydrogen cyanide, nitrogen oxides and total hydrocarbons (Rhône-Poulenc, 1983a, 1983b). Table 5.5.12 provides a comprehensive overview of the heat evolved and of the gases produced from MDI and TDI. A nonisocyanate control material of similar elemental content, hexamethylene diamine (HMD), was included for comparison.

The Tewarson apparatus has been improved over recent years in respect of the design of the chimney, gas sampling arrangements, sample holder capacity



**Figure 5.5.11** The Tewarson apparatus and gas analysis unit. Reproduced, with permission, from *The behaviour of commercially important di-isocyanates in fire conditions. Part 1: Toluene di-isocyanate (TDI)*. Marlair, Prager and Sand, 1993. © John Wiley & Sons, Ltd

(now 30 g) and ignition procedure. A test of 80/20 TDI with this apparatus was included in the MISTRAL 2 phase of work, the results of which confirmed the data from the earlier work. A selection of comparative points is given in Table 5.5.13.

The Tewarson small-scale test data, like the INERIS large-scale test data, confirm that, like other organic materials of similar elemental content, diisocyanates burn if subjected to radiant heat and the application of an ignition

**Table 5.5.12 TDI and PMDI: Tewarson test results.**

Material	Test conditions		Maximum heat release rate kW/m <sup>2</sup>	Maximum gas concentrations				
	Heat flux kW/m <sup>2</sup>	Oxygen level % (v/v)		O <sub>2</sub> % (v/v)	CO <sub>2</sub> % (v/v)	CO ppm (v/v)	NO <sub>x</sub> ppm (v/v)	HC total ppm (v/v)
TDI	5	21	735	0.65	0.60	200	50	<2
PMDI	5	21	a	a	a	a	a	a
HMD	5	21	1097	0.97	0.62	>50	64	<2
TDI	5	15	242	0.23	0.20	67	67	<2
PMDI	5	15	a	a	a	a	a	a
HMD	5	15	446	0.40	0.27	<50	40	<2
TDI	10	21	1116	1.0	0.9	400	58	10
PMDI	10	21	660	0.57	0.53	250	43	≤2
HMD	10	21	1860	1.6	1.0	80	76	<2
TDI	10	15	353	0.32	0.28	100	28	<2
PMDI	10	15	177	0.17	0.15	67	13	≤2
HMD	10	15	902	0.80	0.50	50	55	≤2
TDI	30	21	1432	1.23	1.3	1060	50	30
PMDI	30	21	1037	0.90	0.82	530	25	40
HMD	30	21	3057	2.80	1.85	450	260	30
TDI	30	15	1320	1.20	1.13	1600	43	35
PMDI	30	15	614	0.53	0.50	350	35	10
HMD	30	15	2557	2.20	1.47	450	168	80

a = no ignition took place.

HC = hydrocarbon.

**Table 5.5.13 Tewarson apparatus testing of 80/20 TDI: original procedure (1979) compared with new procedure (1995).**

Procedure	Unit	1979 <sup>a</sup>	1995 <sup>b</sup>
<b>Equipment</b>			
Sample holder area	m <sup>2</sup>	Aluminium (0.0023)	Glass (0.0048)
Sample weight	g	10	30
Ignition source		pilot flame	electric arc
External flux applied	W/cm <sup>2</sup>	0.5 to 3.0	–
<b>Results</b>			
Total heat evolution	kJ/g	17.0 to 18.2	18.6 to 19.6
Gas production	g/kg sample burned		
CO <sub>2</sub>		1700 to 1900	1600 to 1900
CO		30 to 80	40 to 80
NO <sub>x</sub>		5 to 11	13 to 15
HCN		5 to 16	0.5
TDI		2 to 5	9 to 12

<sup>a</sup>Rhône-Poulenc, 1983a, 1983b<sup>b</sup>Costa C, Rhône-Poulenc, CRIT Décines, 1996. Personal communication as part of MISTRAL 2 project.

source. After ignition, they burn readily, generating quite dense smoke. The gases emitted are mainly carbon dioxide and carbon monoxide, with variable smaller levels of  $\text{NO}_x$ , HCN and the diisocyanate itself. The concentrations and relative proportions of these gases depend upon the fire conditions.

INERIS carried out further experimental work (Marlair *et al.*, 1999) using the latest version of the Tewarson apparatus (Figure 5.5.12) designated since January 2000 as *ASTM E 2058 Fire Propagation Apparatus (Factory Mutual 2000)*. The work was part of an on-going programme for the French Ministry of the Environment, dealing with the development of a comprehensive methodology to evaluate environmental issues concerned with oxygen-controlled fires. It was envisaged that such fires could arise in warehouses, tunnel configurations and other enclosures.



**Figure 5.5.12** The Tewarson apparatus (ASTM E2058, INERIS 1997)

In small developing fires, fuel-controlled conditions are defined by ISO TR 9122-4 (ISO 1993b) as being freely ventilated and having a CO<sub>2</sub>/CO combustion gas effluent ratio of 100 or more. In large fully developed fires in buildings, low ventilation-controlled fires can occur, and are found to have a CO<sub>2</sub>/CO ratio of 10 or less. However, under these conditions a ratio of more than 10 would be indicative of relatively high ventilation.

#### References regarding the Cone Calorimeter

Babrauskas (1992, 1995), ISO (1993e), Paul (1994). The procedure is described in ISO 5660, which also puts the value to be ascribed to the data into clear perspective. It has not yet been developed for toxic gas assessment studies.

A series of seven single-burn experiments was performed using 30 g quantities of TDI at different air flows (40 to 200 l/min) and a calibrated external heat flux of 25 kW/m<sup>2</sup>. The findings (Marlair *et al.*, 2001) show that oxygen availability in the burning region significantly influences most fire parameters. TDI is similar to many other test substances in this respect. Combustion efficiency, rate of heat release, and quantities of CO<sub>2</sub> and NO<sub>x</sub> produced, all decreased as the equivalence ratio (fuel/air ratio) increased, whereas the amounts of some gases, such as CO and HCN, significantly increased. These changes are not specific to TDI but reflect general trends also observed for other chemicals.

It can be concluded that oxygen-controlled fires of TDI compared to fuel-controlled conditions lead to reduced thermal threat but potentially increased chemical threat to an extent related to the particular characteristics of the enclosure and its oxygen depleted environment.

The other small-scale test that has come into prominence for defining the fire behaviour of materials is the Cone Calorimeter. In this test the rate of heat release from a material is measured when it is burnt in a set of prescribed positional and environmental modes. Considerable importance is ascribed to this property by a number of fire scientists. The experimental arrangement is shown in Figure 5.5.13.

The Institut Scientifique de Service Public, Belgium, tested TDI as part of the MISTRAL 2 project, using a 30 ml sample in a stainless steel container of 0.0113 m<sup>2</sup> cross-sectional area. The external flux applied was 15 kW/m<sup>2</sup>. Table 5.5.14 records the results, including *ad hoc* toxic gas measurements additional to the rate of heat release main assessment.

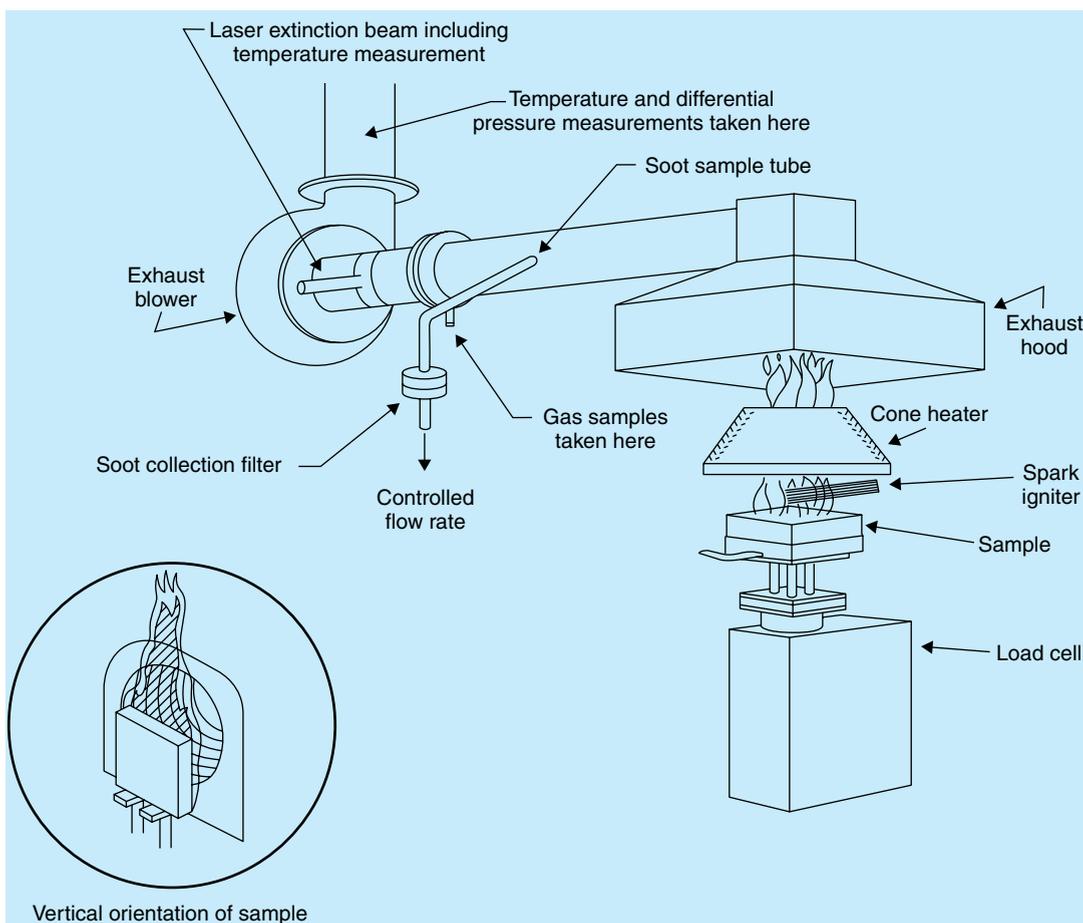
**Table 5.5.14 80/20 TDI: Cone Calorimeter test results.**

Rate of heat release	kW/m <sup>2</sup>	
Maximum		351 to 445
Average		250 to 328
Estimated heat of combustion	MJ/kg	21.0 to 22.5
Total heat	kJ	750 to 836
Gas yields	g/kg	
CO <sub>2</sub>		1680 to 1760
CO		85 to 89
HCN		35 to 44

The MISTRAL project has included other laboratory tests in the search for suitable small-scale methods to predict large-scale events accurately. TDI has been included in brief evaluations by TNO (Bartelds *et al.*, 1993) and IBMB Braunschweig using the DIN 53436 Furnace at 600 and 900 °C (University of Braunschweig, 1996). The fire performance of TDI in these tests was similar to that of other organic materials of similar elemental content.

### Assessment of combustion gas yields

All organic chemical compounds produce carbon dioxide in considerable quantities during the burning process. Carbon monoxide is the main component



**Figure 5.5.13** The Cone Calorimeter. © Society of Fire Protection Engineers. Reprinted with permission from Babrauskas (1995)

**Table 5.5.15** INERIS gallery: burning rates, heat release and toxic gas yields.

Material	Pool area m <sup>2</sup>	Burning rate kg/m <sup>2</sup> /min	Heat release rate kW/m <sup>2</sup>	Gas yield g/kg					Residue %
				CO <sub>2</sub>	CO	NO <sub>x</sub>	HCN	MDI or TDI	
PMDI	1.0	0.9	280	1800	44	12	3.5	3.5	83
TDI	0.25	1.4	488	2090	41	11	1.2	6	Nil
TDI	1.0	2.1	560	1620	36	2	4.0	0.8	Nil
TDI	1.5	2.4	–	1690	34	11	7	–	Nil
TDI	2.0	2.1	625	1500	29	6	4	–	Nil

of the toxic gases and there are variable smaller quantities of other gases based on the relevant hetero atom. Nitrogen oxides, hydrogen cyanide and the monomeric diisocyanates themselves are produced in the case of MDI and TDI. Table 5.5.15 summarizes yields determined in the full-scale tests.

*Sources for further information on indices of emergency exposure*

1. US Environment Protection Agency: Acute Exposure Guideline Levels (AeGL)
2. US NIOSH: Immediately Dangerous to Life or Health Levels (IDLH)
3. US American Industrial Hygiene Association: Emergency Response Planning Guidelines (ERPG) Levels
4. ECETOC: Emergency Exposure Indices (EEI)
5. German Vereinigung zur Förderung des deutschen Brandschutz: Einsatz-toleranzwerte (ETW)
6. TCL<sub>0</sub>. Threshold levels consistent with no impairment in ability to escape over a 30 min period of exposure (Marlair *et al.*, 1994).

*References giving guidance on fire-fighting*

Marlair *et al.* (1993), Marlair *et al.* (1994), ISOPA (2002).

Marlair *et al.* (1996) gave data on the INERIS pool fire assessment of a number of organic chemicals, classified by having at least one hetero atom fixed to their hydrocarbon structure. PMDI and TDI were two of the materials described, together with a number of N-, P-, S- or halogen-containing organic herbicides and pesticides, as well as acetonitrile and adiponitrile. All these compounds showed a similar combustion pattern, with modest rather than vigorous behaviour.

The ultimate exposure risk depends upon the sum of the toxicities of the fire gases inhaled. Various criteria have been proposed at this time to translate individual toxic gas component concentrations (Fractional Effective Dose, FED) into an overall hazard statement for a fire scenario. However, there is no agreement on which limiting factors should be best used for that purpose. Hirschler (2000) has summarized the confusion in understanding fire hazard and smoke toxicity issues and their relationship to the irritancy to, and the incapacitation of, exposed personnel. In the absence of any agreed preferred method of data analysis, no conclusions are drawn here.

Use of the proposed different criteria in the total hazard summation expression,  $\Sigma$ FED, leads to different total hazard and different component contributions to the total hazard.

## Conclusions

### **Fire behaviour of MDI and TDI**

The above data and discussion are the authors' best current understanding of the behaviour of PMDI and 80/20 TDI under well-aerated unconfined fire conditions, as summarized below.

- Neither MDI nor TDI has an explosive tendency.
- Both MDI and TDI require thermal stimulation for ignition.
- After ignition, sooty smoke is given off, particularly by TDI.
- Polymeric MDI is significantly less easily ignitable than TDI.
- A TDI pool fire assumes a dynamic equilibrium that is then maintained until all the product is consumed.
- A polymeric MDI pool fire, on the other hand, displays only a short classic steady state burning period, after which char formation becomes increasingly influential in dampening the fire, ultimately smothering the flames and leaving a considerable carbonaceous solid foam residue (50 to 80 % by weight).
- An MDI fire is approximately half the intensity of a comparable TDI fire and releases heat at a lower rate.

It must be emphasized that the toxic gases produced in a fire vary with the controlling parameters of the particular fire. Clearly it must be the rule for fire fighters to be provided with fresh air breathing equipment and full protective clothing when called upon to deal with MDI or TDI fires. Such fires might also pose downwind problems for personnel local to the incident. Guidance on these matters is more fully explained in the literature.

If drums are involved in a developing fire, precautions must be taken to ensure that they are kept cool to prevent rupture. Such ruptures can be quite vigorous, with drums even being projected into each other or up into the air.

None of this behaviour is specific to PMDI and TDI: it is the effect of heating any type of chemical in a closed container to the bursting point of the drum. The stronger the drum, the longer it will withstand the heating process, but the more violent will be the subsequent rupture.

### **Suitability of small-scale predictive tests**

Data from selected small-scale tests go some way towards predicting full-scale fire behaviour, but fire experts find that they are not adequate replacements for full-scale tests at this time (ISO, 1993e; Babrauskas, 1996).

- The Tewarson test gives a fairly close prediction of the gas production of the large-scale pool tests. However, the rates of heat release found are very variable and sensitive to test conditions.
- The Cone Calorimeter is better in its prediction of fire vigour in terms of rates of heat release, but it shows considerable inaccuracies in the prediction of gas production.

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## 5.6 Occupational exposure limits, stack limits and community limits

### Occupational exposure limits

The workforce must be protected from levels of exposure to chemicals which could cause injury. This is particularly important when there may be long-term (chronic) effects without indications from short-term (acute) exposure. A working life with given chemicals may extend to 50 years of full-time work exposure, so this is the time frame which must be considered. The route of exposure may be important. For a given chemical, the effect of ingestion or of skin contact may be quite different from that of contact with the respiratory tract. Further, a short high-level exposure may give different effects from the same dose (total amount of chemical taken in) received over a longer period: the body's clearance mechanisms may be able to deal with a long-term, low exposure, but not with the short-term exposure of the same total amount of material.

Occupational exposure limits (OELs) are estimates of safe working exposures. They are also known by other terms, including *permissible exposure limits*, *occupational exposure standards* and *maximum workplace limits*. They relate to exposure to chemicals, and also to physical agents in the workplace. They are calculated and set from the results of laboratory animal studies combined with human data, as obtained from clinical cases or epidemiological studies. OELs may be calculated by regulators, by academic bodies or by industry. Regulators in most countries have set mandatory workplace maximum concentrations for the workplace for many substances. OELs are re-examined if significant new information becomes available. Historically, the lead institution in this field is the American Conference of Government Industrial Hygienists (ACGIH), which prepared its first set of Threshold Limit Values (TLV<sup>®</sup>s) in 1946. This and subsequent lists of recommendations were adopted and adapted widely by a number of other institutions and governments.

In broad concept, occupational exposure limits are maxima below which the workforce should be able to work safely, even for a lifetime. However, humans display a very wide range of susceptibility to specific influences and exposures, even when in good health. In cases of poor health of an individual or the exposure to a second chemical which reduces the threshold level of the target exposure, the individual may have less protection from occupational exposure levels appropriate for a healthy workforce exposed to the target chemical only. A very useful explanation of the philosophy of maximum exposure levels is given by the ACGIH (2001), and is reproduced below:

*Threshold Limit Values (TLVs) refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed day after day without adverse health effects. Because of wide variation in individual susceptibility, however, a small percentage of workers may experience discomfort from some substances at concentrations at or below the threshold limit; a smaller percentage may be affected more seriously by aggravation of a pre-existing condition or by development of an occupational illness. Smoking of tobacco is harmful for several reasons. Smoking may act to*

*enhance the biological effects of chemicals encountered in the workplace and may reduce the body's defense mechanisms against toxic substances.*

*Individuals may also be hypersusceptible or otherwise unusually responsive to some industrial chemicals because of genetic factors, age, personal habits (smoking, alcohol, or other drugs), medication, or previous exposures. Such workers may not be adequately protected from adverse health effects from certain chemicals at concentrations at or below the threshold limits. An occupational physician should evaluate the extent to which such workers require additional protection.*

*These limits are not fine lines between safe and dangerous concentrations, nor are they a relative index of toxicity. They should not be used by anyone untrained in the discipline of industrial hygiene.*

**Time frames** The main time frames used globally follow the ACGIH recommendations, which are:

**TLV-C<sup>®</sup>** *Threshold Limit Value: Ceiling. The exposure which should not be exceeded during any part of the working exposure.*

**TLV-STEL<sup>®</sup>** *Threshold Limit Value: Short-term Exposure Limit. The concentration to which workers can be exposed continuously for a short period of time without suffering from 1) irritation, 2) chronic or irreversible tissue damage, or 3) narcosis of sufficient degree to increase the likelihood of accidental injury or impair self-rescue. This 15-minute limit is not a separate limit: rather it supplements the TLV-TWA limit where there are recognized acute effects from a substance whose toxic effects are primarily of a chronic nature. STELs are recommended only where toxic effects have been reported from high short-term exposures in either humans or animals.*

**TLV-TWA<sup>®</sup>** *Threshold Limit Value: Time-weighted Average. The time-weighted average concentration for conventional 8-hour workday and a 40-hour workweek, to which it is believed that nearly all workers may be repeatedly exposed, day by day, without adverse effect.*

### **Types of exposure**

In this book references to OELs are limited to exposure to chemicals only. In that context they are very predominantly related to airborne exposure of the respiratory tract. However, OEL tables of chemicals are often annotated to give information on other aspects of risk, such as the significance of dermal exposure: they also indicate whether the substance is a proven or suspect human carcinogen. There may also be information on uptake by the body or elimination from the body, as indicated by concentrations of chemicals or metabolites in blood or urine.

### **The UK Maximum Exposure Limit**

The UK HSE has adopted an exposure limit, which is called the Maximum Exposure Limit (MEL). This is based on the philosophy that MELs should

be allocated to substances *for which no threshold level of exposure for the effect can be identified and for which there is no doubt about the seriousness of the hazard(s) posed by the substance*. Isocyanates are listed within the MEL classification because they are respiratory sensitizers. Whilst the protection of the health of the employee is the primary consideration of the UK HSE, it also acknowledges that socio-economic factors need to be taken into account and a cost–benefit assessment is prepared in order to assess the acceptability of exposing the workforce to a given chemical (HSE, 2001).

### **Regulatory limits for MDI and TDI**

Regulatory authorities in many countries have devised and adopted occupational exposure limits in air for MDI and TDI. These are commonly 20 ppb (short-term exposure limit) and 5 ppb (for 8 h time-weighted average value) for both MDI and TDI. In some countries the OELs are based on the notional total reactive isocyanate group (TRIG) concentration (see later). It should be re-emphasized that the OELs cannot be considered as ‘safe’ for the entire workforce and especially not for those already suffering from a diisocyanate-related ailment. The above limits have been based on respiratory effects. In ACGIH (2001) the effects cited for MDI are *irritation, lung edema and sensitization*; those for TDI are *irritation and sensitization*.

OELs for airborne species, such as MDI and TDI, are expressed both as *volume in volume* and as *weight in volume*. The concept of *volume in volume* expressed either as parts per million (ppm) or parts per billion (ppb) is used very widely, and is very convenient because both MDI and TDI values can be expressed with the same number. For example, ACGIH gives the TLV-TWA for both MDI and 2,4-TDI as 0.005 ppm ( $\equiv$  5 ppb). However, the physico-chemical concept can be used only for airborne species in the vapour form. Aerosols, unlike gases, can be expressed only in terms of weight in volume, for example as  $\text{mg}/\text{m}^3$ . However, it is not uncommon for aerosol concentrations to be cited *incorrectly* as volume in volume, even by regulators.

In Table 5.6.1 are given some typical values of OELs, as short-term (C or STEL) or time-weighted average (TWA) values. These indicate a broad global consensus of the values appropriate for the workplace, although some regulators simply adopt ACGIH values without re-evaluation. In a number of cases, only 2,4-TDI is considered and the level of 2,6-TDI is not subject to regulation or recommendation. However, in some workplace scenarios, notably in flexible foam slabstock manufacture, 2,6-TDI may be at a higher concentration than 2,4-TDI (see *Part 2, Releases to atmosphere from polyurethane manufacturing sites*). In its *Notice of Intended Changes for 2001* ACGIH has announced that the current limits will apply to 2,4-TDI, 2,6-TDI or mixtures of these isomers. It is likely that other agencies will adopt this change. Both the ACGIH and the MAK Senatskommission of Germany are re-assessing (2002) the exposure limits to be applied to TDI. These examples show that the values given in Table 5.6.1 are subject to change and should be used only as indicators: current local regulations should always be consulted for compliance purposes. Vincent (1998) has reviewed the philosophy, the limit-setting procedures and the role of occupational hygiene within the framework of global occupational exposure levels.

**Table 5.6.1 Some occupational exposure limits for MDI and TDI.**

Current regulations should always be consulted for compliance purposes.

	MDI limit (ppb)		TDI limit (ppb)	
	Short-term (C or STEL)	Time-weighted average (TWA)	Short-term (C or STEL)	Time-weighted average (TWA)
Austria	10	5	–	10
Canada, Ontario	20	5	20	5
Denmark	–	5	–	5
France	20	10	20	10
Germany	10	5 <sup>a</sup>	– <sup>b</sup>	– <sup>b</sup>
Italy	–	5	20	5
Japan	–	5	20	5
Malaysia	–	5	–	5
Netherlands	20	5	20	5
Norway	10	5	10	5
P R China	20	–	20	–
R O Korea	–	5	20	5
Sweden	10	5	10	5
Switzerland	10	5	10	5
USA				
ACGIH (TLV)	–	5	20	5
OSHA (PEL) <sup>c</sup>	20	–	20	–
Conversion factors (vapour only)	20 ppb = 0.02 ppm ≡ 0.21 mg/m <sup>3</sup> 5 ppb = 0.005 ppm ≡ 0.052 mg/m <sup>3</sup>		20 ppb = 0.02 ppm ≡ 0.14 mg/m <sup>3</sup> 5 ppb = 0.005 ppm ≡ 0.036 mg/m <sup>3</sup>	

<sup>a</sup>As inhalable aerosol.

<sup>b</sup>Under review (2001): there is a proposal to halve the current TWA values for 2,4-TDI and 2,6-TDI, and to change the peak concentration limits.

<sup>c</sup>Permissible Exposure Limit.

### Ways of expressing airborne diisocyanate concentrations in the workplace

Units of *weight in volume* can be converted into *volume in volume* by use of the gas laws. It is not possible to express aerosol concentrations in terms of *volume in volume*.

#### Conversion of MDI concentrations

For MDI vapour at 20 °C  
 1 mg/m<sup>3</sup> is equivalent to 0.096 ppm  
 or 1 ppm is equivalent to 10.4 mg/m<sup>3</sup>

#### Conversion of TDI concentrations

For TDI vapour at 20 °C  
 1 mg/m<sup>3</sup> is equivalent to 0.14 ppm  
 or 1 ppm is equivalent to 7.2 mg/m<sup>3</sup>

### Total reactive isocyanate group (TRIG) concentration

The ACGIH approach which is substance-specific covers only a small number of monomeric isocyanate species (currently 4,4'-MDI, 2,4-TDI and four other diisocyanates) and does not address the wide variety of isocyanate species and mixed isocyanate exposures which are common in the workplace.

One approach by some regulators to remedy this deficiency is to view the isocyanate group in isolation, without regard to the chemical substrate to which

### Conversion of MDI or TDI concentrations

#### MDI

The gram molecular weight (molar weight) of MDI is 250 g (250 000 mg). Applying the gas laws, and assuming that MDI is an ideal gas:

250 000 mg occupy 22 400 ml at 273 K (0 °C) and 760 mmHg (760 Torr)

Then at 293 K (20 °C)

250 000 mg occupy  $22\,400 \times \frac{293}{273}$  ml = 24 040 ml

∴ 1 mg occupies 0.096 ml

∴ **1 mg/m<sup>3</sup> ≡ 0.096 ppm or 1 ppm ≡ 10.4 mg/m<sup>3</sup>**

#### TDI

The conversion figures for TDI can be obtained by substituting the gram molecular weight of TDI (174 g) for that of MDI in the above derivation.

#### Note

These conversion figures are for the diisocyanate vapour at 20 °C (293 K) and 760 Torr (760 mmHg). However, they are often used as the standard conversion figures cited for use even when temperature and atmospheric pressures are different from those above. The errors incurred by not making corrections would normally be negligible compared to those arising from occupational hygiene sampling and analysis procedures.

it may be attached. The philosophy is that health effects are more closely related to the isocyanate group concentration than to the individual chemical species such as MDI or TDI. The concept is notional: isocyanate groups can exist in air only as part of a larger molecule. Whilst this total reactive isocyanate group (TRIG) concentration approach rectifies one deficiency, it does not take into account that polymeric species may be less toxic than monomeric species (see *TRIG concentration limits (vol/vol) and isocyanate functionality*, below).

When there is only one isocyanate species present, isocyanate group concentration is directly proportional to the molecular concentration. However, when there are mixed gaseous species present this is not the case if concentration is expressed as weight in volume. In such cases it is normal to use a method which allows isocyanate concentration to be estimated directly without deriving the figure from the

contributing species and concentrations. Analytical methods which allow the TRIG concentration to be determined without the separate determination of individual molecular (eg MDI, TDI) concentrations are called *TRIG methods*.

TRIG limits have been adopted by four countries as the regulatory limits (Table 5.6.2).

**Table 5.6.2 TRIG concentration limits.**

Country	All isocyanates (as –NCO)	
	Short-term mg/m <sup>3</sup>	Long-term mg/m <sup>3</sup>
Australia	0.07	0.02
Finland	0.035	–
Ireland	0.07	0.02
UK	0.07	0.02
<b>Conversions</b>		
MDI	1 mg/m <sup>3</sup> MDI = 0.34 mg/m <sup>3</sup> NCO group	1 mg/m <sup>3</sup> NCO group = 3 mg/m <sup>3</sup> MDI
TDI	1 mg/m <sup>3</sup> TDI = 0.48 mg/m <sup>3</sup> NCO group	1 mg/m <sup>3</sup> NCO group = 2 mg/m <sup>3</sup> TDI

**TRIG concentration equivalents (wt/vol) for MDI and TDI**

If the sampled air contains only MDI or TDI (or any other single isocyanate species), the TRIG concentration can be calculated direct from the concentrations of the single species.

**TRIG concentrations (wt/vol)****MDI**

**1 mg/m<sup>3</sup> MDI is equivalent to 0.34 mg/m<sup>3</sup> of isocyanate group**

**TDI**

**1 mg/m<sup>3</sup> TDI is equivalent to 0.48 mg/m<sup>3</sup> of isocyanate group**

**Calculation of total reactive isocyanate group concentration for MDI in air**

1 molecule of MDI contains two isocyanate groups  
The gram molecular weight (molar weight) of MDI is 250 and of the isocyanate group is 42

∴ 1 g MDI contains  $\frac{2 \times 42}{250}$  g (= 0.34 g) of isocyanate group

∴ **1 mg/m<sup>3</sup> MDI contains 0.34 mg/m<sup>3</sup> isocyanate group**

A similar calculation can be made for TDI using its gram molecular weight of 174

**Calculation of total reactive isocyanate group concentration for a mixed MDI/TDI atmosphere***Example*

In a factory atmosphere, the following concentrations were determined using a non-TRIG method:

	0.3 μg/m <sup>3</sup> MDI	
	5 μg/m <sup>3</sup> TDI	
MDI	0.3 μg/m <sup>3</sup> MDI in air	≡ 0.3 × 0.34 μg/m <sup>3</sup> isocyanate group in air = 0.1 μg/m <sup>3</sup> isocyanate group in air
TDI	5 μg/m <sup>3</sup> TDI in air	≡ 5 × 0.48 μg/m <sup>3</sup> isocyanate group in air = 2.4 μg/m <sup>3</sup> isocyanate group in air
	∴ TRIG concentration	= 2.5 μg/m <sup>3</sup>

**TRIG concentration limits (vol/vol) and isocyanate functionality**

When expressed in *volume in volume* terms, the concentration of isocyanate equivalent to the parent molecule depends only on the isocyanate functionality. Since both MDI and TDI have two isocyanate groups, then 20 ppb MDI or TDI is equivalent to 40 ppb isocyanate group. For a monofunctional isocyanate, 20 ppb mono-isocyanate (e.g. tolyl isocyanate) the concentration of -NCO group is 20 ppb. Thus, for a given TRIG limit (e.g. 20 ppb) the allowable concentration of a mono-isocyanate species is double that of a diisocyanate species (10 ppb), such as TDI.

**TRIG concentrations (vol/vol)****MDI**

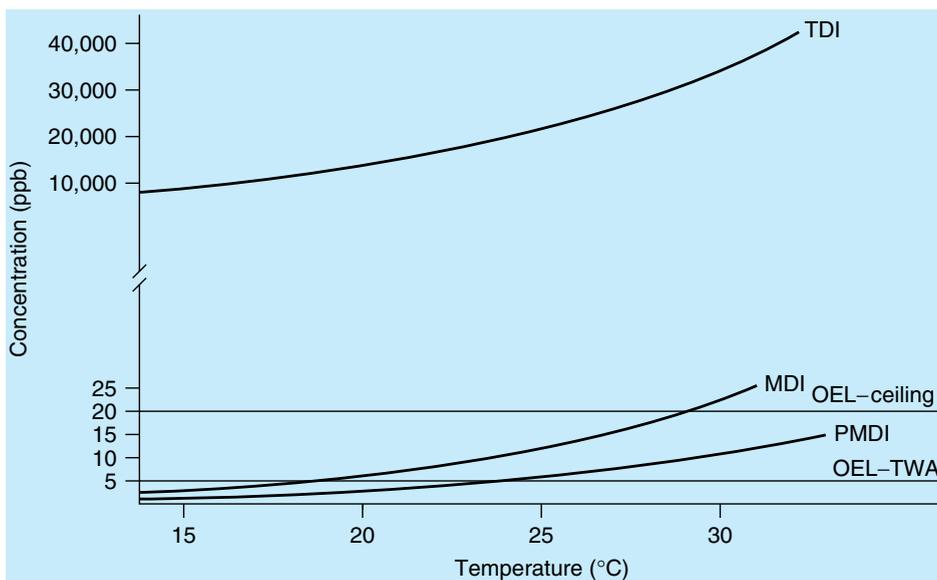
**0.01 ppm is equivalent to 0.02 ppm of isocyanate group**

**TDI**

**0.01 ppm is equivalent to 0.02 ppm of isocyanate group**

### **Occupational exposure limits and saturated vapour concentrations**

The saturated vapour concentration (SVC) of a chemical is the concentration in air of that chemical when *in equilibrium* with the liquid or solid phase of the chemical at a given temperature. An understanding of the SVCs of MDI and TDI relative to their occupational exposure limits is critical to an understanding of occupational hygiene. In Figure 5.6.1 are given the SVC curves for monomeric MDI, polymeric MDI and TDI. The isomer ratio of the TDI has little effect on the SVC of the TDI mixture. In Table 5.6.3 are given ratios of SVC/STEL for MDI and TDI at two temperatures.



**Figure 5.6.1 SVC curves for monomeric MDI, polymeric MDI and TDI**

Even in the worst cases, which are very rarely attained except in a confined space such as in a drum, monomeric MDI vapour exceeds the short-term limit (20 ppb) only above about 28 °C and the long-term limit above 19 °C. In the case of polymeric MDI (containing 50 % 4,4'-MDI) the temperatures at which the limits are exceeded are even higher, that is at 35 and 24 °C, respectively. The ratios of SVC to OELs given in Table 5.6.3 reflect this. It is well-established experience that MDI vapour concentrations in the workplace often fall below commonly used detection limits of less than 1 ppb. Modelling studies of the concentration profiles above pools of MDI at given temperatures

**Table 5.6.3 Saturated vapour concentration (SVC) and occupational exposure limit ratios at 20 and 30 °C.**

	Polymeric MDI		MDI		TDI	
	20 °C	30 °C	20 °C	30 °C	20 °C	30 °C
$\frac{\text{SVC (ppb)}}{\text{STEL (ppb)}}$	$\frac{3.1}{20} = 0.16$	$\frac{12.0}{20} = 0.6$	$\frac{6.1}{20} = 0.3$	$\frac{24.0}{20} = 1.2$	$\frac{14\,000}{20} = 700$	$\frac{35\,000}{20} = 1750$
$\frac{\text{SVC (ppb)}}{\text{TWA (ppb)}}$	$\frac{3.1}{5} = 0.6$	$\frac{12.0}{5} = 2.4$	$\frac{6.1}{5} = 1.2$	$\frac{24.0}{5} = 4.8$	$\frac{14\,000}{5} = 2800$	$\frac{35\,000}{5} = 7000$

and their relationship to OELs also align with the above conclusions (Robert and Roginski, 1994).

### **Regulatory compliance and sampling strategy**

It is possible that a time-weighted average exposure limit be complied with, even if there have been repeated and unacceptable excursions above the short-term exposure limit. Clearly, the short-term and time-weighted average limits have to be linked to ensure protection of the workforce. The relationship is expressed by ACGIH (2001) in the following way:

*A STEL is defined as a 15-minute TWA exposure which should not be exceeded at any time during a workday even if the 8-hour TWA is within the TLV-TWA. Exposures above the TLV-TWA up to the STEL should be not longer than 15 minutes and should not occur more than four times a day. There should be at least 60 minutes between successive exposures in this range.*

This is important in the case of MDI and TDI, since it is believed that peak over-exposures, as distinct from lower long-term exposures, are particularly significant as causes of diisocyanate asthma.

### **Possible overexposures may go undetected**

Short periods of overexposures may remain undetected if only 8 h time-weighted average values are monitored. For example, if exposures of 40 ppb diisocyanate occur for a total time period of 30 min during an 8 h working day when the exposure level is otherwise 2.5 ppb, the 8 time-weighted average exposure is 4.8 ppb. This value suggests compliance with a 5 ppb occupational exposure limit, even though a long period of over-exposure may have occurred.

Furthermore, an underestimation effect may occur if a paper tape, continuously moving past a sampling window, is used to monitor personal exposure levels which fluctuate significantly over a short period of

time. Such a situation could occur, for example, if a worker enters a high exposure area briefly to take a sample. A short-term exposure lasting, say, 30 seconds will be measured over the average time that the paper tape segment takes to pass the sampling window (which may, in older instruments, take several minutes). This can result in a significant underestimation of the true exposure levels (Dharmarajan and Rando, 1980).

### **Biological working tolerance levels**

Airborne exposure limits relate to *potential intake* of a chemical such as MDI or TDI into the body. A different approach to exposure is to establish levels of the material *actually taken into* the body, monitored by measuring how much of a given material is being excreted from the body. It is well known that MDI and TDI react in the body, so excretion rates of the diisocyanates cannot be used as a criterion. However, the German government has established a biological working tolerance level (Biologische Arbeitsstofftoleranzwert) for MDA in the urine of workers, as an indicator of the level of exposure of a worker to both MDA and MDI, it being assumed that hydrolysis of reactants of MDI adducts in the body will be converted to MDA (see *Part 3, Health: biomonitoring of MDI and TDI*).

### **Stack release limits and community limits**

Airborne releases from the workplace may affect both the environment and the community. Clearly, workplace exposure limits are not relevant in these cases, so new criteria need to be considered regarding maximum exposure levels. In the case of MDI or TDI the potential environmental impact is very low (see *Part 4, The environment*), especially at the extremely low release concentrations which are encountered. Accordingly, regulatory bodies have based the requirements for MDI and TDI almost exclusively on community health issues.

A small number of countries have regulations which apply to the maximum concentration of MDI or TDI which may be released from stacks (see Table 5.6.4). However, release concentration is a poor criterion of the potential impact on human health, since no account is taken of the physical form of the chemical, its distribution in the atmosphere, which depends upon a diversity of factors including the location of the workplaces, or the proximity of the community. The use of community limits, also known as *community exposure limits*, *fenceline limits*, *acceptable ambient limits* or *off-property limits* is a much more meaningful approach.

### **Community limits**

Occupational exposure limits apply to a special group of individuals. These people, the workforce, fall within a limited age range, work within limited

**Table 5.6.4 Stack concentration limits.**

Country	MDI mg/m <sup>3</sup>	TDI mg/m <sup>3</sup>	TRIG mg/m <sup>3</sup> of NCO group
Germany <sup>a</sup>	20	20	–
Belgium <sup>a</sup>	20	20	–
France <sup>a</sup>	20	20	–
Italy <sup>a</sup>	5	5	–
Spain <sup>a</sup>	20	20	–
UK	–	–	0.1
Sweden	–	–	0.1
Conversion factors	MDI 0.1 mg/m <sup>3</sup> of NCO group $\equiv$ 0.3 mg/m <sup>3</sup> of MDI TDI 0.1 mg/m <sup>3</sup> of NCO group $\equiv$ 0.2 mg/m <sup>3</sup> of TDI		

<sup>a</sup>TA Luft requirements are used by Germany and followed by some other countries. The limit depends on the exhaust flow rate, and the class into which the chemical is entered. In the above examples, Italy has entered MDI and TDI into a TA Luft equivalent class requiring more rigorous control than practiced elsewhere. The TA Luft limits requirements on releases of chemicals is currently (2001) under review.

hours and are normally healthy. Desirably, the workforce is subject to health surveillance. The workforce is normally aware of the chemicals with which it is working, and their health effects, and is able to report related symptoms.

The community, that is those people beyond the factory fence line who may be exposed to releases from the factory, is very different from the workforce. In the community there may be individuals who spend almost all a lifetime in the same location. The group will normally include the young, the old, the pregnant, and those with severe medical conditions. These individuals may not know to what they are exposed or the associated health symptoms. Accordingly, the community must be considered more vulnerable than the workforce and must therefore be protected by more rigorous exposure controls. It will be seen that, whilst workplace exposure limits are commonly in the range parts per billion, community limits are in the range parts per trillion (ppt), in alignment with this philosophy.

#### Calculation of UK factor

The best practical means was based on the then TLV-C (20 ppb) multiplied by a factor.

The factor of 1/60 was calculated from:

$$\begin{aligned}
 &1/2 (= \text{period of life in} \\
 &\text{factory/lifetime}) \\
 &\times 1/3 (= \text{period of day in} \\
 &\text{factory/length of day}) \\
 &\times 1/10 (= \text{safety factor})
 \end{aligned}$$

#### Community exposure limits

It is difficult to assess what maximum exposure limits should be set for the workforce. It is even more difficult to set meaningful community limits. It is possible, but not easy, to characterize workplace exposures and associated diisocyanate-induced health effects. It is very difficult to characterize community exposure to released diisocyanates and to investigate causal relationships with health effects, given the diversity of confounding effects, socio-behavioural, physical or chemical. However, limits have been set. The first such attempt was made by the UK Alkali Inspectorate in the 1970s

(BRMA, 1977). It was required that the community should not be subjected to concentrations of MDI or TDI greater than 330 parts per trillion (ppt), which was 1/60th of the TLV-C of 0.02 ppm at that time.

Australia has adopted a fenceline of  $1/30 \times$  maximum allowable workplace concentration. The USEPA and a number of US States and Canadian Provinces have introduced community limits for MDI and TDI. These are based on risk assessments of different levels of sophistication. The following is the approach of North Carolina (Hayward, 2001):

### Sample risk assessment for MDI for North Carolina.

---

No Adverse Effect Level 0.2 mg/m<sup>3</sup>

Safety Factors

- noncontinuous exposure adjustment 5.6
- differences between rats and humans 10
- accounting for sensitive humans 10

**Acceptable Ambient Level** =  $(0.2 \text{ mg/m}^3) / (5.6 \times 10 \times 10) = \mathbf{0.00036 \text{ mg/m}^3}$

---

The no adverse effect level is that found in rat studies using MDI aerosol (see *Part 3, Health*). The complete rationale for MDI is available.

The USEPA has developed criteria whereby community air limits can be calculated. The *Reference Concentration* (RfC) is based on more sophisticated calculations than those used above. It is appropriate only for noncancer endpoints. In Table 5.6.5 are given US (Federal) RfC values for MDI and TDI as well as other community limits. Some US States simply adopt the Federal values. A summary of US air regulations for selected polyurethane industry chemicals has been prepared by API (2001).

**Table 5.6.5 Some North American community exposure limits.**

Authority	MDI		TDI	
	$\mu\text{g}/\text{m}^3$	ppt	$\mu\text{g}/\text{m}^3$	ppt
US Federal (RfC)	0.6	60	0.20	29
N. Carolina	0.36	36	0.20	30
California	0.7	70	0.07	10
Canada (Ontario)	1.0	100	1.0	142
Conversion factors (vapour only)	1 ppt $\equiv$ 0.010 $\mu\text{g}/\text{m}^3$ 1 mg/m <sup>3</sup> $\equiv$ 100 $\mu\text{g}/\text{m}^3$		1 ppt $\equiv$ 0.007 $\mu\text{g}/\text{m}^3$ 1 mg/m <sup>3</sup> $\equiv$ 138 ppt	

### Determination or estimation of community exposure

The RfC is part of the USEPA *Integrated Risk Information System (IRIS)*. This is a publicly available, chemical-specific, electronic database containing health risk and regulatory information. IRIS is a tool that provides hazard identification and dose–response assessment information. When combined with specific exposure information it may be used for characterization of the public health risk. IRIS may contain descriptive and quantitative information on reference doses for chronic noncarcinogenic health effects, supplementary data on acute health hazards and physical/chemical properties. The RfC is an estimate of a daily exposure to the human population that is likely to be without appreciable risk of deleterious effects during a lifetime. It is calculated by taking the ratio of a *no observed effect level* and a *lowest observed adverse effect level* (NOEL/LOAEL), then multiplying or dividing by a number of factors to take into account the variation in sensitivity among the members of the human population, the uncertainty in extrapolating laboratory animal data to humans, the uncertainty in extrapolating from data obtained in a study that is of less-than-lifetime exposure, the uncertainty in using LOAEL data rather than NOAEL data, and the inability of any single study to address all possible adverse outcomes in humans adequately. Further, a factor is used to represent the degree to which the hazard database for the chemical is complete.

The determination or estimation of community exposure (fenceline concentrations) is problematical, whether undertaken by direct analysis of MDI or TDI at the fenceline or by modelling the distribution of releases from the stack. Recent developments have allowed direct analysis to be used to detect levels of MDI or TDI down to the 10 ppt level, provided that sampling is undertaken over a long period. However, it would be necessary to undertake a major statistical sampling programme to characterize exposure of the complete fenceline taking into account daily, seasonal and yearly changes in distribution pattern of the released diisocyanate. Further, it would be necessary to take into account patterns of diisocyanate usage on the site. How-

ever, direct analysis is the only way in which compliance can be confirmed.

### Modelling of releases to atmosphere

The general approach to modelling is given in Figure 5.6.2.

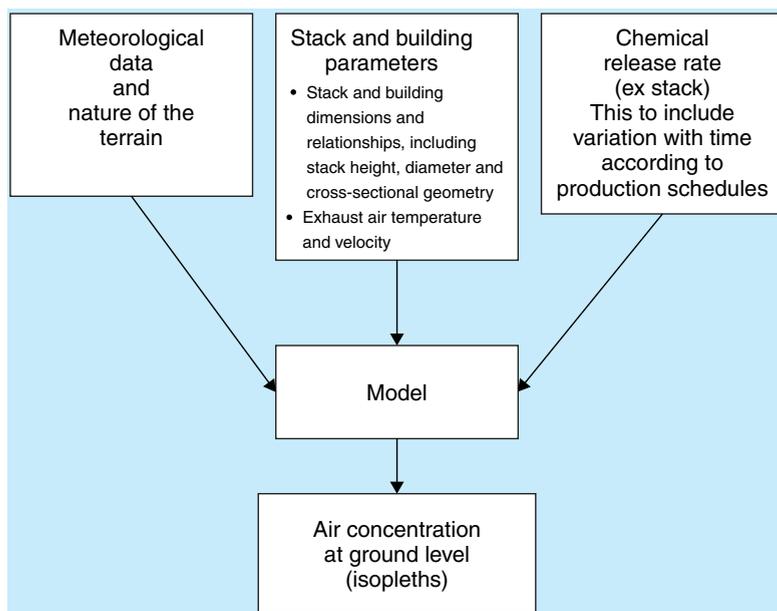


Figure 5.6.2 Modelling of releases

There is a very wide range of mathematical models available, but the models which may be used are normally specified in situations where compliance is in question. Middleton (1998) used the Industrial Source Complex (ISC) Short Term Dry Deposition Model to calculate average MDI concentrations from two stacks associated with diisocyanate processing. The version of the ISC model used by Middleton has been recommended by the USEPA for regulatory compliance purposes.

The ISC Short Term Dry Deposition Model requires emissions and meteorology input data and information on the site environment. The model needs release rates, stack configurations and other physical parameters such as stack temperature and building shape. Also, typical meteorological data for a full year are required. The site environment (rural versus urban) and terrain also need to be specified for the calculations. The modelling requires that aerosol diameters be specified when MDI is assumed to be in the particulate phase.

Middleton modelled the MDI release distributions from two facilities. One facility produced boats and the other produced oriented strand board for building applications. Both factories were rural and in flat terrain. The calculations assumed that they were operating throughout the year with constant release levels, and used maximum measured figures of MDI concentration and mass release rate. Details of the two situations are given in Table 5.6.6 and details of the modelling, and results, are given in Table 5.6.7.

**Table 5.6.6 Details of two facilities releasing MDI.**

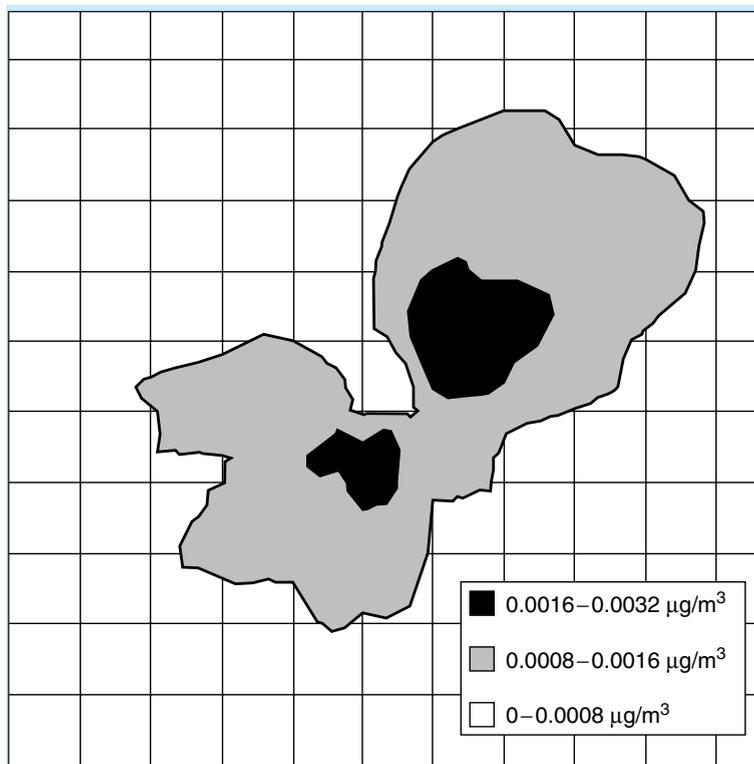
Terrain	Boat building facility		Building board facility	
		Flat, rural		Flat, rural
Stack				
Diameter	m	0.84		1.43
Height	m	4.9		15.2
Air temperature	K	296		312
Air speed	m/s	11.8		26.7
Building				
Height	m	5.8		15.3
Maximum release rate	g/s	0.000073		0.012

In Figure 5.6.3 is given the composite map isopleths (profiles of equal concentration) for  $10\ \mu\text{m}$  particles, around the building board facility. In Figure 5.6.4 are given the composite maps of the isopleths for the boat building facility. It is interesting to note that, whilst both facilities are situated in flat rural terrain, the forms of the isopleths are different, that of the former being mono-nodal and that of the latter bi-nodal.

Detailed information on the modelling of releases in locations of different geographical location and weather conditions is given in *Part 4, The environment*. Details of MDI and TDI stack releases measured in the exhaust ventilation of a range of processes are given in *Part 2, Handling: releases to atmosphere from polyurethane manufacturing sites*.

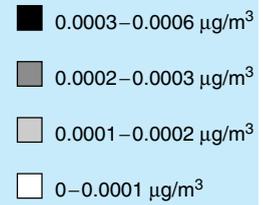
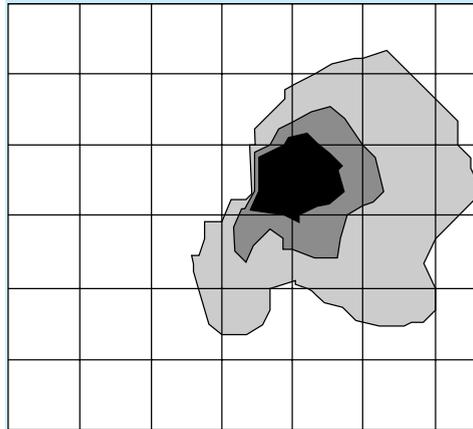
**Table 5.6.7 Modelling of releases.**

	Boat building facility	Building board facility
<b>Modelling parameters used</b>		
Form of MDI	Vapour and aerosol of 0.1, 1.0, 10 and 50 $\mu\text{m}$ diameter	
Meteorology	Use of hourly surface data and twice-daily upper air data	
Mathematical model	ISC Short Term Dry Deposition model	
<b>Results</b>		
Release		
• rate	g/s	0.000073
• concentration	$\mu\text{g}/\text{m}^3$	11.0
Maximum concentration range		
	0.0005 to 0.0007 $\mu\text{g}/\text{m}^3$ at 200 m from site	0.003 to 0.005 $\mu\text{g}/\text{m}^3$ at 500 m from site
<b>Regulatory requirement</b>		
Maximum concentration (RfC)	0.6 $\mu\text{g}/\text{m}^3$	0.6 $\mu\text{g}/\text{m}^3$

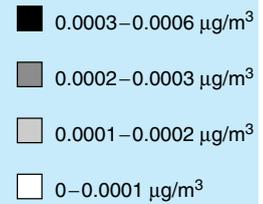
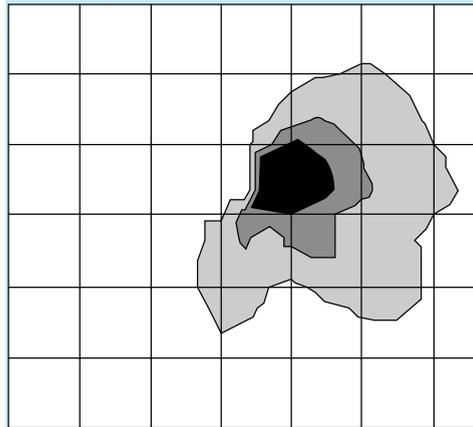


**Figure 5.6.3** Composite map isopleths for 10  $\mu\text{m}$  particles around a building board facility. Figure based on a personal communication from the Alliance for the Polyurethanes Industry, USA

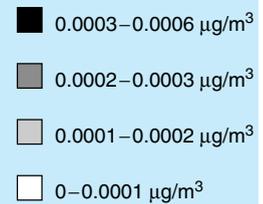
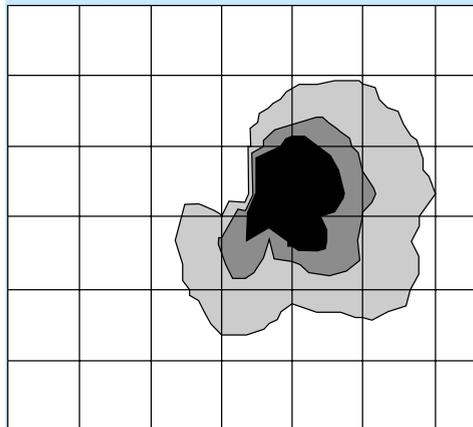
1 micron diameter particles.  
300 metre grid units.



10 micron diameter particles.  
300 metre grid units.



50 micron diameter particles.  
300 metre grid units.



**Figure 5.6.4** Composite maps of the isopleths for a boat building facility. Figure based on a personal communication from the Alliance for the Polyurethanes Industry, USA

## Reading

- ACGIH (2001). 2001 TLVs and BEIs: threshold limit values for chemical substances and physical agents and biological exposure indices. American Conference of Governmental Industrial Hygienists, Inc., Cincinnati.
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## 5.7 Sampling and analysis

Sampling and analysis are carried out for a variety of purposes, including assessment of worker exposure, compliance with regulatory exposure limits, determination of airborne concentrations in the workplace or in releases from various processes, during toxicological or human challenge studies, and evaluation of monitoring methods and instruments. Effective and representative sampling is a prerequisite to all understanding of exposure. In the case of diisocyanates there are particular problems such that sampling must be carried out with understanding and care.

The following text covers the sampling and analysis of MDI and TDI in air, water, soil, bulk diisocyanates and polyurethane products. Occupational hygiene scenarios predominantly require the sampling and analysis of air, and this is reflected in the degree of detail on this important sector. There is also a review of past analytical methodology used in health studies in the light of current knowledge.

### Materials to be measured

MDI is available commercially as pure MDI, as a range of polymeric MDIs and as a range of modified MDIs. Whilst pure MDI is essentially the 4,4'-isomer with a very small percentage of the 2,4'-isomer, polymeric MDIs and modified MDIs may contain many species; see *Part 5.1, Chemistry of*

*manufacture of MDI and TDI* for further information. The most common types of polymeric MDI contain about 50 % diisocyanate, about 25 % triisocyanate, with the remainder being higher molecular weight species. Polymeric MDIs for different applications may vary significantly in the content of the various component species. Fortunately, it is seldom necessary to know the detailed composition of a polymeric MDI. For most purposes it is usually sufficient to know the total concentration of isocyanate species that is present in a given sample, and the methods described below are satisfactory for this purpose. If more detailed specific information is required at any time, it will be necessary to discuss the requirements with the manufacturer of the particular product.

The commercial TDI product most widely used is a mixture of isomers, comprising 80 % 2,4-TDI and 20 % 2,6-TDI. The corresponding mixture of 65 % 2,4-TDI and 35 % 2,6-TDI is also used: 2,4-TDI alone is used for special applications and 2,6-TDI is not a commercial product. Several methods are available to measure TDI concentrations in the atmosphere. Care needs to be taken with some colorimetric methods, since the two isomers may not behave identically in colour development with the analytical reagent. This can lead to problems in determining exposure levels, unless the method is known to measure each isomer correctly.

There are many modified MDI and TDI products available commercially. Some of these are discussed in *Part 5.1, Chemistry of manufacture of MDI and TDI*. The compositions of most of these materials are proprietary. The full characterization of some of the products involves sophisticated analytical techniques which are beyond the scope of this book.

## Airborne MDI and TDI species

### Chemistry

MDI and TDI normally undergo addition reactions with substances containing *active hydrogen* atoms. However, studies have shown that there is no evidence that MDI or TDI are hydrolysed to MDA or TDA in air. Further, these diisocyanates do not usually react with other species which are commonly found in workplace air. Dharmarajan (1995, personal communication) tested for the presence of MDI and MDA in the emissions from a strand board manufacturing plant, where MDI-based resins were used as binders. The test emissions were from a process using supersaturated steam. Only MDI was detected in these emissions; no MDA was found. Holdren *et al.* (1984) at the Battelle Laboratories studied the fate of TDI in a variety of atmospheres including simulated urban air, with a very wide range (7 % to 70 %) of relative humidity. No TDA was detected in any experiment, corresponding to a conversion of less than 0.05 %. This clearly indicates the absence of hydrolysis in the vapour phase.

In the presence of hydroxyl radicals found in air the diisocyanates break down mainly to water, carbon dioxide and nitrogen oxides. The half-lives of decomposition are of the order 12 to 24 h, so no losses of diisocyanate occur during the sampling process. Becker *et al.* (1988) studied the hydroxyl free-radical reaction with TDI, whilst Klamt (1993) and Bailey (1993) carried out calculations on the corresponding reaction with MDI and TDI. The results

See *Part 4, The environment* for further details.

of these calculations and study, together with the conclusions of Holdren *et al.*, indicate that the mechanism of loss of MDI from the atmosphere would also be by free-radical attack and that hydrolysis of MDI to MDA would not occur.

Whilst MDI and TDI do not form the respective amines in air, MDA or TDA may be formed as an artefact in sampling and analytical procedures by hydrolysis of MDI or TDI, if care is not taken to exclude water. MDI and TDI once trapped on a filter may also react with other molecules.

### **Physical form**

MDI or TDI species may be present in atmospheres as vapour, as a mixture of vapour and aerosols or as a component of a reacting mixture. The most common application in which aerosol is produced is that of spraying a reacting polyurethane mixture (Booth and Dharmarajan, 1996).

#### **Physical states of MDI and TDI in the air.**

TDI	Vapour
MDI	Vapour and/or aerosol
Spray applications with MDI or TDI	Primarily aerosol

Much of the following text deals with the complexities of aerosol measurement. However, very small aerosols (up to about 0.5  $\mu\text{m}$  diameter) are termed *gas-like* and may even be measured using methods which are not normally acceptable for aerosols, using paper-tape monitors, for example.

### **Types of aerosol**

The differences in the physical state of airborne MDI in the workplace were not fully appreciated until 1978, when Dharmarajan and Weill (1978) pointed out that airborne MDI in a workplace environment may exist as an aerosol. Further laboratory studies by Tucker and Arnold (1982), Booth *et al.* (1983) and Dharmarajan *et al.* (1987) showed that MDI vapour atmospheres could give rise to condensation aerosols.

Several types of aerosols containing diisocyanates are possible theoretically in workplace situations. They may be reacting aerosols, for example:

- those produced when spraying a mixture of diisocyanate and polyol component onto a substrate to produce a coating. The diisocyanate content of such aerosols will decrease rapidly with time as the polyurethane formation proceeds.
- aerosols of dusts, wood, etc. which have a diisocyanate adsorbed onto their surfaces.

Nonreacting aerosols can also occur:

- very fine aerosols of MDI, such as condensation aerosols which may be formed by the cooling of a warm, saturated atmosphere of MDI in the

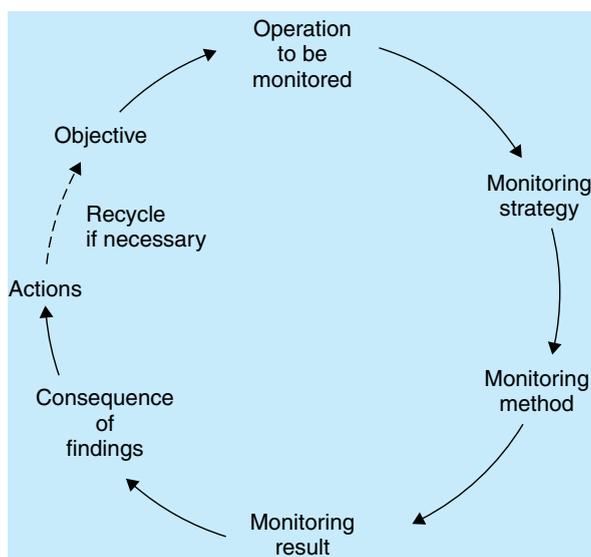
presence of available nuclei. However, rarely does cooling alone cause condensation aerosols to form, as dilution by air prevents it.

- liquid droplets of MDI or TDI formed during spray applications of diisocyanate. These are very unlikely in most polyurethane processes.
- MDI dusts generated by handling pure MDI in its solid state, for example when handling flaked pure MDI or when sweeping up a spill of pure MDI.

Mass concentrations of particulates are normally measured by drawing air through a suitable filter. The aerodynamic diameter of an aerosol particle is primarily responsible for determining deposition within the respiratory tract. Aerodynamic size distribution is frequently determined by the use of particle impactors (see below).

### Choice of methods for the sampling and analysis of MDI and TDI in air

The choice of methods depends on the several interdependent factors. This may be illustrated as follows (Figure 5.7.1).



**Figure 5.7.1** Analytical methods: decision circle

The selection of sampling and analysis methods is critically and integrally dependent upon the objectives of sampling and the operation that is sampled. The precision, accuracy and required detection limits are also very closely dependent on the objectives. Thus, in the case of an accidental spill of TDI from a tank car in a remote area, the rapid detection of airborne diisocyanate is more important than precision or accuracy, as the objective is to determine the potential evacuation area. Many other practical considerations, such as the availability of sophisticated instruments and trained personnel to perform analysis, also affect the choice of methods.

**Table 5.7.1 Choice of sampling methods**

Details of equipment and techniques are given later in the text

**Routine work:** Paper tapes are often satisfactory for routine work, but may significantly underestimate exposure if aerosols are present, depending on the particle diameter range. The combination of an impinger backed with a coated filter is always satisfactory.

Operation	Objective	Diisocyanate	Method
Drumming and transport operations. Polyurethane production.	Routine long- or short-term measurements.	MDI: vapour only	Impinger + filter. Paper tape. Sorbent tube. Reagent-coated filter with field desorption.
		MDI: vapour + aerosol	Impinger + filter. Reagent-coated filter with field desorption.
Fugitive emissions into the workplace.	Personal or area monitoring.	TDI	Impinger + filter. Paper tape. AVM. Sorbent tube. Reagent-coated filter.
	Testing for possible emissions.	MDI vapour	Any tape instrument.
Stack sampling.	Measurement of diisocyanates in exhaust air.	TDI vapour	Paper tape. AVM. Dräger tube. GMD Sure-Spot. K&M TDI badge.
		MDI, TDI	Impinger + filter. Isokinetic sampling is required if aerosols are present.

**Emergency situations:** A rapid response method is essential. The objective is to establish if diisocyanate is present in the air, rather than to determine an accurate value for the amount present. Paper tape monitors can be used; or, for TDI only, AVM or Dräger tubes.

Tables 5.7.1 and 5.7.2 provide summaries of the various types of methods and equipment that are available for the sampling and subsequent analysis of MDI and TDI in air. In Table 5.7.2 the approximate costs of analytical equipment, including accessories such as tapes, are categorized into bands and may be influenced by the amount of auxiliary equipment decided upon. The cost bands in US dollars are:

Low: <\$150  
 Medium: \$150 to \$10 000  
 High: >\$10 000

Manufacturers should be asked to indicate tape costs and running time. The running time of tapes is dependent on whether the tape moves forward only when positive diisocyanate detection occurs, or whether the tape runs continuously.

In some countries there are recommended methods for compliance measurement of airborne diisocyanates. US Government recommended methods are listed in Table 5.7.3.

**Table 5.7.2 Monitoring methods for MDI and TDI in workplace atmospheres.**  
*Details of equipment and techniques are given later in the text*

Method	Suitable for	Comments	Sampling/resolution time	Claimed range	Cost range
<b>PAPER TAPE</b>					
<b>Passive badge systems</b>					
GMD Sure-Spot TDI dosimeter badge	TDI	Portable, immediate results Direct read colorimetric badge using direct diffusion exposure. Specific chemical colour reaction measured using a colour comparator. Passive, only sampling the air which passes directly over the badge. Gives employees visual warning of exposure. Very simple to operate.	Each shift (8h)	10 to 385 ppb hour (accuracy $\pm 25\%$ )	Low
K&M TDI detection badge	TDI		Each shift (8h). 15 min to 24 h sampling	5 to 700 ppb hour (accuracy $\pm 17\%$ )	Low
<b>Active sampler</b>					
GMD Sure-Spot Test Kit	MDI, TDI	For continuous area (fixed point) monitoring. Gives short period and/or TWA results. Paper tape placed in a holder, while a precalibrated pump draws a measured air sample through. Dose estimator measures colour change. Simple to operate. Can be carried by worker on supplied belt pouch and can therefore also be used for personal monitoring.	5 minutes (25 samples of 5 min per full charge)	1 to 72 ppb (accuracy $\pm 25\%$ )	Pump test kit: medium Test cards: low

(continued overleaf)

Table 5.7.2 (continued)

Method	Suitable for	Comments	Sampling/resolution time	Claimed range	Cost range
<b>Moving tape systems</b>					
MDA Model 7100 Paper Tape Monitor	MDI, TDI	Real time concentrations on display and hard copy. Dual level alarms. Minute by minute concentrations. Shows peak concentrations. Can be fixed or portable. Fast response. Can be used outdoors.	Less than 10 s	1 to 200 ppb	Test kit: medium Tapes: low
MDA SPM (Single Point Monitor)	MDI, TDI	Operates on direct current with battery back up. 'Strobing' visual alarm. LCD shows self-diagnostic data. Up to 8 h sampling data can be stored in internal memory. Calculates 8 h and 15 min TWA. Memory and printer option gives capability to send output to a printer.	Less than 10 s	2 to 60 ppb	Test kit: medium Tapes: low
GMD RIS (Remote Intelligent Sensor)	MDI, TDI	Operates on direct current with battery back up. 'Strobing' visual alarm. LCD shows self-diagnostic data. Up to 8 h sampling data can be stored in internal memory. Calculates 8 h and 15 min TWA. Memory and printer option gives capability to send output to a printer.	4 min at OEL. 12 s at high concentrations.	1 to 2000 ppb	Test kit: medium Tapes: low
GMD Autostep	MDI, TDI	Portable. With fast response mode. Minimum response time of 15 s. Real-time data logging with down-loading via a computer interface unit. Can display, store or print hard copy of peak concentration events and time. Useful for leak detection, leak sourcing and fast surveys of suspect areas. US Underwriters Laboratory approved for Class 1, Division 1.	15 s	1 to 200 ppb	Test kit: medium Tapes: low

**GAS TUBE**

Dräger Tube	TDI	Simple to operate. Cheap, portable, immediate results. Limited accuracy, only a general indicator of concentration.	Can be read 15 min after sampling	20 to 200 ppb	Low
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**IMPINGER AND/OR FILTER METHODS**

Modified Marcali method	MDI, TDI	Sampling by impinger. Uses conventional laboratory equipment including a colorimeter or spectrophotometer (UV absorbance). Fairly flexible and simple. Quick results. Significant errors for TDI if 2,6-/2,4-TDI ratio is high.	10 min	2 to 40 ppb (can be extended)	Medium/high
1,2-MP derivatization followed by HPLC with dual detection. MDHS 25/3 <sup>a</sup>	MDI, TDI TRIG	A measured volume of air is drawn through a glass fibre filter impregnated with 1,2-MP solution. HPLC analysis is carried out on the solvent desorbate. Can also measure individual monomers. Equipment expensive. Skilled analyst needed. Results only after laboratory analysis. Suitable for personal monitoring.	15 min	0.1 to 140 µg NCO/m <sup>3</sup> for 15 litre sample (EC detector)	High

(continued overleaf)

Table 5.7.2 (continued)

Method	Suitable for	Comments	Sampling/resolution time	Claimed range	Cost range
MAP derivatization followed by HPLC with dual detection <sup>b</sup>	MDI, TDI TRIG	Can also measure individual monomers. Equipment expensive. Skilled analyst needed. Results only after laboratory analysis.	15 min	0.3 to 6000 µg/m <sup>3</sup> for 15 litre sample (UV or fluorescence detector)	High
Use of dual filter with 1,2-MP derivatization for aerosol and MAMA derivatization for vapour, followed by HPLC separation <sup>c</sup>	MDI, TDI TRIG	Can also measure individual monomers. Equipment expensive. Skilled analyst needed. Results only after laboratory analysis.	15 min	0.7 to 140 µg/m <sup>3</sup> for 15 litre sample (fluorescence detector)	High
<b>SORBENT TUBES</b>					
Nitroreagent on glass powder or glass fibre	MDI, TDI	Sampling tubes have to be made up by a skilled analyst and must be stored carefully. Desorbed derivatized diisocyanates are analysed by HPLC.	Typically, 1.7 l/min for 1 to 2 h	Greater than 0.2 µg per tube	Tubes: low HPLC: high
<b>ION-MOBILITY SPECTROMETRY</b>					
Graseby AVM	TDI	Near real-time monitoring. Portable. No longer sold, but still in frequent use. Not very suitable for compliance with OELs.	1 to 2 s	4 to >48 ppb	(Medium, but no longer available)

<sup>a</sup>HSE (1999).<sup>b</sup>Streicher *et al.* (1996).<sup>c</sup>Lesage *et al.* (1992).

**Table 5.7.3 US Government recommended methods for the sampling and analysis of MDI and TDI in the workplace.**

Government Body	MDI	TDI	TRIG <sup>a</sup> concentration
OSHA	Method 18	Method 18	
	Method 33	Method 33	
	Method 47	Method 42	
NIOSH	Method 5521	Method 5521	Method 5522
		Method 2535	

<sup>a</sup>Total reactive isocyanate group: see Part 5.6, *Occupational exposure limits, stack limits and community limits*.

OSHA Method 18:	Nitroreagent–toluene impinger sampling/HPLC-UV analysis for MDI and TDI. Nitroreagent is <i>N</i> -(4-nitrobenzyl)- <i>N</i> -propylamine.
OSHA Method 33:	A confirmatory test for MDI and TDI nitroreagent urea. The urea collected from HPLC elution is injected into GC, and the GC eluent is analysed by a thermal energy analyser. In this method, the urea is pyrolysed at 875 °C to give nitric oxide, which is reacted with ozone to produce chemiluminescence, which is measured.
OSHA Method 42:	1-(2-Pyridyl)piperazine (1,2-PP)-coated filter sampling/HPLC-UV analysis for TDI only.
OSHA Method 47:	1,2-PP-coated filter sampling/HPLC-UV analysis for MDI only.
NIOSH Method 2535:	Nitroreagent-coated glass wool sampling/HPLC-UV analysis for 2,4- and 2,6-TDI.
NIOSH Method 5521:	1-(2-Methoxyphenyl)piperazine-toluene (1,2-MP) impinger sampling/HPLC-UV and/or electrochemical detector for monomeric isocyanates including TDI, MDI and HDI.
NIOSH Method 5522:	Tryptamine–toluene impinger sampling/HPLC-UV or electrochemical detector for monomeric and oligomeric isocyanates or TRIG.

Some methods are being considered as international standard methods (see Table 5.7.4). The International Organization for Standardization (ISO) has established a working group (ISO/TC 146/SC 2/WG 4) to recommend and prepare ISO Norms for the measurement of workplace atmospheres, which cover airborne mono-, di- and poly-isocyanates. Four methods have been under consideration by the group (Table 5.7.4), of which the UK HSE method (HSE, 1999) has been accepted as an ISO method: it is a total reactive isocyanate group method. The group is also preparing a text, *Guide for selection of isocyanate measurement methods*.

The European Community Bureau of Reference initiated a project in 1993 on the preparation of certified reference material for the determination of diisocyanates in air, using reversed phase HPLC. The derivatization agent selected was 1-(2-methoxyphenyl)piperazine, and four

diisocyanates, including 4,4'-MDI, 2,4-TDI and 2,6-TDI, were prepared as their 1,2-MP derivatives. Laboratories participating in the 'round robin' analysis used reversed phase HPLC with UV or diode-array detection. It is intended that samples of reference material should be made available.

The UK HSE has established WASP, the Workplace Analysis Scheme for Proficiency. This scheme provides a means of external quality assurance for laboratories carrying out chemical analysis of workplace air. A number of representative analytes are used, and MDI is included as a HPLC analyte. Sample materials are sent to participating laboratories for analysis, and the results are assessed in confidence by the UK Health and Safety Laboratory. Participation in the scheme is open to analysts worldwide (HSE, 2000).

**Table 5.7.4 Methods under consideration by ISO for the sampling and analysis of airborne diisocyanates (September 2001).**

Source of method	Reagent	Status
UK HSE	1-(2-methoxyphenyl)piperazine	ISO Standard
IRSST/Omega Co.	Iso-Chek™	Proceeding to NWIP stage <sup>a</sup>
US NIOSH	1-(9-anthracenylmethyl)piperazine	Proceeding to DIS <sup>b</sup>
Skarping <i>et al.</i>	Dibutylamine	Proceeding to NWIP stage

<sup>a</sup>NWIP is *New Work Item Proposal*.

<sup>b</sup>DIS is *Draft International Standard*.

### Sampling considerations

Extremely low exposure limits, combined with high diisocyanate reactivity, high absorptivity and the possible presence of vapour aerosols and reacting mix in some situations, pose problems in the sampling of airborne MDI and TDI, and the subsequent preparation, storage, shipping and analysis of the samples.

Analytical results are only as good as the sample collected. If the sample collected is not representative or its integrity is somehow compromised, the analysis, however sensitive, precise and accurate, will not correctly answer the question for which the sample was collected. The three methods that are used for sampling atmospheres of diisocyanates are:

- paper tape systems;
- impingers containing a derivatizing reagent;
- filters or sorbent tubes, usually impregnated with a derivatizing reagent.

Most derivatizing agents are secondary amines with molecular structures capable of being quantitated by colorimetric, UV or other spectroscopic methods. Each of the above methods is subject to some constraints, which are discussed later in this section.

MDI and TDI are often present only at trace levels in air, as parts per billion (ppb) or even as parts per trillion (ppt). As a general rule, the percentage errors encountered in trace atmosphere analysis are usually higher than the errors in bulk sample analysis. Several steps are involved, which can lead to cumulative errors. Some subtleties and insights associated with airborne sampling and analysis are listed below.

- (1) Often the exposure profiles are episodic and it may not be possible to repeat the sampling.
- (2) Diisocyanates can coexist with other potentially reactive species at low concentrations in the air phase of the workplace or environment. Such species include airborne acids, catalysts, polyols and, especially, water. However, reactions with diisocyanates may commence when these species are brought together on a surface or in a liquid such as found in a filter, impinger or sorbent tube. Such reactions, which may be accelerated further in the presence of collected catalysts, may reduce the amount of diisocyanate available for derivatization and thus cause under-estimation of the airborne concentrations.
- (3) Alkaline sites on glass-fibre filters react with MDI and TDI.

- (4) Dust and other species collected by the filter can react with the analyte of interest.
- (5) Evaporation of the analyte from the surface of the filter can occur during long-term sampling and shipping.
- (6) Large particles can become detached from the filter during sampling and shipping.

In general, use of sampling line extenders or probes in front of the sampler must be avoided because both MDI and TDI readily adsorb irreversibly to various surfaces (untreated glass, PVC and other plastic materials) leading to loss of material. In situations where the use of extenders cannot be avoided, the length must be kept to a minimum, ideally less than 15 cm (6 inches). Polytetrafluoroethylene, silanized-glass, or stainless steel tubing coated with reagent and diethylphthalate may be used. Sampling tubes should be rinsed with a derivatizing reagent in a solvent such as acetonitrile, and the rinsings included in the analysis.

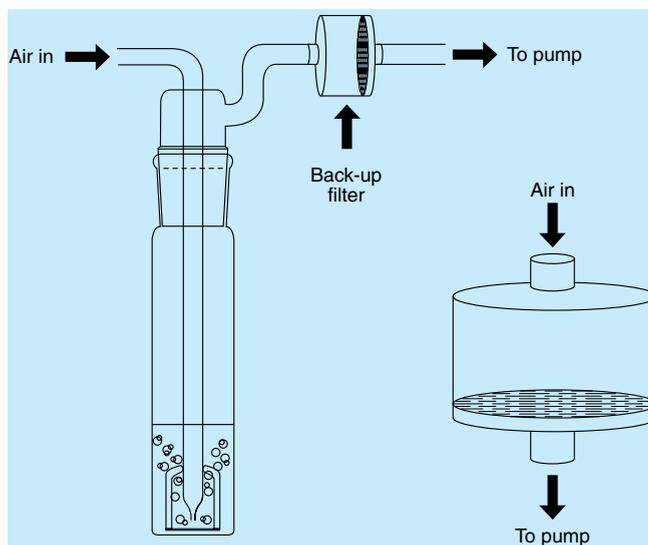
**CAUTION.**

If dimethylsulphoxide is used, any trace of water will cause hydrolysis of MDI or TDI to the respective diamines and other species (see Part 5.3, *Chemical reactions of MDI and TDI*).

The sampling of airborne vapours is usually achieved either by the use of a paper tape monitor, or by the capture of a sample in an impinger or on a filter for later analysis. These methods can also be used for aerosols, but the sampling of these can pose problems.

Impingers are unsuitable for sampling the full range of diisocyanate particle sizes likely to be encountered in the workplace because particles of less than about  $1\ \mu\text{m}$  diameter are inefficiently collected. Similarly, isocyanate species present in large particles ( $>10\ \mu\text{m}$ ) and collected on reagent-coated filters may not be efficiently derivatized. For this reason it is advisable to desorb the filter immediately after sampling with a solution of the derivatizing agent. However, the combination of an impinger followed by a reagent-coated filter should collect both isocyanate aerosols and vapours satisfactorily.

For the combination of an impinger backed by a filter (Figure 5.7.2) a sampling rate of 1 l/min is suggested. If using an impinger and filter



**Figure 5.7.2** Sampling with an impinger/filter combination

combination, the filter must be placed after the impinger otherwise the filter will clog. This combination has the effect that small amounts of derivative solution are constantly transferred to the filter, thus co-adsorbing with the sample aerosols, dissolving them and reacting with them on the filter surface. With high-volume multi-jet or rotary impingers, a secondary turbulence improves the washing effect (Brenner and Bosscher, 1995).

### **Paper tape monitors**

In these instruments, the sample air is drawn by a pump at a fixed rate through a paper tape impregnated with a derivatizing agent. The diisocyanate reacts with the reagent in the paper to give a stain of a characteristic colour, which is quantified by an optical system. The monitors require to be calibrated as regards flow rate and light setting. The instruments provide a measure of the diisocyanate concentration in the sampled air. In most paper tape monitors the tape moves past a sampling port either continuously or in a stepwise manner. Tape monitors can be fitted with alarms to indicate that a specified concentration of diisocyanate has been exceeded. Some examples of commercial paper tape monitors are shown in Figure 5.7.3.

Paper tapes are widely used because of their advantages:

- easy to use and do not require skilled analysts to operate them;
- operate continuously and unattended;
- give rapid results and can thus be used for leak detection and in emergency situations;
- some instruments can give audible warnings of high concentrations.

They have disadvantages:

- may read incorrectly at very high or very low humidities;
- are unsuitable for aerosols under many conditions;
- may not be accepted for purposes of regulatory compliance.

Paper tape monitors have been designed to measure diisocyanate vapour and so are suitable for measuring TDI in the air and also MDI, if aerosols are absent. If aerosols are present erroneous results may be produced unless the tape system has been specially calibrated for that particular set of conditions, as two studies have shown (Károly *et al.*, 2000; Hext, 1996).

The problems of measuring aerosols are related to both sampling and analysis. Tape instruments, like many other methods, fail to collect a representative sample of the target air, because of nonisokinetic sampling and inlet design. Once the sample of aerosol has been deposited onto the tape it may not diffuse within the paper and may even obscure the tape colour development from the optical system. Aerosols having different particle size distributions and different chemical compositions may respond differently in the colour development process.

As paper tapes move at a fixed speed across a sampling port they can, in principle, measure short-term variations in vapour concentrations, e.g. peak excursions. Some problems associated with the measurement of peak releases are discussed in *Part 5.6*.



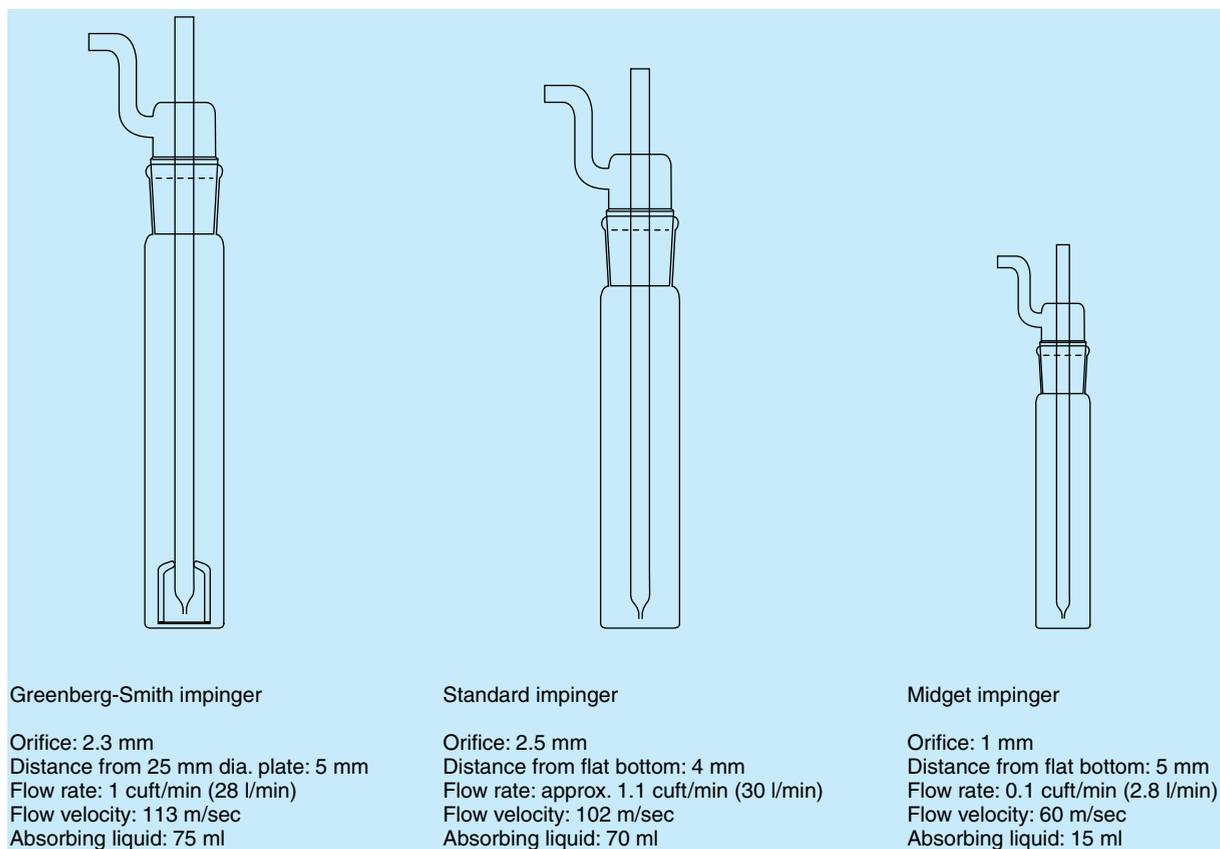
**Figure 5.7.3** Some commercial paper tape monitors: (a) GMD Remote Intelligent Sensor (RIS) (picture courtesy of Scott/Bacharach, Pittsburgh, PA, USA); (b) GMD Autostep Plus (picture courtesy of Scott/Bacharach, Pittsburgh, PA, USA); (c) MDA Scientific Series 7100 single point monitor (picture courtesy of Zellweger Analytics, Lincolnshire, IL, USA); (d) MDA Scientific SPM (picture courtesy of Zellweger Analytics, Lincolnshire, IL, USA)

Papers impregnated with a derivatizing agent can also be used in personal exposure monitors. These are of two types, one in which a pump draws the air to be sampled through a paper disc, and one in which the air to be sampled is allowed to diffuse into a paper disc. In both cases, the colour developed is a measure of the diisocyanate vapour in the sampled air.

### Impingers

The diisocyanate vapour in the atmosphere to be sampled is drawn through a solution of a derivatizing reagent contained in an impinger. After the sampling has been completed, the solution is analysed in one of several ways discussed later in *Methodology: practical aspects of the analysis of MDI and TDI*.

The terms *bubbler* and *impinger* are used synonymously by several authors. However, there are significant differences between them. A bubbler can be of any size, whereas an impinger is a bubbler with very specific dimensions. The impaction collection efficiency is intimately related to the impinger-jet diameter, the strike distance between the jet and the bottom of the impinger, and the flow rate, which determines the velocity of the aerosol in the impinger jet (see Figure 5.7.4). For example, a Greenberg–Smith Impinger (Bureau of Mines, USA) is a bubbler with sample inlet tube of 15 mm diameter tapering to a 2.3 mm internal diameter jet hole. The strike distance from the jet to a



**Figure 5.7.4** Impingers for sampling diisocyanates

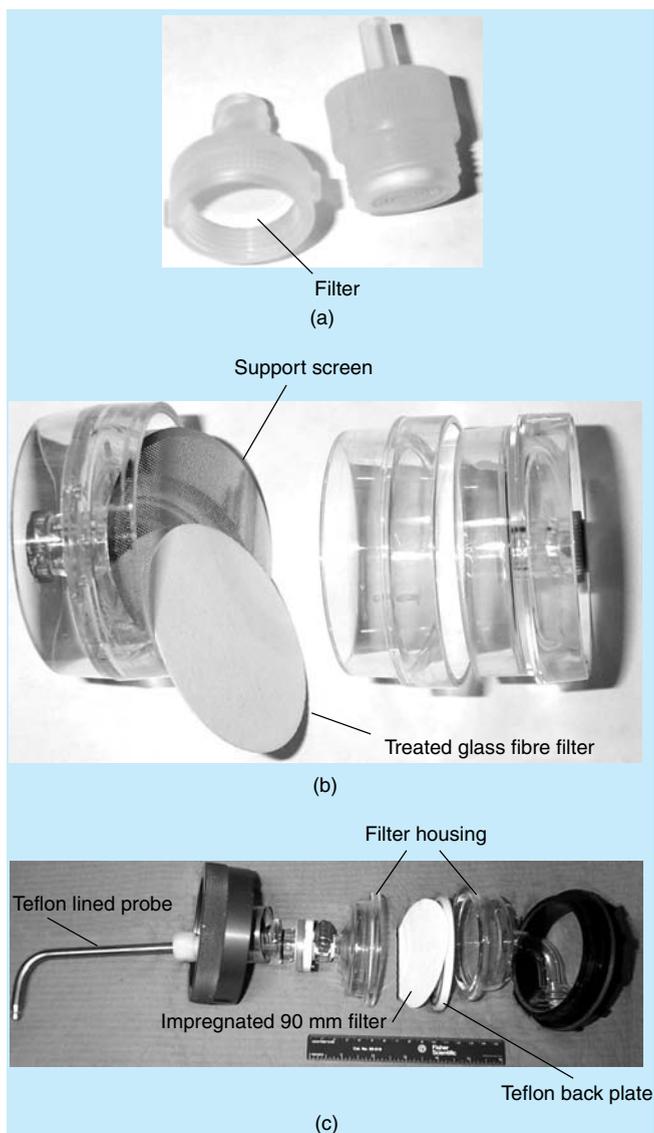
specially constructed flat plate is 5 mm, the diameter of the impinger body is 51 mm and the height is 183 mm. The flow rate for sampling is 1 ft<sup>3</sup>/min (28.4 l/min) or flow velocity of 113 m/s. A standard impinger (Verein Deutscher Ingenieure, Germany) is a bubbler with an inlet tube of 15 mm diameter and a jet size of 2.5 mm internal diameter and a strike distance of 4 mm (velocity = 60 m/s). The flow rate for a standard impinger is 30 l/min. A midjet impinger (Bureau of Mines) is a bubbler of around 30 ml with an inlet tube of 5 mm diameter and a jet size of 1.0 mm internal diameter and a strike distance of 5 mm (flow rate 2.8 l/min, velocity 60 m/s). Also there are high volume impingers which may be useful for short-term measurements, such as testing the emissions from fires or soldering, or for measurements at lower concentrations or for fence-line measurements.

The impinger sampling mechanism for vapours is based on diffusion. Impinger methods show greater than 95 % sampling efficiency for TDI. Since airborne TDI in the workplace environment is generally present as a vapour, TDI molecules inside the air bubbles caused by impinger sampling diffuse to the surface of the bubbles and dissolve in the reagent solution. However, with airborne MDI aerosol, the impinger sampling efficiency is dependent on several factors, such as MDI particle sizes and their distribution, the impinger dimensions and sampling flow rates. For particles with an aerodynamic diameter greater than about 1 µm, the mechanism of collection in an impinger is by impaction, rather than diffusion. The wettability factor for aerosols is important and can be adjusted by selection of the solvent for the reagents. For example, water and hydrochloric acid do not dissolve MDI and TDI, which is why dimethylformamide or acetonitrile is sometimes used as a solvent in impingers. MDI condensation aerosols (range of diameter around 0.1 to 1 µm) are not collected efficiently by a standard impinger because neither the impaction nor the diffusion collection mechanism is effective in this particle-size range. Booth *et al.* (1983) generated a condensation aerosol atmosphere of MDI and sampled it simultaneously with impinger and coated-filter methods and found that the collection efficiencies of impingers used in the Marcali method were 29 and 17 % at MDI concentrations of 30 and 70 ppb, respectively. However, at 5 ppb MDI concentration, the impinger technique was greater than 95 % efficient. The findings of Booth *et al.* have been supported by the studies of Hext (1996) in which MDI atmospheres were generated in the range of diameter of 0.1 to 1 µm in a wind tunnel and sampled using various techniques, including impingers.

Impinger sampling methods have been recommended for sampling in an isocyanate-based paint spray mist environment. The reason for this is that the relatively large aerosols in a spray mist are efficiently collected by the impinger, the particles are immediately dissolved in the impinger solvent, and the isocyanates are stabilized by the reagent.

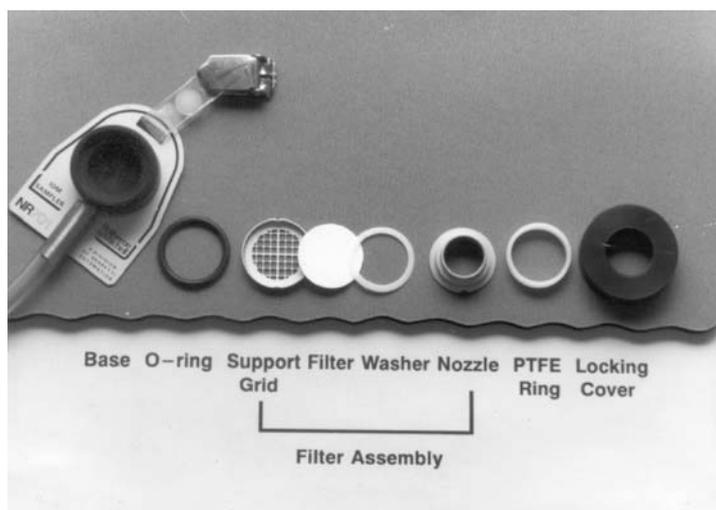
### Filters

Aerosols are usually sampled by drawing the atmosphere to be tested through a glass fibre filter which has been coated with a derivatizing reagent. After the sampling process has been completed, the filter is washed with a suitable solvent. The diisocyanate–reagent reaction product is then analysed using one of several laboratory methods. Commonly used filter designs are shown below (Figures 5.7.5 and 5.7.6).



**Figure 5.7.5** Commonly used filters for sampling diisocyanates: (a) 13 mm filter; (b) 37 mm filter; (c) 90 mm filter

When aerosols comprising reacting diisocyanate mix are collected on a reagent-coated filter, a problem arises due to competitive reactions: the continuing polyurethane formation and the reaction of the derivatization reagent with the diisocyanate. The latter can take place only on the surface of the collected aerosol particle, whereas the polyurethane reaction continues throughout the particle. This explains the observation that samples of reacting mix collected on filters which were not desorbed in the field gave consistently lower results than those collected in impingers. Studies in which filter samples were desorbed in the field immediately after sampling show that such filter samples and impinger samples gave comparable results (Karoly, 1998).



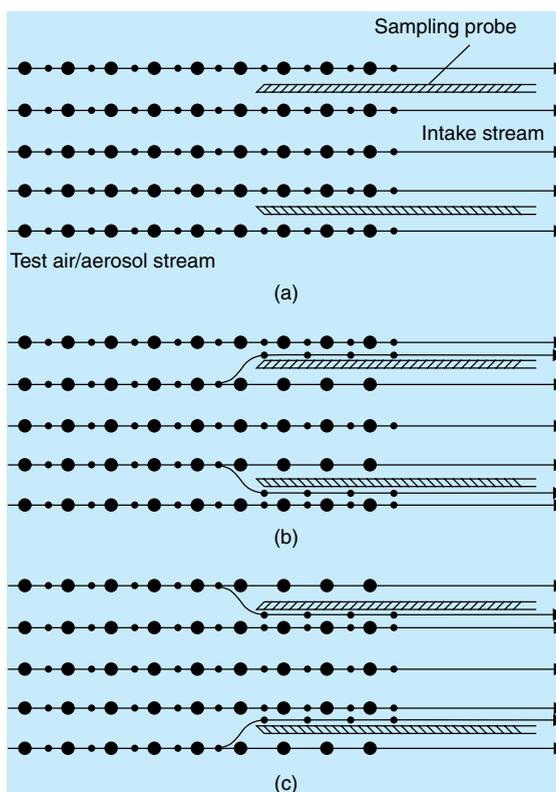
**Figure 5.7.6** Institute of Occupational Medicine (IOM) sampler. This sampler is designed to be clipped to a subject's chest

### **Aerosol sampling**

When an air stream is sampled, the intake velocity of the sampler relative to the velocity of the air stream is a significant factor. Sampling is said to be *isokinetic* if the probe intake stream has the same velocity as the air stream, and *anisokinetic* if the two velocities differ. Relative air stream velocities are important only in aerosol sampling and Figure 5.7.7 illustrates what happens when a given air stream containing an aerosol is sampled using the same sampling probe, but with different intake velocities. The figure shows notional mixed streams of very small, light, gas-like particles and large, much heavier, particles in air. In Example 1 (Figure 5.7.7 (a)), the test stream (air/aerosol) and the sampling intake stream move at the same speed (isokinetic sampling) and the sample taken in by the probe is representative of the test stream. In Example 2 (Figure 5.7.7 (b)), the intake stream moves much more slowly than the test air/aerosol stream (anisokinetic sampling). The larger particles are not diverted from their path because of their greater momentum. The excess of the test stream flows around the probe, taking with it the gas-like particles of lower momentum and thus, this gives rise to *under-sampling* of the aerosol. In Example 3 (Figure 5.7.7 (c)), the intake stream moves much faster than the test stream. Excess test stream enters the probe taking with it excess of the gas-like aerosols. Thus, this gives rise to *over-sampling* of the aerosol.

### **Comparisons of aerosol sampling methods**

When impingers alone are used for measuring the MDI concentrations, the results are lower than those obtained using reagent-coated filter methods. Several studies by various investigators showed anomalous and contradictory results when different sampling and analysis methods for MDI were compared in the field and in laboratory generated atmospheres. The experimental methods and results from selected studies are summarized in Table 5.7.5.



**Figure 5.7.7** Isokinetic sampling. (a) Isokinetic sampling: the intake stream and the air/aerosol stream move at the same speed. (b) Anisokinetic sampling: the intake stream moves much slower than the air/aerosol stream. (c) Anisokinetic sampling: the intake stream moves much faster than the air/aerosol stream

In some MDI atmospheres impingers performed better than coated filters and in others the reverse occurred. The same impinger and coated filter methods did not show these differences in their efficiencies for TDI in either laboratory generated or field atmospheres. From all of these studies it became apparent that the collection efficiency of a sampler was highly dependent on the MDI aerosol size distribution.

When aerosols were sampled by the use of a filter or an impinger alone, the particle size distribution of the aerosol had a significant effect on the accuracy of the results. This, together with lack of information on whether the aerosols were sampled under isokinetic conditions, may explain many of the confusing results in Table 5.7.5.

### Determination of particle size

It is often important to characterize the size distribution of aerosols for several reasons. The sizes of particles are important determinants of the sites of deposition in the respiratory tract. Aerosol size also determines the stability of the aerosol in air, important in determining fallout in a workplace or in the environment. Finally, the methods used for sampling depend very much on the physical characteristics of the aerosol.

Table 5.7.5 Selected studies comparing sampling methods for MDI aerosols.<sup>a</sup>

Sampling / analysis	Aerosol generation methods	Aerosol-size measurement method	Results	Reference
1. Marcali impinger / colorimetry 2. Teflon filter + Marcali impinger / colorimetry	Spray foaming of PMDI	None	MDI in air in aerosol form	Dharmarajan and Weill (1978)
1. MAMA-coated XAD-2 / HPLC 2. MAMA-coated sponge / HPLC 3. MAMA impinger / HPLC 4. Nitro-impinger / HPLC 5. Nitro-coated filter / HPLC	(1) Lab-nebulizer / pure MDI (2) Field-spray operation / PMDI	TSI 3020 Condensation Nuclei Counter (CMAD = 0.1 μm)	Laboratory: Impingers < MAMA XAD-2 Impingers < MAMA sponge Field: Nitro filter < impinger	Andersson <i>et al.</i> (1982, 1983)
1. Nitro-coated filter / HPLC 2. Nitro-coated glass wool / HPLC 3. Nitro-impinger / HPLC 4. Nitro-fritted bubbler / HPLC	Heating pure MDI to 135 °C and diluting MDI vapour with room temperature air	MMAD = 0.6 GSD = 2.2 TSI 3030 aerosol size counter	Impinger < filter Impinger < glass wool Bubbler < filter	Tucker and Arnold (1982)
1. Nitro-coated filter / HPLC 2. Nitro-impinger / HPLC 3. H <sub>2</sub> SO <sub>4</sub> -coated filter / HPLC 4. Marcali impinger / colorimetry	Heating pure MDI (65 to 115 °C) and diluting vapour with room temperature air	80 % of aerosols < 1.9 μm MMAD. (parallel stage impactor)	In static atmosphere: Impingers < coated filters In dynamic atmosphere: Impingers ≅ coated filters	Booth <i>et al.</i> (1983), Dharmarajan <i>et al.</i> (1987)
1. Nitro-coated filter / HPLC 2. Filter / gravimetry 3. Acid impinger / colorimetry 4. Nitro-coated glass wool / HPLC 5. Nitro-impinger / HPLC	Nebulizer / PMDI	Berkeley QCM cascade monitor	Impinger < gravimetric filter Impinger ≅ nitro-coated filter Impinger < glass wool Filter < glass wool Glass wool ≅ gravimetric	Reuzel <i>et al.</i> (1986)
1. Nitro-impinger / TLC or HPLC 2. Gravimetric filter / photometry 3. 13 mm 1,2-PP and DEP coated filter	Nebulizer Heating MDI (90 to 120 °C) and diluting with air	Particles > 3 μm removed with a cyclone. MMAD = 0.8 μm Parallel stage impactor	Impinger > 3 μm removed with a cyclone. MMAD = 0.8 μm Impinger > 1,2-PP-coated filter Impinger ≅ DEP + 1, 2-PP coated filter	Aufsatz <i>et al.</i> (1981) Coyne <i>et al.</i> (1988)

<sup>a</sup> These studies should be compared with that of the later International Isocyanate Institute study (below) which used aerosols of known particle size distribution, and included isokinetic sampling.  
< = worse than.  
> = better than.

≅ = about the same as.

Nitro- = nitroreagent.

DEP = diethylphthalate.

XAD-2 is a cross-linked styrene polymer (Amberlite™ XAD-2) manufactured by Rohm and Haas.

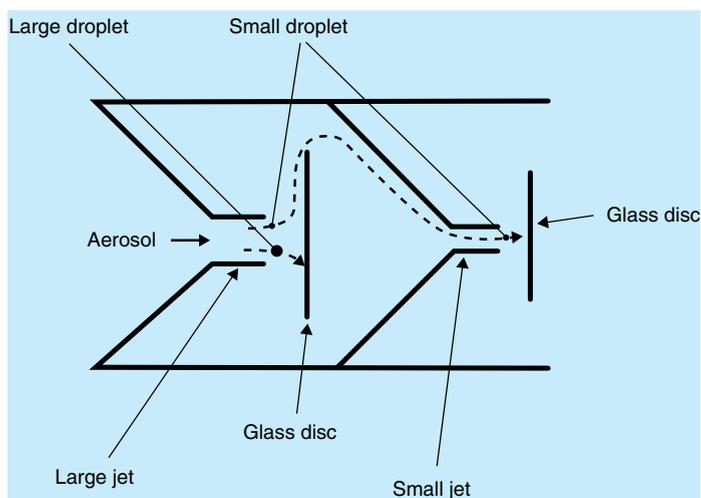
GSD = geometric standard deviation.

MMAD = mass median aerodynamic diameter.

CMAD = count median aerodynamic diameter.

See later for detailed discussion of the reagents MAMA, nitroreagent, 1,2-PP and the Marcali method.

Mass concentrations of particulates are normally measured by drawing air through a suitable filter. The particle size distribution of diisocyanate aerosols has usually been determined by the use of a cascade impactor, for example, see Bürkholz *et al.* (1977). This device consists of a series of air jets of decreasing diameter, with each jet followed by a removable disc. When the aerosol passes through each jet, the larger particles strike, and collect on, the disc, whilst the smaller particles remain in the air stream until the next jet. The decreasing size of the jets, with a corresponding increase in velocity of the particles, leads to the collection of ever smaller particles (Figure 5.7.8).



**Figure 5.7.8 Cascade impactor: droplet separation mechanism (figure reproduced by courtesy of Bayer AG)**

Experimental parameters have to be adjusted so that the amounts deposited are not more than a few milligrams. The sampling time, which has to be determined by the aerosol concentration, may be several minutes up to 2 h (Bürkholz *et al.*, 1980). The mean particle size deposited on each disc is a fixed parameter, known from calibration measurements. It can also be theoretically determined. If only a few particles collect on a disc they can be counted, but gravimetry or chemical analysis are more usual. The particle size distribution is determined by comparing the weights on the discs, and the mass median aerodynamic diameter (MMAD) of the aerosol can be calculated. The total aerosol concentration can also be calculated from the sampling volume. The cumulative number distribution of particles can be used to calculate the number mean aerodynamic diameter (NMAD), and hence the MMAD.

*Aerodynamic diameter* is a term related to the settling characteristics of an aerosol particle and is not the same as the physical size of the particle. Aerosol distributions are usually defined by one or more of the following terms:

- MMAD mass median aerodynamic diameter;
- CMAD count median aerodynamic diameter;
- NMAD number mean aerodynamic diameter.

The TSI laser velocimeter APS 3300 has also been cited for monitoring aerosol mass and for particle size analysis in animal studies using 4,4'-MDI and polymeric MDI (Pauluhn and Mohr, 1994; Pauluhn *et al.*, 1999). This real time particle size analyser is based on the principle of particle lag

in an accelerating flow. The airborne aerosol passes through an orifice into a chamber at reduced pressure. Immediately after the nozzle the particles lag behind the air due to their inertia, and the degree of lag is dependent on the particle aerodynamic diameter. The velocity of the particles is measured by a two-spot laser Doppler velocimeter. A particle passing through the two beams produces two pulses, with the time difference between the pulses indicating the particle velocity. The velocities are electronically converted to aerodynamic diameters and hence the number particle size distribution. The size range measured is 0.5 to 15  $\mu\text{m}$  (Remiarz *et al.*, 1983).

Light scattering can also be used for particle size determinations. A measuring cell, through which the aerosol flows, is illuminated by a sharply focused beam, and each particle scatters light according to its size. This scattered light is collected and analysed. The method has been used to analyse 4,4'-MDI aerosols (Bürkholz *et al.*, 1980), but it is normally used to monitor aerosol concentration. A Simslin aerosol light-scattering photometer was used in a polymeric MDI chronic inhalation toxicity and carcinogenicity study (Reuzel *et al.*, 1994).

### The International Isocyanate Institute study

A detailed study was carried out by the International Isocyanate Institute (III) (Hext, 1996, Hext, 2002) to evaluate the collection efficiencies of various sampling methods routinely used for polymeric MDI. Aerosols of various aerodynamic diameters:

small	0.1 to 3 $\mu\text{m}$
large	5 to 30 $\mu\text{m}$
very large	>30 $\mu\text{m}$

Aerosols of up to about 5  $\mu\text{m}$  are respirable and can pass into the lungs. Larger particles have a lower capability of penetrating the respiratory system; see *Part 3, Health*.

were generated. Insofar as it was experimentally possible, two target concentrations (0.1 and 1.0  $\text{mg}/\text{m}^3$ ) were chosen for study at each diameter range. The performances of test samplers were compared to that of an isokinetic reference sampler, which was a 25 mm diameter glass-fibre filter coated with 1,2-MP. The samplers used are listed in Table 5.7.6.

As it is very difficult to produce aerosols to a specification of concentration or size, the study strategy was to generate an MDI atmosphere and measure the size and concentration simultaneously with a reference and the test methods. The aerosol size distribution was determined for every run using a Marple™ cascade impactor.

### Conclusions from the III study on MDI aerosol sampling

- The IOM sampler was the most consistent sampler, but was prone to over-sample when used as an area monitor unless a backing disc was present to compensate for the fact that the sampler was designed for personal monitoring.
- All the samplers showed some variability in collection efficiencies. All were adequate for PMDI particles around 1 to 20  $\mu\text{m}$  in size; variability was high with very large particles.

**Table 5.7.6 Samplers used in the International Isocyanate Institute study.**

Sampler	Sampling rate l/min	Derivatizing reagent
Institute of Occupational Medicine (IOM)	2	1, 2-MP + DEP
13 mm filter	1	1, 2-MP + DEP
13 mm filter	1	1, 2-PP + DEP
37 mm filter	1	1, 2-MP + DEP
37 mm filter	1	1,2-MP <sup>a</sup>
Mini-impinger	1	1,2-MP
Mini-impinger/filter	1	1, 2-MP + DEP
Glass tube	2	Nitroreagent
Glass tube/filter	2	1, 2-MP + DEP
Isokinetic sampler	1.18	1, 2-MP + DEP
Isokinetic sampler	1.18	1, 2-PP + DEP <sup>b</sup>
Paper-tape monitors (a) GMD-RIS (b) MDA-SPM	Manufacturers' recommended settings	

<sup>a</sup>Used only for large particles.

<sup>b</sup>Used when experimental runs included 13 mm filter impregnated with 1,2-PP + DEP reagent.

1,2-MP: 1-(2-methoxyphenyl)piperazine.

DEP: diethylphthalate.

1,2-PP: 1-(2-pyridyl)piperazine.

Nitroreagent: (*N*-4-nitrobenzyl-*N*-*n*-propylamine).

- The paper tape monitors showed low total efficiencies with all particle sizes, with the larger particle sizes showing least efficiency.
- The mini-impinger had poor collection efficiency for the small particle size range.
- The glass tube using nitroreagent had good collection efficiency at 0.1 mg/m<sup>3</sup>.
- Over-sampling often increased with increasing particle size. This was most pronounced with the 37 mm filter (largest filter area).
- With all filter samplers, the holders did not contribute significantly to the total efficiency at the small particle size range.
- With all filter samplers, the holders contributed significantly to the total efficiency over the large and very large particle size ranges.
- At the small particle size range and 0.1 mg/m<sup>3</sup> concentration, there were no statistically significant differences in total efficiencies between any of the samplers.

More detailed conclusions on the samplers tested are given below.

#### **Paper tape monitors for MDI**

The paper tape monitors (MDA Scientific Inc., Model SPM and GMD Systems Inc., Model RIS, both operated at the flow rates recommended by

**Table 5.7.7 Performance of paper tape monitors with aerosols of polymeric MDI.**

Paper tape monitor	Particle diameter range of the test atmosphere <sup>a</sup> μm	Target atmosphere concentration mg/m <sup>3</sup>	Efficiency <sup>b</sup> %
MDA SPM	0.3 to 1.2 (small)	0.1	35 ± 13 (n = 8)
MDA SPM	0.2 to 1.0 (small)	1	22 ± 4 (n = 11)
MDA SPM	5 to 23 (large)	0.1	1 ± 2 (n = 7)
MDA SPM	5 to 29 (large)	1	2 ± 3 (n = 5)
MDA SPM	31 to 117 (v. large)	1	4 ± 7 (n = 5)
GMD RIS	0.3 to 1.2 (small)	0.1	45 ± 18 (n = 9)
GMD RIS	0.2 to 1.0 (small)	1	23 ± 11 (n = 11)
GMD RIS	12 to 19 (large)	0.1	31 ± 36 (n = 4)
GMD RIS	5 to 24 (large)	1	2 ± 1 (n = 4)
GMD RIS	31 to 43 (v. large)	1	3 ± 2 (n = 2)

<sup>a</sup>Mass median aerodynamic diameter.

<sup>b</sup>n = number of experiments.

the manufacturer) did not work very efficiently for aerosols of polymeric MDI in any size range in this study (Table 5.7.7).

The efficiency was defined as

$$\frac{\text{Concentration of isocyanate by paper tape analysis}}{\text{Concentration of isocyanate by isokinetic analysis}} \times 100$$

where the concentration of isocyanate by isokinetic analysis is the sum of the diisocyanate and triisocyanate concentrations measured using the isokinetic sampler. It should be borne in mind that the design of the study required the use of inlet tubes on the paper tape monitors at the maximum length recommended by the manufacturers. This may have resulted in some adsorptive or deposition losses on the tube surfaces.

With small particles the tape monitors under-sampled, sampling efficiencies ranging from 22 to 45 % for the monitors tested at both concentrations. The study also showed that paper tape monitors significantly underestimated polymeric MDI concentrations in atmospheres with particle diameters greater than 5 μm. For the large and the very large particles the efficiency was generally low, typically less than 7 %.

#### **IOM filter sampler**

*Institute of Occupational Medicine (IOM) sampler with 25 mm glass-fibre filter coated with 1-(2-methoxyphenyl)piperazine (1,2-MP) and diethylphthalate (DEP) reagent, operated at a flow rate of 2.0 l/min*

- The collection efficiency for the small particles was about 100 %, at both target concentrations. This was attributable entirely to the aerosol collected on the filter.
- For the large particles the collection efficiency of the filter was 86 and 74 % for the 1.0 and 0.1 mg/m<sup>3</sup> concentrations, respectively; however, a portion of the total aerosol collected was on the filter holder (39 and 55 %, respectively).

- For the very large particles there was a marked and variable mean over-sampling by the filter ( $210\% \pm 194\%$ ) with a small quantity collected on the holder ( $22\%$ ).

#### **13 mm filter sampler (1,2-MP reagent)**

*13 mm glass-fibre filter coated with 1,2-MP and DEP in a Millipore Swinnex™ cassette operated at a flow rate of 1.0 l/min*

- The small particles at both target concentrations were collected almost entirely by the filter; a slight over-sampling was noted (collection efficiencies of 135 and 117% were observed for the 1.0 and 0.1 mg/m<sup>3</sup> concentration levels, respectively).
- For large particles there was variation in the total collection efficiency (collection efficiencies of 169 and 137% for the 1.0, and 0.1 mg/m<sup>3</sup>, respectively) and in the quantities of aerosol collected on the filter (82 and 33%, respectively) or holder (87 and 104%, respectively).
- For very large particles there was a marked and variable mean over-sampling by the filter ( $214\% \pm 124\%$ ) with a large but variable quantity collected also on the holder ( $185\% \pm 184\%$ ).

#### **13 mm filter sampler (1,2-PP reagent)**

*13 mm glass-fibre filter coated with 1-(2-pyridyl)piperazine (1,2-PP) and DEP in a Millipore Swinnex™ cassette, operated at a flow rate of 1.0 l/min*

- The small particles at both target concentrations were collected predominantly by the filter. Under-sampling was apparent at the target concentration of 1.0 mg/m<sup>3</sup> (collection efficiency 76%) whereas at 0.1 mg/m<sup>3</sup> over-sampling was observed (collection efficiency 117%).
- For large particles some variation was seen between the collection filter (collection efficiencies of 3 and 52% for the 1.0 and 0.1 mg/m<sup>3</sup>, respectively) and the filter holder (collection efficiencies of 56 and 29% for the 1.0 and 0.1 mg/m<sup>3</sup>, respectively). The whole assembly under-sampled (total collection efficiencies of 59 and 81% for the 1.0 and 0.1 mg/m<sup>3</sup>, respectively).
- At the very large particles, aerosol was collected on both filter and holder with the total efficiency showing under-sampling (total collection efficiency of 77%).

#### **37 mm filter sampler (1,2-MP reagent)**

*37 mm glass-fibre filter coated with 1,2-MP and DEP in a Millipore™ cassette, operated at a flow rate of 1.0 l/min*

- For small particles there was under-sampling at 1 mg/m<sup>3</sup> (collection efficiency of 70%) whereas there was over-sampling at 0.1 mg/m<sup>3</sup> (collection efficiency of 171%).
- Over-sampling became pronounced for the large particles (collection efficiencies of  $751\% \pm 1077\%$  and  $480\% \pm 491\%$  for the 1.0 and 0.1 mg/m<sup>3</sup> respectively) and very large particles (collection efficiency  $1491\% \pm 1276\%$ ).

**Mini-impinger (1,2-MP reagent)**

*Mini-impinger containing 1,2-MP in toluene backed up with 25 mm glass-fibre filter coated with 1,2-MP in a closed-face cassette operated at a flow rate of 1.0 l/min. A back-up filter impregnated with 1,2-MP reagent was attached to the exiting air from this sampler to detect any breakthrough by the test aerosol.*

- For small particles 60 to 65 % of the aerosol passed through the impinger and was trapped on the back-up filter. Total collection efficiencies for these concentrations were 109 and 113 %, respectively.
- For the large particles the majority of the aerosol collected was trapped in the impinger medium. Mean total collection efficiencies were 142 and 111 % at 1.0 and 0.1 mg/m<sup>3</sup>, respectively.
- For the very large particles variation of 93 to 293 % between total collection efficiencies for individual samplers was seen with limited breakthrough onto the back-up filter. The mean collection efficiency at this particle size was 186 %.

**Glass tube (nitroreagent)**

*Glass tube containing glass wool coated with nitroreagent (N-4-nitrobenzyl-N-n-propylamine) backed up with 25 mm glass-fibre filter coated with 1,2-MP in a closed-face cassette operated at a flow rate of 1.0 l/min. A back-up filter impregnated with 1,2-MP reagent was attached to the exiting air from this sampler to detect any breakthrough by the test aerosol.*

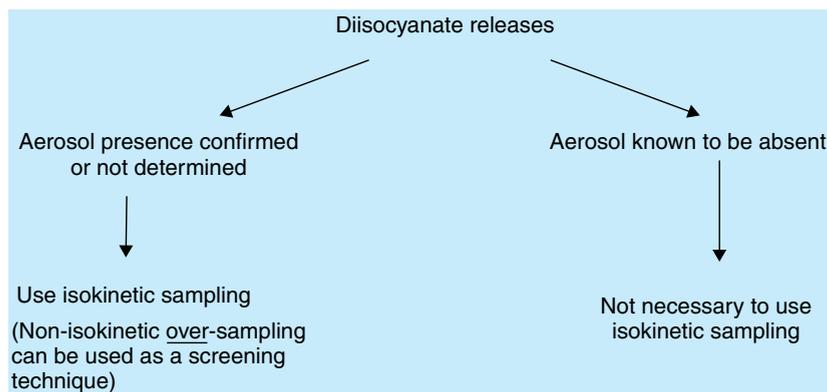
- For small particles there was evidence of a small breakthrough (4 to 7 %). Total collection efficiencies for the 1.0 and 0.1 mg/m<sup>3</sup> concentrations were 48 and 106 %, respectively.
- Mean total collection efficiencies for the large particles were virtually identical at both concentrations (72 and 70 % for the 1.0 and 0.1 mg/m<sup>3</sup>, respectively) although there were variations between individual samplers with respect to breakthrough onto the back-up filter.
- For the very large particles there was a marked variation between individual samplers with evidence for both under-sampling and over-sampling (collection efficiency 121 % ± 110 %).

**Stack monitoring**

Monitoring is carried out to determine the concentration of materials entering the atmosphere from workplace operations. In some countries regulations relating to MDI and TDI require the reporting of ex stack concentrations, the mass loss rates from the stack, or even the calculated concentration of material in the air at the fence line of the production site. Low concentrations only of MDI and TDI are normally released from stacks of polyurethane operations.

In a small number of operations aerosols may be present in the exhaust air. It is important to recognize that the passage of aerosols through the exhaust ducting depends on the aerosol size distribution. Large aerosol particles tend to be deposited onto the ducting, especially where bends in the ducting give rise to turbulent conditions. In such situations, concentrations of aerosol will decrease along the ducting and stack. The smaller the aerosol, the more gas-like is the behaviour in the ducting and ex stack.

In situations where aerosols are emitted from the stack, it may be necessary to consider isokinetic sampling (Figure 5.7.9). One regulatory authority indicates that, if aerosols are of diameter less than  $3\ \mu\text{m}$ , specific aerosol capture is not required. Measurements to characterize the air released should be made just before the stack outlet. It may also be necessary to model the deposition of aerosols in fence-line concentration calculations (see *Part 5.6, Occupational exposure limits, stack limits and community limits*).



**Figure 5.7.9 Sampling stack releases of diisocyanates**

The USEPA has submitted a very cumbersome sampling method (Draft Method 207–1) for adoption. This method is difficult to operate and involves the use of an extremely large sampling train (Figure 5.7.10), which is too big to mount onto some stacks.

#### Sampling method for isocyanates: USEPA Draft Method 207-1

In this method (USEPA, 1998a) isocyanates, as vapour or aerosol, are sampled from the stack at an isokinetic sampling rate and are collected in a multi-component sampling train. The components of the train include a heated probe, impingers containing the derivatizing agent, 1-(2-pyridyl)piperazine in toluene, an empty impinger, an impinger containing charcoal and an impinger containing silica gel. The collected samples are analyzed by HPLC, as described in USEPA Draft Method 207-2 (USEPA, 1998b).

#### Screening method for MDI: USEPA Conditional Test Method 31

In this method (USEPA, 1999) MDI emissions, as vapour or aerosol, are sampled from the stack at a sub-isokinetic sampling rate. They are collected on a 13 mm glass-fibre filter coated with 1.0 mg of either 1-(2-methoxyphenyl)piperazine or 1-(2-pyridyl)piperazine. The sampling train includes a glass nozzle with a  $90^\circ$  bend, a filter cassette and a personal sampling pump. The collected samples are analysed by HPLC, as described in OSHA Method 47.

The USEPA has been collaborating with industry on releases of MDI from stacks, focusing on total MDI released per annum, rather than on ex stack concentrations. In view of the difficulty of using Draft Method 207-1, industry submitted for acceptance a screening method for use with MDI (USEPA Conditional Test Method 31), which is sub-isokinetic. Since the method tends to give over-sampling, industry may perform this less expensive procedure. As stated in the method, if the obtained results are less than the regulatory limit a more rigorous method is not necessary. However, if the results are near the limit a method such as Draft Method 207–1 will have to be employed.

In the case of TDI, however, several

**Method for measurement of TDI: USEPA Conditional Test Method 36**

In this method (USEPA, 2000) TDI emissions are withdrawn from the emission source at an isokinetic sampling rate and are collected on a 90 mm glass-fibre filter coated with 10 to 12  $\mu\text{g}/\text{mm}^2$  of 1-(2-pyridyl)piperazine or 1-(2-methoxyphenyl)piperazine. The primary components of the sampling train include a filter cassette and a sampling pump. The collected samples are analysed by HPLC.

options may be available depending on the local regulations. One method for TDI (CTM 36) has been accepted by the USEPA as an alternative for Draft Method 207-1.

Four other methods, listed in Table 5.7.8, have been passed through the USEPA Method 301 validation programme (API, 2000).

**Methodology: practical aspects of the analysis of MDI and TDI**

This section discusses the methods, both current and past, that have been used to analyse MDI and TDI. Because in several methods the sampling and analysis stages are intimately connected, it is appropriate to discuss them together. The general principles for sampling vapours and aerosols which have already been discussed will therefore need to be borne in mind when considering the details of several of the analytical methods below. Whilst some of the methods are no longer preferred by many analysts, a discussion is included so that readers are able to make informed judgments on the relevance of some of the older results published in the literature.

Air monitoring techniques for MDI and TDI may broadly be classified as either direct-reading or indirect methods. The following steps comprise all monitoring methods, whether direct or indirect:

- representative sampling of the air;
- efficient collection of the analyte;
- trapping and stabilization of the analyte;
- proper storage of the collected analyte;
- preparation of the sample for analysis;
- analysis of the sample collected;
- reporting of the concentration of the analyte in the air.

In direct-reading methods, most of the above steps are accomplished almost simultaneously and *in situ* by the use of appropriate instruments or techniques. In indirect methods, the MDI and TDI are collected on some suitable sampling medium and the samples are then passed to an analytical laboratory, where they are processed and analysed by techniques such as high performance liquid chromatography, gas chromatography or spectrophotometry. Thus the results of measurements are obtained long after sampling in the case of indirect methods. The indirect methods yield a single time-weighted average concentration of the analyte, averaged over the sampling period, whereas many direct-reading instruments can give both the instantaneous airborne concentrations of MDI and TDI and their variation over a time period. Direct-reading methods are also capable of giving the time-weighted average concentration of the analyte over the sampling period as do the indirect methods. Although indirect methods are labour intensive, they are used routinely by many hygienists

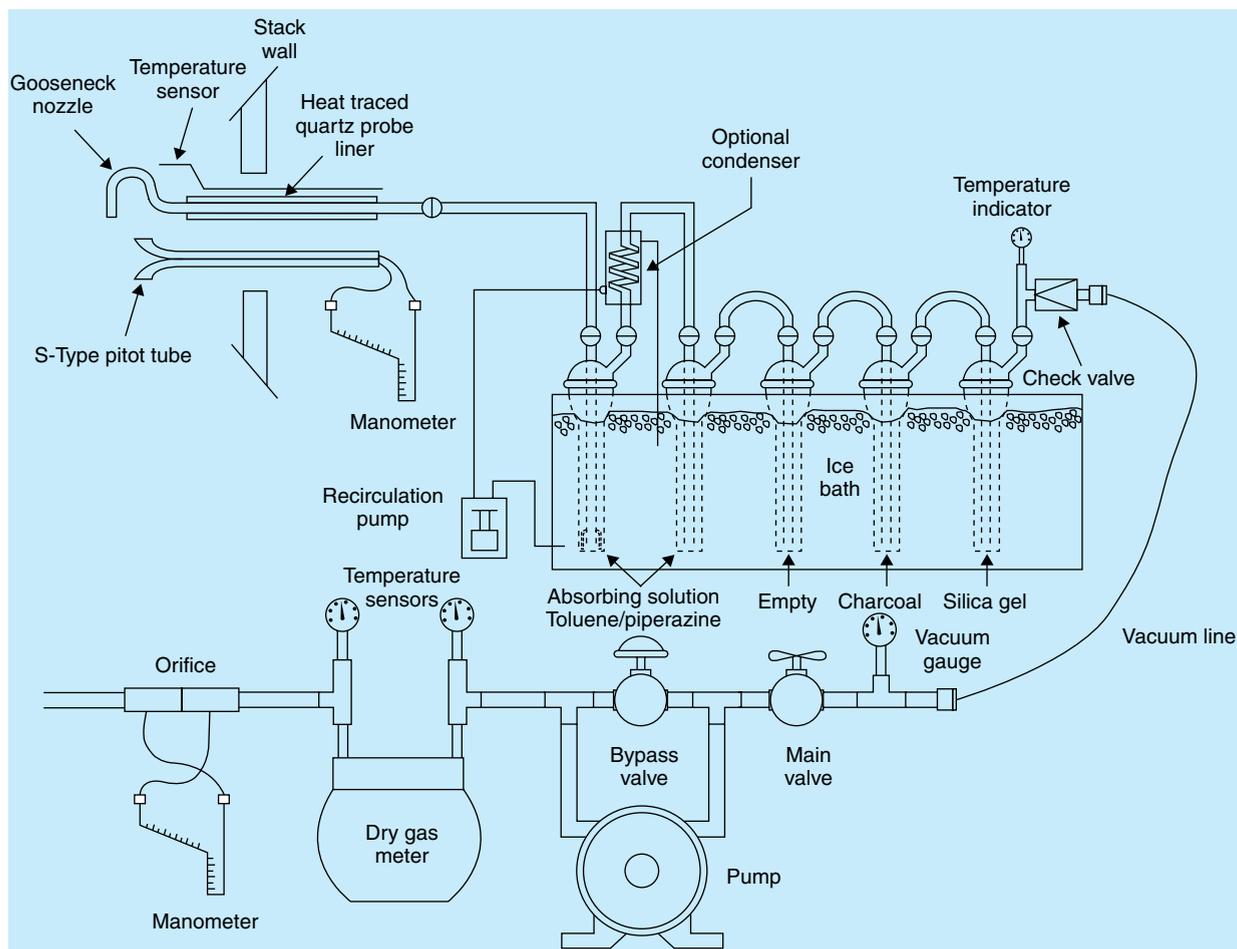


Figure 5.7.10 USEPA stack sampling train (adapted from the US Federal Register 1997, volume 62, no. 235)

Table 5.7.8 Summary of test methods validated by USEPA method 301.

Method identification <sup>a</sup>	Sampling protocol
NIOSH 5521	Midget impingers charged with 1-(2-methoxyphenyl)piperazine in toluene
OSHA 18	Midget impingers charged with <i>N</i> -4-nitrobenzyl- <i>N</i> - <i>n</i> -propylamine in toluene
MDHS 25/2	Midget impinger charged with 1-(2-methoxyphenyl)piperazine in toluene
OSHA 42	37 mm glass-fibre filter impregnated with 1-(2-pyridyl)piperazine

<sup>a</sup>All methods employ high performance liquid chromatography with a UV detector for analysis of diisocyanates.

because government agencies require their use to verify compliance with exposure standards.

### **Direct-reading methods for monitoring MDI and TDI**

#### ***Paper tape methods***

At the present time paper tape monitors are the most widely used direct-reading instruments available for MDI and TDI. Manufacturers of paper tape monitors for MDI and TDI include MDA Scientific, a subsidiary of Zellweger Analytics, and Scott/Bacharach.

Paper tape monitors are based on the collection of diisocyanates onto chemically impregnated filter paper tapes which move continuously or step wise across a sampling port. The diisocyanates react with the chemicals on the tape to produce a characteristic colour stain. The intensity of the colour stain is proportional to the concentration of diisocyanates in the air and is measured photometrically. Portable paper tape monitors run on rechargeable batteries and use a paper tape cassette which can be used continuously for many hours. The diisocyanate concentration measured is displayed and there may be audible and visual warning signals of excursions above a regulatory exposure limit. The readings may be stored electronically in data-logging systems. At the end of a sampling session, the data stored electronically can be retrieved and can be printed out or downloaded to a computer. The data stored can be analysed electronically in several ways to provide useful information such as the time-weighted average, and the occurrence and duration of concentrations above a set limit. Graphs of concentrations against time may be displayed instantaneously to give an indication of the exposure profile, which is useful to detect leaks, or other problems in procedures, processes or locations. The area (stationary) paper tape monitors essentially perform all of the above operations for periods as long as 1 month without change of tape.

#### **Paper tape monitors: hints on use**

- Check all of the manufacturer's recommended settings, especially the sampling flow rate, and the optical calibration.
- Do not use time-expired tapes. Store tapes according to the manufacturer's instructions.
- Tape monitors may not be effective in very dry or very wet atmospheres. Follow the manufacturer's specifications.
- Avoid the use of probe-extension tubing. If extension is unavoidable, use a silanized-glass probe of maximum length 15 cm (6 inches) to minimize adsorption losses.
- If the monitoring situation is unfamiliar take the tape cassette out of the monitor and inspect the coloured spots closely. Tape monitor readings may not be accurate in aerosol, spray or dusty environments and in the presence of interfering chemicals such as chlorine, and oxides of nitrogen and of sulphur. If the colours of the spots are not characteristic of the stain produced by MDI or TDI, there may be some

interfering species in the air causing the discoloration or bleaching of the tape, which may lead to over- or underestimation of the diisocyanate concentrations. Therefore the area should be monitored by other methods to determine the source of the interference.

- Do not assume that tape monitors are suitable for local regulatory compliance purposes.

Although the basic concept of paper tape monitors is sound, they may have limitations of which the user should be aware. The main problems relate to relative humidity, aerosols and chemical interferences. Several studies have been performed to evaluate paper tape monitors. Most of these studies have been carried out on monitors which are no longer available commercially, having been replaced by updated instruments. The studies are nevertheless discussed below because some of the findings are still relevant.

#### *Evaluation of paper tape monitors*

Neilson and Booth (1975);  
Miller and Mueller (1975);  
Momborg and McCammon (1976); Dharmarajan and Rando (1980); Walker and Pinches (1981);  
Dharmarajan (1996);  
Hext (1996).

Evaluation of personal continuous monitors then available from GMD Systems (now Scott/Bacharach) as GMD-PCMs™ (Dharmarajan, 1996) and from MDA Scientific as the Isologger™ (Booth and Dharmarajan, 1996) in dynamically generated TDI atmospheres indicated that humidity significantly affected the responses of the paper tape monitors. The chemistries of the paper tapes used by MDA and GMD were different, and the effects of humidity were also different on these monitors. At 50 % relative humidity (RH), the Isologgers™ read the TDI concentrations correctly. However, at lower humidities they read about 20 % lower than, and at higher humidities (75 % RH) they read 20 % higher than, the true concentrations. At humidities greater than 75 % the Isologger™ used a high-humidity calibration table to correct for the effects of humidity on the tape. In contrast, the GMD-PCM™ monitors tended to read the TDI concentrations correctly at lower humidities (approximately 30 % RH), but at higher humidities the responses of the GMD-PCMs™ were generally lower than the true concentrations. The effect of humidity on the performance of paper tape monitors for MDI has not been critically evaluated.

Paper tape monitors have been found to be satisfactory for MDI vapour over the range of air temperatures associated with most polyurethane processes. For polymeric MDI this relates to 3 to 22 ppb (saturated vapour concentration at 20 to 35 °C).

In general, tape manufacturers calibrate instruments for MDI using 4,4'-MDI. However, for many applications polymeric MDI is used which contains approximately 50 % diisocyanate, about 25 % triisocyanate and the remaining 25 % is made up almost entirely of higher molecular weight isocyanates (see Figure 5.1.1). There are a number of calibration curves available for polymeric species.

In concentrations of less than 0.1 mg/m<sup>3</sup> (which is less than about 10 ppb) where 4,4'-MDI is present predominantly as vapour, the paper tape instruments may be used. In greater concentrations where aerosols may be present, great care should be exercised in interpreting the readings of paper tape instruments. In spite of all the limitations of paper tape instruments, they are still useful instruments for screening purposes and for the measurement of spike exposures (1 to 5 min).

Initially, the manufacturers of paper tape monitors recommended their instruments for all sampling of MDI, based on calibrations performed in their own laboratories. However, evaluation of the paper tape monitors in other laboratory-generated atmospheres produced unreliable and inconsistent results when aerosols were present. It became apparent that the inconsistencies observed with MDI tape monitors may have been due to differences in the size distribution of MDI aerosol atmospheres between those used for calibration and those used for testing. The manufacturers of paper tape instruments have made several modifications to their instruments to improve the capture efficiency of airborne MDI and the reaction of MDI with the paper tape. An extensive study has been carried out of two particular paper tape monitors with aerosols of polymeric MDI (see *The International Isocyanate Institute study* above). In this study, these particular instruments severely underestimated the true concentrations of polymeric MDI.

The reliability and accuracy of paper tape instruments may be affected by the presence of interfering chemicals such as nitric oxide, nitrogen dioxide and sulphur dioxide (Dharmarajan and Rando, 1980). Nitric oxide, nitrogen dioxide and chlorine interfere positively: for example, 2 ppm of chlorine gave a reading equivalent to about 22 ppb of TDI, 8 ppm of nitrogen dioxide produced a response of about 12 ppb TDI and 40 ppm of nitric oxide gave a reading about 13 ppb of TDI with the MDA Model 7000<sup>TM</sup> TDI monitor. Excessive amounts of dust (such as foam dust, sand from foundry moulding using MDI), paint spray aerosol (especially coloured paint) and even water droplets in the air may affect the photometric measurement in a paper tape monitor, thereby affecting the readings. Aromatic amines, phosgene, monochlorobenzene, carbon monoxide, and other chemicals used in the manufacture of MDI and TDI do not cause interferences in the paper tape method. Commonly used catalysts and solvents in polyurethane industries also do not interfere with the paper tape monitors for TDI (Walker and Pinches, 1981).

Various other direct-reading devices based on paper tape technology are available. Chemically impregnated filter paper in the form of a disc can be used in a static mode. Such discs can be placed across the port of a sampling device, or can be used as a personal badges.

### **GMD Sure-Spot<sup>TM</sup>**

In the GMD Sure-Spot<sup>TM</sup> equipment (Figure 5.7.11) air is drawn through a chemically impregnated filter paper at 1.5 l/min for up to 10 min using a battery-operated pump. The isocyanates react with the reagent on the filter paper to produce a coloured stain. The stain intensity on the paper is measured either visually by comparison with a colour intensity reference chart, or electronically using a simple optical densitometer.

The Sure-Spot<sup>TM</sup> technique affords a simple and inexpensive method for the quick screening of MDI and TDI concentrations in air. The factors that affect paper tape monitors in general will also affect the Sure-Spot<sup>TM</sup>. The manufacturers of the Sure-Spot<sup>TM</sup> have issued calibration data obtained using MDI vapour and fine aerosols of MDI. However, there are no peer-reviewed studies of the performance of Sure-Spot<sup>TM</sup> units with vapour or with condensation aerosols of MDI.

### **TDI vapour detection badges**

TDI vapour detection badges are simple and inexpensive devices which can be used routinely by workers for visual warning of exposure. The badges are



**Figure 5.7.11** GMD Sure-Spot™ test kit (picture courtesy of Scott/Bacharach, Pittsburgh, PA, USA)

not suitable for use where aerosols may be present because droplets make the interpretation of badge colour change difficult. Badges have, therefore, not been developed for use with MDI. The occupational hygienist must ascertain the interferences by other chemicals present in the workplace where these devices are used.

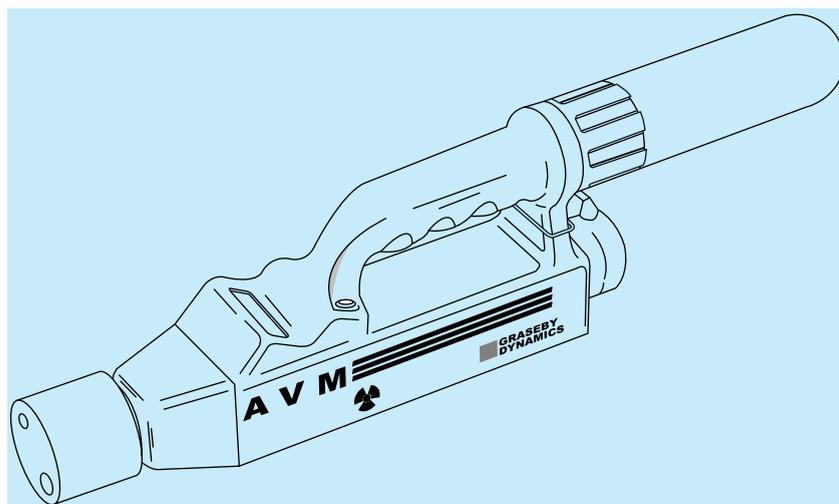
In the *Sure-Spot™ dosimeter badge* (Scott/Bacharach), TDI diffuses into the badge and reacts with the impregnated paper, producing a colour change. A reference spot on the badge is subjected to the same conditions as the measurement spot except as regards exposure to the TDI. The stain intensity is measured using an optical densitometer or a visual colour chart to determine the quantity of TDI.

The *SafeAir™ TDI badge* (K&M Environmental Inc) is designed to indicate the presence of TDI vapour in air at levels of 2.5 ppb h and above. The presence of TDI is shown on the badge by a colour change, the intensity of which is proportional to the amount of TDI present. There is a colour comparator with a scale from 2.5 to 700 ppb h (Kirolos *et al.*, 1999).

### ***Ion-mobility spectrometry-based TDI monitors***

Graseby Dynamics developed a direct reading airborne organic vapour monitor (AVM) based on ion-mobility spectrometry (IMS): see Figure 5.7.12. This instrument can be used for TDI vapour but not for MDI or aerosols (Dharmarajan, 1988; Brokenshire *et al.*, 1990). The Graseby AVM instrument is no longer marketed. However, because of the near real-time capability of the equipment, it remains in frequent use in some locations.

A small battery-operated pump draws air through an inlet nozzle. The incoming air sweeps over the surface of a thin, heated membrane; the test vapour permeates through the heated membrane into the ionization region. A  $^{63}\text{Ni}$  radioactive source ionizes the air, leading to complex ion–molecule reactions, resulting in the formation of ion clusters of relatively low mobility. A pulsed gating grid allows some of these ions to enter a drift tube and move towards a collecting electrode. The mobility of ion clusters migrating to the collector electrode is related to the mass, size, and the nature of the neutral species within the drift region, and to the temperature and pressure. By



**Figure 5.7.12** Direct reading airborne vapour monitor (AVM) from Graseby Dynamics, UK

electronic processing of the ion mobility spectrum from the collector-electrode current, the signal from the target chemical can be quantified and calibrated to display concentrations. Typically, there is a 1 to 2 s delay in displaying the concentration of TDI in the sampled air.

The AVM has been tested in dynamically generated TDI atmospheres (Brokenshire *et al.*, 1990). Atmospheres of different concentrations (3 to 42 ppb) of 2,4-TDI, 2,6-TDI and of 80/20 TDI at various humidities (0 to 68 % RH) were generated and simultaneously sampled with a nitroreagent impinger reference method, a GMD paper tape monitor and a Graseby AVM. The results of the testing are shown in Table 5.7.9. At the time of these evaluations, the responses of the AVM were displayed on LCD screens as bars. The number of bar segments displayed was proportional to the TDI concentration. The relation of bar segments to the TDI ppb concentration ranges is also shown in Table 5.7.9. It is clear from Table 5.7.9 that the range of TDI concentrations corresponding to bar segments from 4 to 8 covers a wide range of concentrations from 4 ppb to greater than 48 ppb of TDI and therefore it is difficult to use the AVM for compliance with governmental exposure standards. Tests were carried out to check whether common constituents of polyurethane production workplace air, such as amine catalysts, interfered with the TDI measurements. There were no significant interferences.

In summary:

- The AVM was simple to use, rugged, and portable, weighing only approximately 2.5 kg (6 lb).
- The AVM could be used for the near-real time measurement of TDI. The AVM responded quantitatively and specifically to both 2,4- and 2,6-TDI isomers.
- The AVM did not have a significant memory effect. After exposure to low concentrations of TDI, it returned to zero within seconds and at higher concentrations (40 to 50 ppb) within 1 min.

**Table 5.7.9** Graseby AVM compared to other methods of TDI determination.

TDI type used	Number of AVM bars displayed	AVM concentration range ppb TDI	Tape monitor <sup>a</sup> ppb TDI	Nitro-impinger ppb TDI
2,4-	2	1 to 2	1 to 2	3
2,4-	3/4	2 to 4 or 4 to 8	6	5
2,6-	4	4 to 8	5	5
2,6-	6	15 to 26	13	12
2,6-	6/7	15 to 26 or 26 to 48	>20	23
2,6-	7	26 to 48	>20	27
2,6-	7	26 to 48	>20	37
2,6-	7/8	26 to 48 or >48	>20	42
80/20	4/5	4 to 8 or 8 to 15	7	–
80/20	6	15 to 26	11	–
80/20	6	15 to 26	13	–
80/20	6/7	15 to 26 or 26 to 48	26	–
80/20	7	26 to 48	45	–
2,4-	5/6	8 to 15 or 15 to 26	–	13
2,4-	6	15 to 26	–	18
2,4-	4	4 to 8	–	6

<sup>a</sup>GMD PCM 600-60™ and Autostep™ were both used in this study.

- At zero humidity, the AVM significantly underestimated TDI concentrations. The manufacturer's recommended operating range was 5 to 90 % RH.
- Whilst the AVM evaluated did not have provision to store the exposure data, it could be linked to equipment to provide information such as time-weighted averages, percentage time above ceiling limit, and exposure/time profiles which are routinely given by paper tape instruments.

Since this study, Graseby Dynamics designed the AVM to read in ppb of TDI. The <sup>63</sup>Ni radioactive source used in the Graseby AVM caused licensing and transportation problems around the world. Graseby is now developing IMS equipment in which a nonradioactive source is used to create the ion clusters.

#### **Direct-reading colorimetric or colour indicating tubes**

Colorimetric detector tubes have been the most popular direct-reading monitor for industrial hygienists for more than 50 years. A detector tube is a glass tube containing an inert substrate (such as silica gel, diatomaceous earth, glass beads, molecular sieve, charcoal, Tenax™ or Amberlite™ XAD-2) coated with one or more chemical reagents. A known volume of air is drawn through the tube with a pump. The analyte reacts with the chemical reagent in the tube to produce a characteristic colour stain for qualitative detection. The length of the stain quantifies analyte concentration. The colorimetric tubes are relatively inexpensive and can be used by nonprofessionals.

Dräger produces a colorimetric tube for TDI (Drägerwerk, 1994). TDI concentrations from 20 to 200 ppb can be measured in about 20 min and Dräger claims the relative standard deviation of the measurement to be 30%. The colour change of the indicating layer is from white to orange. Two different

built-in reagent ampoules have to be broken to wet the indicating layer before sampling. The minimum measurable concentration with this tube is 20 ppb for TDI, which is four times the typical 8 h time-weighted average exposure limit for TDI. Therefore the use of colorimetric tubes for TDI is limited. However, for several applications, such as leak detection, or the quick screening of an accidental TDI spill, detector tubes can be very useful.

### **Indirect sampling and analysis of diisocyanates in air**

#### ***Chromatographic methods of separation***

Chromatography is a technique to separate different chemicals dissolved in a solution or to separate individual vapours or gases from a mixture of vapours or gases. All chromatographic techniques have a stationary substrate and a mobile solvent phase or gaseous phase. The mobile phase containing the mixture of chemicals to be separated percolates through the stationary phase, and the differential rate of migration causes the chemicals to separate. The separation or migration rate is dependent upon a number of chemical and physical characteristics of both the mobile and the stationary phases and of the analytes, including:

- the molecular sizes, the structures and the polarities of the chemicals being separated;
- the pH, polarity, temperature and flow rate of the mobile phase, and its affinity for the substrate;
- the physical and chemical properties of the column substrate, including its pore size.

After separation, the chemicals are detected and quantitated by a variety of techniques such as thermal conductivity, flame ionization, electron capture, UV or visible-light absorption, electrochemical fluorescence or mass spectrometry. All chromatographic techniques are highly specific and sensitive. Modern electronic detectors have made possible the determination of chemicals at concentration levels of parts per billion.

#### **High performance liquid chromatography (HPLC)**

High performance liquid chromatography became a routine analytical technique in the 1970s. In this technique, the analyte of interest, after appropriate treatment of the sample, is dissolved in a solvent which does not absorb UV strongly, and the solution is injected onto a column. The column contains a substrate, such as silica, which is coated with a high molecular weight chemical. Octadecylsilane, for example, has been used as a coating material. The analyte is carried through the column using a suitable mixture of solvents, such as acetonitrile and buffered water. As the solution moves through the column, differential partitioning causes the analyte to be separated from other species. The analyte in solution, separated from other species, leaves the column and passes through a detector cell. The retention time of the analyte in the column, compared to standards eluted similarly, establishes the identity of the diisocyanate. The intensity of the detector signal quantitates the analyte. All modern HPLC detector systems have the capability to monitor the retention time continuously and detect, record and integrate the detector signals as each eluent leaves the column. Several detection systems, based on

UV absorption, fluorescence, electrochemical oxidation or reduction, and mass spectrometry, have been used with HPLC. Modern computer-controlled HPLC systems can inject and analyse several standards and samples, and compute analyte concentrations, all automatically.

### Ethanol method

The ethanol method, an unpublished HPLC method, was probably the first method used for the sampling and analysis of diisocyanates in air (referred to by Goldberg, 1981). Reactions between aromatic diisocyanates and ethanol to form the ethyl urethanes have been used advantageously to sample MDI and TDI. Ethanol in an impinger served both as the derivatizing reagent and the absorbing medium (Bagon and Purnell, 1980). After completion of the sampling, the ethanol was evaporated and the urethane derivatives were redissolved in methylene chloride and analysed using HPLC. A silica-gel column was used with a methanol/dichloromethane or ethanol/isooctane eluent system. The ethanol impinger had 100 % collection efficiency and the method could detect MDI and TDI at approximately  $2 \mu\text{g}/\text{m}^3$  airborne concentrations. This method did not become widely used because the reaction rates of amines with diisocyanates are considerably faster than that of ethanol, and amines in the atmosphere collected by the ethanol competed for reaction with diisocyanates.

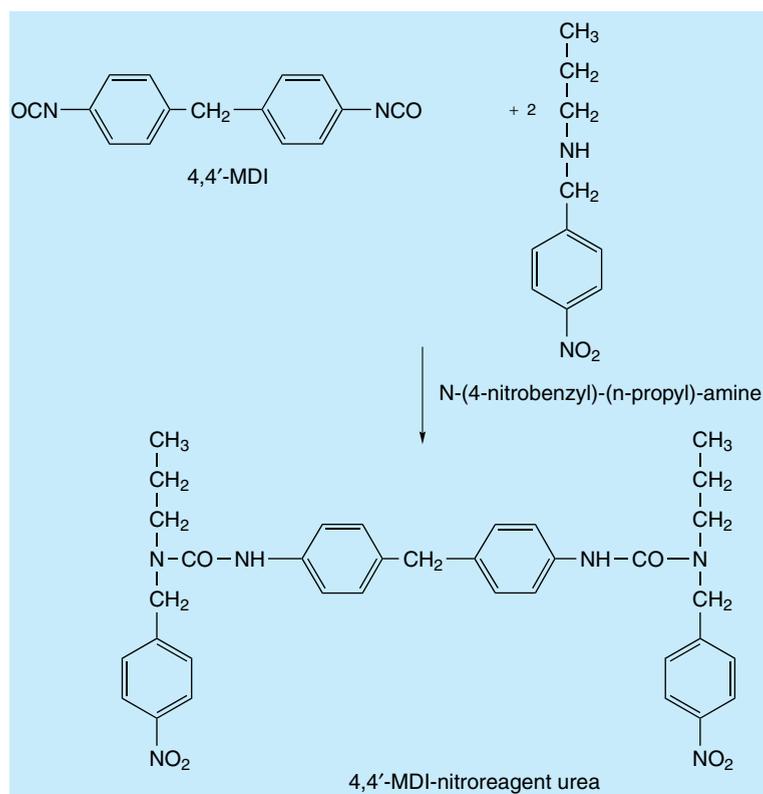
### Nitroreagent HPLC method

The first published HPLC method for MDI and TDI based on nitroreagent was published by Dunlap *et al.* (1976). This method was an extension to HPLC of their nitroreagent-TLC method. The method required the sampling of air at 1 l/min with an impinger containing  $2 \times 10^{-4}$  M nitroreagent in toluene. The nitroreagent reacted with the diisocyanates to form their ureas (see Figure 5.7.13). The toluene solvent was evaporated from the sample under vacuum, and the residue was dissolved in 1.0 ml of acetonitrile and analysed with HPLC using a UV detector at 254 nm wavelength.

The nitroreagent HPLC method originally published was based on unmodified silica-gel column chromatography. The unmodified silica-gel columns are generally difficult to work with and they are poisoned easily. Several methods have been published since which improve the chromatography of the nitroreagent method using the more stable reverse-phase columns. In 1980, OSHA incorporated the nitroreagent impinger method into their *Manual of Analytical Methods* as *Method 18* for 2,4-TDI and MDI (Cummins, 1980).

There are several limitations of the nitroreagent impinger method. Nitroreagent is light sensitive, and exposure to direct sunlight and fluorescent light must be avoided. The nitroreagent degradation products interfere with the chromatographic analysis. Impinger sampling is not ideal for the sampling of MDI aerosol particles less than  $5 \mu\text{m}$  in size. MDI sampling losses of greater than 70 % can occur when condensation aerosols (less than about  $1 \mu\text{m}$ ) are sampled with midjet impingers. The impingers must be backed up with a coated filter for sampling MDI. A nitroreagent coated glass-fibre filter method has been developed by NIOSH for the sampling of MDI (Tucker *et al.*, 1981). The method consists of impregnating a 13 mm binder-free glass-fibre filter with  $2 \times 10^{-2}$  M nitroreagent in hexane and drying the filter at room temperature. The filter is loaded into Millipore Swinnex™ cassettes for sampling. Experience has shown that dry nitroreagent degrades faster than nitroreagent in solution. Therefore, extreme care has to be exercised with coated filters, such as covering

*Use of reverse-phase columns with nitroreagent HPLC*  
Sangö (1979); Graham (1980); Bagon and Purnell (1980).



**Figure 5.7.13** Reaction of nitroreagent with MDI

the filter cassette with black tape and desorbing the filters as soon as possible after sampling.

A solid sorbent tube method based on nitroreagent was published by NIOSH as *Method 2535* (Tucker, 1994). In this method, two portions of glass wool coated with nitroreagent were compressed into a 4 cm × 6 mm internal diameter glass tube, to form front and back sections. The glass tube was covered with black tape to protect the nitroreagent from light. The method was recommended for TDI only.

An alternative sorbent tube can be made up from glass powder (20/40 mesh) coated with nitroreagent applied in methylene chloride solution. The glass is held in place by pieces of a fine metal sieve. After sampling for about 1 to 2 h at 1.7 l/min air flow rate, extra nitroreagent solution in methylene chloride is trickled onto the glass powder from the inlet side to ensure complete derivatization of the diisocyanate. The derivatized diisocyanates are washed off the glass by methylene chloride and then quantitated by HPLC.

#### Nitroreagent impingers: hints on use

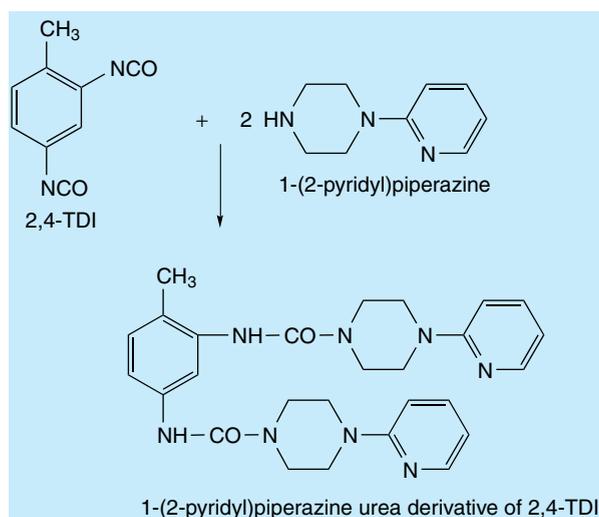
- A nitroreagent impinger by itself should not be used for sampling aerosols of MDI with particle diameter less than 5.0 μm, because there

- will be significant sampling losses. If impingers have to be used, they should be backed up with a coated filter to capture the aerosols which have passed through the impinger.
- Generally, for impinger sampling, a small length of PVC tubing is used to connect the impinger outlet to a battery-operated pump. Air samples are then drawn through the impinger at about 1 l/min. Several precautions are recommended:
    - (a) The solvent recommended for the nitroreagent impinger method is toluene. During sampling, significant amounts of toluene vapour evaporate from the impinger and condense on the tubing and the internal parts of the pump. Many commercially available battery-operated pumps are made of plastic materials which are not suitable for use with toluene. The toluene can damage the pump, and can cause fluctuations in the flow rate during long-term sampling. The user is advised to check with the pump manufacturer that the pump internals are suitable for use with toluene. A large charcoal trap between the impinger and the pump minimizes the amount of toluene reaching the pump.
    - (b) During sampling, toluene vapours can condense in the PVC tubing, and frequently the condensed toluene droplets roll back into the impinger. When this happens, the toluene leaches out some plasticizers from the PVC tube. The suggested solution to this problem is to avoid using PVC tube or any other tubing material which has not been tested for extractability. The plasticizer problem was found to have been eliminated by the use of fluoropolymer tubing. If this tubing is not readily available, then a loop should be made with the PVC tubing before attaching it to the pump, in such a way that the condensed toluene cannot drain back into the impinger.
  - After sampling, the toluene sample should be transferred into clean Pyrex™ glass brown bottles to minimize light exposure, thereby reducing the degradation of nitroreagent. Caps for the bottles should be lined with PTFE rather than with other liners such as cardboard, polyethylene or other polymers. Toluene can contact these liners during transport, extracting materials which may cause interferences in the HPLC analysis.
  - Syringe filter-cartridges are very convenient to transfer the sample into the HPLC vials before analysis. However, plasticizer leaching has occurred with the use of certain cartridge-housing materials. The filter cartridge should be checked before use by soaking the cartridge for some time in the solvent, and then analysing the extract under the same HPLC conditions as the samples. If plasticizers have been extracted, they will show up in the HPLC chromatogram.

### 1,2-PP method

The use of 1-(2-pyridyl)piperazine (1,2-PP) as a derivatizing reagent for diisocyanates was first introduced by Hardy and Walker (1979) and by Ellwood *et al.* (1981) (Figure 5.7.14). The 1,2-PP reagent, with a boiling point of

283 °C, was found to be more stable and less susceptible to degradation by light than was nitroreagent, and more readily soluble in water and a wide range of polar and nonpolar solvents. Both the TLC and HPLC methods for aliphatic and aromatic diisocyanates were developed using 1,2-PP. The sampling method using the 1,2-PP reagent for both the TLC and HPLC methods was based on an impinger technique using a  $2 \times 10^{-4}$  M solution in toluene. After sampling, the toluene was evaporated and the residue was dissolved in acetonitrile for TLC or HPLC analysis. Both UV and fluorescence detectors can be used with the 1,2-PP derivatives.



**Figure 5.7.14** Reaction of 1-(2-pyridyl)piperazine with 2,4-TDI

OSHA modified the 1,2-PP impinger method by using a 37 mm glass-fibre filter coated with 1,2-PP reagent as the sampling medium for MDI and TDI and published these methods as *Methods 42* and *47* in the *OSHA Manual of Analytical Methods* (Burrigh, 1989a, 1989b). OSHA carried out extensive validation of the coated 1,2-PP filter method for MDI and TDI. It should be noted that OSHA used a vapour spiking technique for TDI but a liquid spiking technique for MDI (without generating an atmosphere of MDI). Adoption of the 1,2-PP-coated filter methods by OSHA made these methods popular in the USA. OSHA recommended coating 37 mm binder-free glass-fibre filters with 0.1 mg 1,2-PP for TDI and 1.0 mg 1,2-PP for MDI. OSHA had originally recommended these methods for compliance purposes only (short-term sampling for a maximum of 15 min at 1 l/min flow rate), but to comply with the 1989 Permissible Exposure Limit (PEL) they increased the recommended sampling air volume to 240 l. However, studies by Dharmarajan and Distasi (1986) and Serbin (1995) have shown that 1,2-PP reagent readily sublimates from the surface of the coated filters during long-term sampling, especially in hot weather. Dharmarajan and Distasi found that drawing hot and humid air (at 29 °C with 80 % RH) through 37 mm 1,2-PP filters for 4 h at 1 l/min caused 67 % of the 1.0 mg 1,2-PP on the filter to evaporate. Based on this finding, it was recommended that 37 mm filters be coated with 2.0 mg of

1,2-PP and sampling be carried out for a maximum of 4 h at 1 l/min. Filter methods with 1,2-PP should not be used for sampling air at temperatures greater than 40 °C, because of the rapid evaporation of 1,2-PP. Ideally, 1,2-PP filters should be used soon after they are prepared. However, they can be stored for 2 weeks in a refrigerator prior to use. Meyer *et al.* (personal communication) showed that the 1,2-PP-coated glass-fibre filter in contact with the mixed cellulose ester (MCE) back-up pad lost up to 85 % of 1,2-PP in 24 h compared to 1 % 1,2-PP loss when suspended in the middle of a cassette with no back-up pad. Further studies comparing 1,2-PP filters contacting stainless steel with those in contact with MCE back-up pads indicated that the loss of 1,2-PP from the filter was due to the capillary transfer of 1,2-PP from the filter into the fibrous MCE pad (Meyer and Czarnecki, 1996).

Based on these studies, the recommendation is to use a 1,2-PP filter with stainless steel back-up or to suspend the 1,2-PP filter in the cassette using the MCE support-pad spacers or O-rings. For routine industrial hygiene surveys, the 1,2-PP filter sampling method has proved to be very popular and efficient. Filter sampling is inherently simpler and more reliable than impinger/bubbler sampling. In personal sampling, the filters are less intrusive and thus more acceptable to workers.

Boyce and Dharmarajan (1992) and OSHA (Burright, 1989a) have evaluated the OSHA 1,2-PP filter method by sampling and analysing of dynamically generated atmospheres of TDI at different concentrations, concurrently using nitroreagent impingers. The results showed excellent correlation. The OSHA 1,2-PP filter method for TDI, modified by using 2 mg of 1,2-PP for coating the filter, was satisfactorily validated by Boyce and Dharmarajan following a validation protocol for an industrial hygiene sampling and analysis method.

Three sets of six 37 mm 1,2-PP filters were spiked with 2,4-TDI at three different concentration levels. Air at 80 % RH was drawn through these filters for 4 h at 1 l/min. The filters were stored for 1 week at ambient temperature and for 3 weeks in a freezer at -20 °C. The filters were desorbed with 2.0 ml of a solution of 90 % acetonitrile and 10 % dimethylsulphoxide and analysed by HPLC. An Alltech™ C8 column and a UV detector at 254 nm wavelength were used. The mobile phase was 50 % acetonitrile and 50 % aqueous buffer with 0.1 M ammonium acetate adjusted to pH 6 with 2.0 ml/min flow rate; 20 µl of the filter desorbate was injected for analysis. The results of analysis are summarized in Table 5.7.10.

**Table 5.7.10 Summary of the laboratory validation of the 1,2-PP coated filter method for TDI.**

Level of spike	2,4-TDI spiked µg	Number of filters spiked	Average recovery % ± SD
Blank	0	3	100 ± 0
Low (at LOQ)	0.38	6	120 ± 3
Medium	1.63	6	92 ± 6
High	5.2	6	92 ± 2

Although OSHA Method 47 recommends the use of a 37 mm 1,2-PP coated filter for the sampling and analysis of airborne MDI, several questions have

been raised about aerosol capture efficiency with a 37 mm diameter filter at a 1 l/min flow rate. At a 1 l/min flow rate through an open-face 37 mm diameter filter, the face velocity is approximately 1.6 cm/s. Levine *et al.* (1995) claimed that, for efficient capture of aerosol, a face velocity of 100 to 150 cm/s was needed. Coyne *et al.* (personal communication) modified the OSHA 1,2-PP method by using a 13 mm glass-fibre filter coated with 1,2-PP and diethylphthalate (DEP) in a Millipore Swinnex™ cassette, which has an inlet diameter of 4 mm. This increased the inlet face velocity to about 130 cm/s. Coyne *et al.* showed that in laboratory-generated atmospheres, the 37 mm 1,2-PP filter underestimated MDI concentrations as compared to the 13 mm 1,2-PP/DEP filter. This depended upon the size of the aerosol generated. For efficient sampling of MDI aerosol, they recommended coating 13 mm glass-fibre filters with about 2 mg 1,2-PP and adding DEP to the filter. It was claimed that DEP provided a hydrophobic environment which reduced hydrolysis of MDI and helped to dissolve and disperse the aerosol particles, thereby improving derivatization kinetics.

However, unpublished studies by Dharmarajan and DiStasi (1986) compared the performances of 37 mm 1,2-PP coated filters to 13 mm 1,2-PP/DEP coated filters in laboratory generated condensation aerosol atmospheres of MDI; no significant differences were found between the 13 mm and the 37 mm filters. Andersson *et al.* (1983) have also investigated the sampling of MDI in laboratory generated atmospheres and industrial spray environments with coated filters, impingers and coated sponge samplers.

Hanus *et al.* (1988) reported the use of 1,2-PP reagent coated on 60–80 mesh Chromosorb WAW™, a common GC column packing material, and packed in a glass tube (60 mm × 4 mm internal diameter) as a sampling medium for MDI and TDI. After sampling of the recommended volume of 30 l, the sorbent material was emptied into a small glass vial and desorbed with 30 % methanol in 0.02 M ammonium acetate buffer at a pH of 6.2, and analysed by HPLC using a UV detector. The method was validated for 2,4-TDI and MDI in laboratory generated atmospheres. The desorption efficiency for liquid-spiked samples was 80 % for MDI and 97 % for TDI. Humidity did not significantly affect the collection or recovery of TDI. Based on studies of aerosol behaviour in respirator cartridges and sorbent tubes, and the MDI study by the International Isocyanate Institute using nitroreagent coated glass wool tubes (Hext, 1996), this 1,2-PP coated sorbent would not be expected to capture MDI aerosol efficiently.

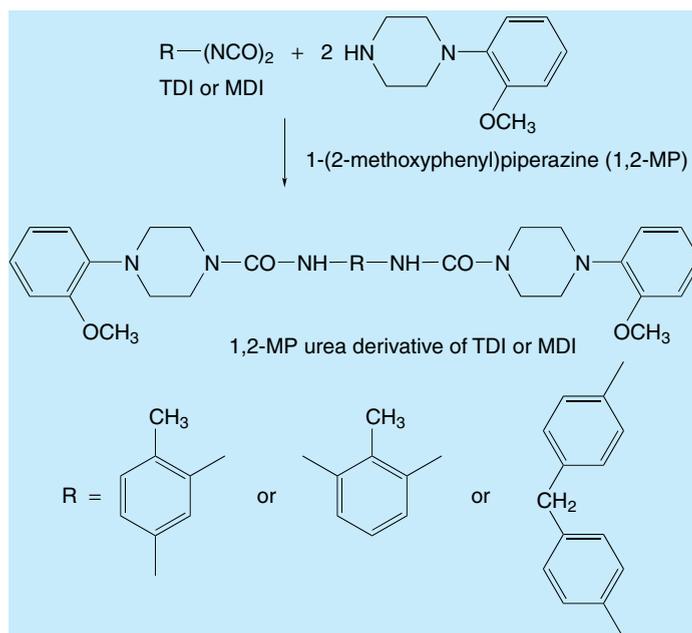
### 1,2-PP coated filter method: hints on use

- Coat 37 mm glass-fibre filters with at least 2.0 mg of 1,2-PP.
- Load the 1,2-PP filter in the plastic cassettes with stainless steel back-up pad, or suspend the filter using MCE support O-rings, because these filters, when in contact with MCE back-up pads, lose a considerable amount of 1,2-PP to the back-up pad by a capillary transfer process.
- Do not sample for longer than 4 h at 1 l/min.
- Do not sample atmospheres at temperatures above 35 °C.

- Desorb the filter samples immediately after sampling.
- Use freshly made filters for sampling because the 1,2-PP coated on the filters sublimates slowly at room temperature and rapidly in hot environments. Do not use 1,2-PP filters which have been stored at ambient temperatures for more than 1 week. Store filters in a refrigerator and use them within 1 month. Filters may be subject to hot environments during transport or storage, and this should be taken into consideration if filters have to be transported before use.
- During HPLC analysis, depending upon the type of column used, excess 1,2-PP can elute before or after the 1,2-PP derivatives of the isocyanates. There is no cause for concern; this is normal and it does not affect the quantitation.

### 1,2-MP method

The derivatizing agent 1-(2-methoxyphenyl)piperazine (1,2-MP) was first introduced by Warwick *et al.* (1981) for the analysis of monomeric isocyanates using UV and/or electrochemical detectors (ECD). The simultaneous UV/ECD dual-detector responses of the 1,2-MP-isocyanate ureas formed (Figure 5.7.15) were used to determine the total reactive isocyanate groups (TRIG) concentration in an air sample. The 1,2-MP method is the standard reference method recommended for TRIG concentration by the UK Health and Safety Executive now refined as MDHS 25/3 (HSE, 1999) and is an ISO recommended standard method for airborne diisocyanates. NIOSH published the 1,2-MP method for the determination of monomeric isocyanates only in their *Manual of Analytical Methods* as *Method No. 5521* (Seymour and Key-Schwartz, 1994).



**Figure 5.7.15** Reaction of 1-(2-methoxyphenyl)piperazine with MDI or TDI

The 1,2-MP HPLC method was based on sampling air in an impinger with 260  $\mu\text{M}$  1,2-MP in toluene. All isocyanate species reacted with 1,2-MP to form their corresponding ureas. The ureas were chromatographed using the same conditions as those used for the pure monomeric isocyanate standards. As the monomeric and the other species were separated and eluted from the column, they were detected with a UV detector and then an ECD connected in tandem. Research showed that the ECD responses of the ureas from isocyanates and 1,2-MP were proportional only to the number of the isocyanate functional groups and were independent of the molecular structure of the rest of the isocyanate molecule. For example, the same molar concentration of the 1,2-MP derivatives of the diisocyanates TDI, MDI and HDI gave approximately the same ECD responses. However, their specific UV responses were quite different, depending upon the aromatic or aliphatic structure of the isocyanate. Within a set of monomers and their monomer-derived prepolymers, the ratio of the ECD to the UV response was almost constant. This phenomenon could be used for identification of prepolymeric and partially reacted polymeric isocyanate species eluted from the column. After the identification of peaks, the precursor monomer calibration line for ECD response could be used to quantitate the total equivalent isocyanate concentration in the sample.

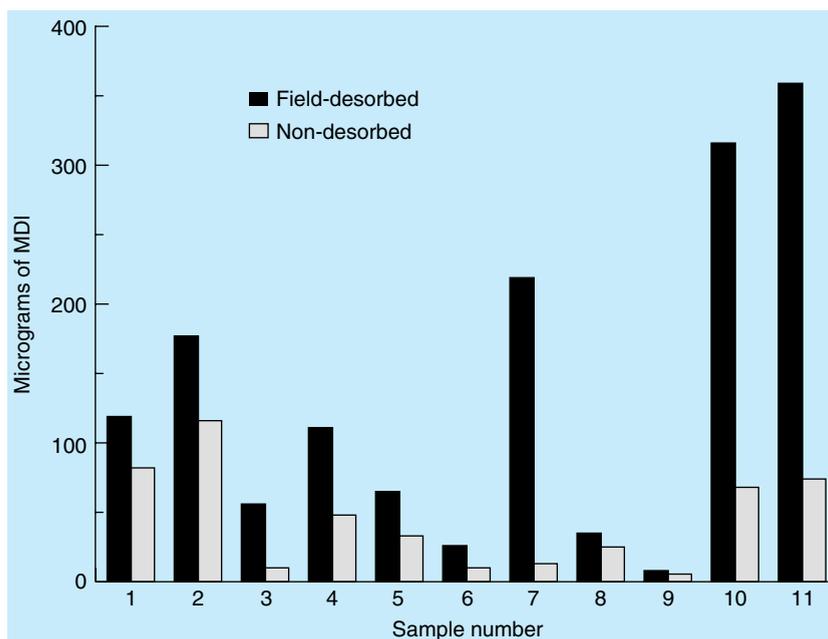
The 1,2-MP method has been evaluated by several investigators and they have reported serious problems with specificity and the inability to deal with TRIG concentrations from mixed parent isomers. It was suggested that contributions to the UV response from other parts of the molecule could lead to misidentification of an isocyanate-derived peak. The method was then modified by extending the ratio range and confirming the identification, made by EC–UV detection, by the use of diode-array UV detection.

It should be noted that the 1,2-MP reagent can also be used for quantitating monomers and prepolymers where standards are readily available, as can the nitroreagent or the 1,2-PP reagent. Studies by Brown *et al.* (1987) have shown that glass-fibre filters impregnated with 1,2-MP can be used for the sampling of isocyanates.

The standard reference methods published by OSHA, NIOSH and UK HSE for the 1,2-MP coated or 1,2-PP coated filter methods for MDI and TDI recommend transporting the filters to the laboratory for analysis after sampling. Karoly (1998) found significant differences between field desorption and laboratory desorption of 1,2-MP coated glass-fibre filters used to sample MDI. These samples were collected in particle board manufacturing plants where a significant amount of MDI collected was from wood dust coated with MDI. The results of this study are summarized in Figure 5.7.16.

The filters which had been desorbed 1 or 2 days after collection were compared with field desorbed filters. The significant underestimation of the laboratory-processed samples was said to be because of the masking of available reaction sites on the filter by the wood dust. This prevented any MDI collected subsequently from reacting with the 1,2-MP on the filter and thus MDI was lost for analysis because it reacted with other materials (such as wood, moisture and catalysts) during shipping and storage. However, this MDI was released for reaction with 1,2-MP when the filter was desorbed in the field, as was particularly clear in samples with high MDI concentrations. This phenomenon may occur with all coated filter methods.

*References on 1,2-MP TRIG concentration evaluations*  
Ohrin *et al.* (1990); Seymour *et al.* (1990); Streicher *et al.* (1995); White *et al.* (1997).



**Figure 5.7.16** Field desorption of 1,2-MP coated filters. Figure reproduced from Karoly (1998), Stability studies of diphenylmethane diisocyanate (MDI) on glass fiber filters, by courtesy of the American Industrial Hygiene Association

### 1,2-MP coated filter method: hints on use

- Although 1,2-MP is less volatile and more stable than 1,2-PP, all the precautions mentioned for the 1,2-PP method above are applicable for the 1,2-MP method also.
- It is recommended that the electrodes of electrochemical detectors be frequently regenerated (Brenner and Bosscher, 1995) and checked by running standards. It is best to leave the ECD in operation continuously. Only recommended electrodes should be used. A porous graphite electrode or a polished glassy carbon electrode is suitable. The electrode surface easily gets poisoned, and it is difficult to clean and polish the electrode to the same condition each time. Therefore, the response of the electrode for the same diisocyanate concentration will be different every time it is used. It is important that standards are run with every sample sequence. When dual detection is used it is usually easier to get reproducible responses by the UV method than by the ECD method.
- It is important to determine the concentration of possible interfering species in the air before sampling for diisocyanates. Brorson *et al.* (1990) studied potential interferences due to catalysts and other chemicals generally found in polyurethane manufacturing facilities. They studied interferences due to diethylamine, dimethylethylamine, *N*-methylmorpholine, triethylenediamine (TEDA), 33% TEDA in polyol, aniline, phenol, and ethanol. The rationale was to determine the relative

competition for TDI by these species compared to 1,2-MP. The study showed that diethylamine at all levels, TEDA at 10 and 100 ppm, and TEDA in polyol at 100 ppm caused underestimation of TDI by about 30 % or more because alkaline substances like TEDA and TEA adsorb almost irreversibly to the ECD. During the HPLC, the portion of the eluent containing the TEDA or TEA should be diverted by an automatic column switch before it reaches the ECD.

## DBA

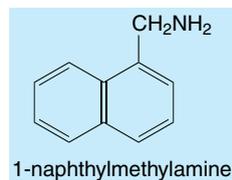
References on  
*di-n-butylamine method*  
 Spanne *et al.* (1996);  
 Tinnerberg *et al.* (1996,  
 1997); Karlsson *et al.*  
 (1998a, 1998b).

A method of monitoring air for isocyanates using di-n-butylamine (DBA) has been developed by Lund University, Sweden, and a definitive version is now being considered as an ISO method. Sampling is by midjet impinger containing DBA in toluene. The DBA reacts with the MDI or TDI to give urea derivatives, which are determined using HPLC.

When using DBA, a high concentration of the reagent can be used, resulting in faster reaction rates compared to other methods. The fact that the excess reagent is evaporated in the work-up procedure means that it does not disturb the chromatographic process.

## HPLC methods using fluorescence detection NMA and MNMA

Levine *et al.* (1979) were the first to publish a HPLC method for aliphatic isocyanates based on fluorescence detection. They used a  $10^{-4}$  or  $10^{-5}$  M solution of 1-naphthylmethylamine (NMA) (Figure 5.7.17) in toluene in an impinger to sample for aliphatic isocyanates in a spray environment. NMA, a fluorescing agent, reacted with isocyanates to form urea derivatives.



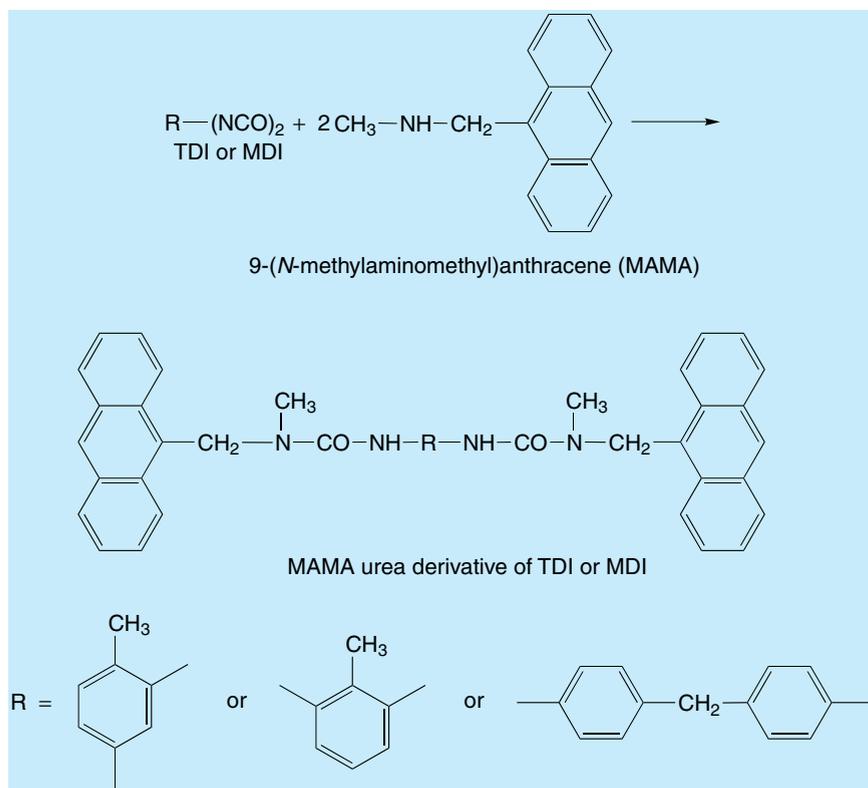
**Figure 5.7.17** 1-naphthylmethylamine

The derivatives were separated from other species using HPLC, after which the isocyanate–ureas were quantitated using a fluorescence detector (excitation wavelength of 216 nm, and emission measured using a UV 30 filter). The sensitivity using a fluorescence detector ( $0.5 \mu\text{g}/\text{m}^3$ ) was 50 times that for UV absorption detection using nitroreagent. Kormos *et al.* (1981) improved the above method by using N-methyl-1-naphthylmethylamine (MNMA), a secondary amine, as the derivatizing agent. MNMA was found to react readily with both aliphatic and aromatic isocyanates, and the possibility of forming more than one derivative with the isocyanates was eliminated by the use of the secondary amine. The sensitivity of detection was reported to be around  $1 \mu\text{g}/\text{m}^3$ . Eliminating the reagent peak by a column switch can improve the performance of the method considerably (see above).

## MAMA

The fluorescing agent 9-(N-methylaminomethyl)anthracene (MAMA), dissolved in toluene was first introduced by Sangö and Zimerson (1980)

for impinger sampling of airborne isocyanates and analysis with HPLC (Figure 5.7.18). This reagent was coated on Amberlite™ XAD-2, and packed in glass tubes (5 cm × 4 mm internal diameter) for sampling gaseous isocyanates by Andersson *et al.* (1982). When approximately 15 l of air had been sampled, the tubes were desorbed with DMF, which was then analysed by HPLC using UV detection. The sampling efficiency of the MAMA-sorbent tube was evaluated by vapour spiking both with TDI, and with MDI at about 150 °C. Under these evaluation conditions, the tubes were found to be adequate for sampling MDI and TDI. However, this evaluation could be misleading, because MDI may be encountered in the workplace in the form of aerosols. As noted above, such tubes may have poor collection efficiency for MDI aerosol, depending on packing and the mesh size of the support.



**Figure 5.7.18** Reaction of 9-(N-methylaminomethyl)anthracene with MDI or TDI

Another important study, performed by Andersson *et al.* (1983), compared the efficiencies of several sampling media both in laboratory generated atmospheres and in the field (a polyurethane insulated pipe manufacturing factory where foam reactants were sprayed, and a factory where MDI foaming mix was poured). The media tested were nitroreagent and MAMA impingers, MAMA coated XAD-2 tube, MAMA coated natural sponges, nitroreagent coated 13 and 37 mm glass-fibre filters, and unimpregnated cellulose acetate and glass-fibre filters. The laboratory MDI atmosphere was generated using

a Collison Nebulizer™ (ISI Inc.). MDI concentration levels were about 1 to 5 mg/m<sup>3</sup>, and the count median aerodynamic diameter of the size distribution was approximately 0.1 μm. The results of the study are summarized below.

*Laboratory studies:*

- The collection efficiency for nitroreagent coated filters was about 100 %.
- The collection efficiency for the MAMA impingers was about 30 % of that of the MAMA XAD-2 tubes and sponges.
- The collection efficiencies of plain glass-fibre and cellulose acetate filters compared to MAMA fritted bubbler samples were highly variable. For glass-fibre filters the efficiency was 80 % ± 53 % when desorbed immediately after sampling and 0 % when desorbed after 48 h; for cellulose acetate filters the efficiencies were 30 % ± 74 % and 0 %, respectively.

*Field studies:*

- Compared to the collection efficiency of nitroreagent impingers those of 13 and 37 mm nitroreagent coated filters were 30 % ± 47 % (*n* = 12) and 40 % ± 78 % (*n* = 8), respectively, in one factory and 60 % ± 36 % (*n* = 7) for 13 mm nitroreagent coated filters in a second factory.
- The results using filters coated with MAMA in amounts ranging from 0.36 to 0.72 mg per filter, using immediate desorption or desorption after 48 h, showed the filter collection efficiencies to be less than 30 % of those of the MAMA impingers.
- The MAMA tube and sponge also showed less than 20 % collection efficiency compared to that of the MAMA impinger.

No satisfactory explanations were given for the contradictory results obtained in the laboratory and field experiments. The presence of a complex MDI moiety in the factory air, which releases MDI in the impinger solution and not in the solvent-free sorbent media was suggested.

Rando *et al.* (1993, 1995) evaluated MAMA as a potential reagent to determine TRIG concentrations. They studied the detector responses of MAMA-derived ureas of 11 isocyanates, including three different polymeric MDIs and one moisture-curing polyurethane varnish based on TDI. Different HPLC detection modes were used: fluorescence at excitation wavelength of 245 nm and emission measured at 414 nm, and UV absorbance at 245 and 370 nm. For all isocyanate-ureas at the same isocyanate molar concentrations the UV absorbance (at 245 and 370 nm) was almost the same but the fluorescence responses varied considerably. Based on this evaluation, it was recommended that MAMA reagent be used for sampling and analysis of TRIG concentrations, with the eluent containing MAMA removed before reaching the fluorescence detector. In an unknown sample, comparing the ratio of the UV absorbance of every peak eluting out at 245 and 370 nm to that obtained from the corresponding isocyanate monomer standard was recommended. If the ratio of UV absorbances of the unknown peak was within ±20 % of the monomer standard, then that peak was identified as due to a moiety containing an isocyanate group. Once all the isocyanate-containing peaks were identified in an unknown, the TRIG concentration was quantitated using the cumulative area from all isocyanate-containing peaks,

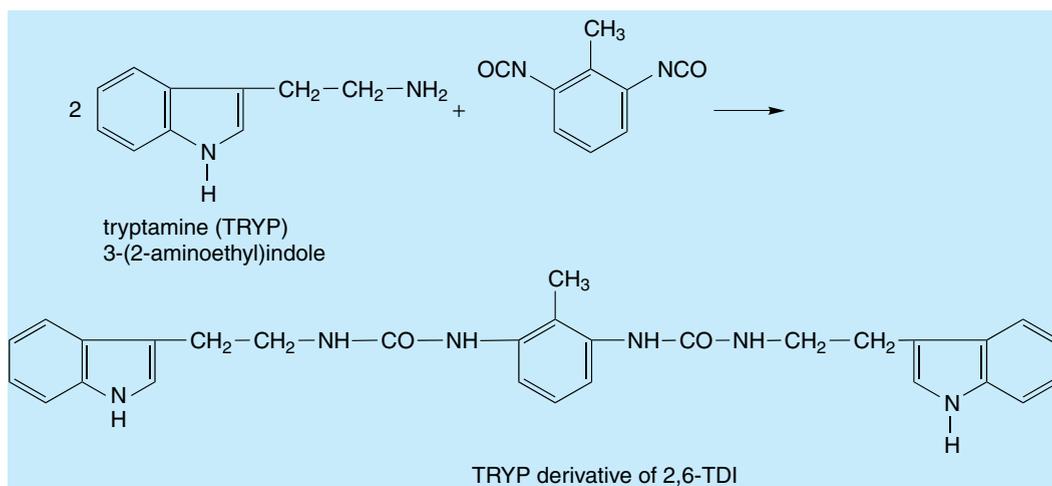
and comparing this to a calibration line of UV absorbances against isocyanate concentrations of a series of monomer standards. The MDI- and TDI-containing materials were tested for the TRIG content by the MAMA-HPLC assay technique and compared with the TRIG or the equivalent isocyanate concentration determined by the standard *n*-butylamine/HCl titrimetric assay (David and Staley, 1969). The analysis for the reactive isocyanate groups by the MAMA-HPLC technique showed excellent agreement with the titrimetric method.

The study indicated that phosgene caused interference by reacting with MAMA to form a product which met the criteria for an isocyanate-containing moiety by this method. One unit of phosgene was equivalent to two isocyanate groups by this method, leading to overestimation.

Brorson *et al.* (1990) studied potential interferences to the MAMA method due to catalysts and other chemicals found in polyurethane manufacturing facilities. The study showed that diethylamine at all levels, dimethylethylamine, TEDA, and TEDA in polyol at 100 ppm, and *N*-methylmorpholine at 10 and 100 ppm, caused underestimation of TDI by 25% or more. Therefore, it is important to determine the concentration of these species in the air before sampling for isocyanates, and eliminating them during the chromatography by peak cutting.

## TRYP

Tryptamine (3-(2-aminoethyl)indole (TRYP)) was first introduced by Wu *et al.* (1987) as a derivatizing agent for the sampling and HPLC analysis of isocyanates using fluorescence and electrochemical detection (Figure 5.7.19). In a series of four papers, Wu *et al.* (1987, 1988, 1990, 1991) investigated the use of TRYP as a potential derivatizing reagent for the sampling of several airborne isocyanates, including polymeric MDI and TDI, using analysis by HPLC-fluorescence and HPLC-amperometric techniques.



**Figure 5.7.19** Reaction of tryptamine with 2,6-TDI

The sampling medium investigated was the mini-impinger with 0.5 mg of TRYP in 15 ml of acetonitrile or toluene. The collection efficiency of the

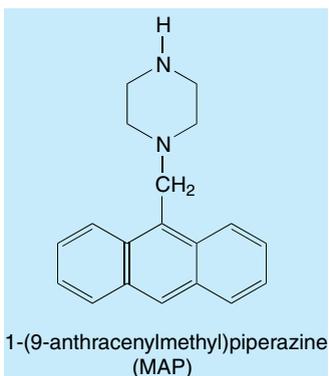
sampling medium for aerosols was not tested. The evaluation of the method was carried out by spiking the TRYP-absorbing solution with isocyanate or the isocyanate–TRYP derivative and drawing air through the impinger. Only TDI was tested by generating an atmosphere. The major conclusions of their studies are given below:

- Tryptamine was a suitable derivatizing agent for isocyanates. It readily reacted with mono-, di- and polymeric isocyanates to form ureas. The ureas could be separated by normal or reversed-phase HPLC and gel-permeation chromatography and quantitated by fluorimetry and amperometry. The dual detection system was a powerful confirmatory test to identify isocyanates of unknown structures.
- The fluorescence intensity of the TRYP–isocyanate derivative was directly proportional to the molar concentration of the tryptamine portion of the derivative, and was independent of the structure of the isocyanate to which it was attached. The fluorescence intensity of the derivative dissolved in methanol was unaffected by quenching effects, which are a common problem encountered in all fluorescence techniques. The use of dual detection for identifying isocyanate peaks was recommended. The TRIG concentrations could then be quantitated by comparing the total area of all isocyanate peaks to a calibration line (equivalent TRYP concentrations compared with peak areas) of the TRYP-derivative standard of TDI.
- The study compared the reaction rates of TRYP, *N*- $\omega$ -methyl-TRYP, 1,2-MP, nitroreagent, and 1,2-PP with phenyl isocyanate. Phenyl isocyanate was chosen because the molecule has only one reaction site. In this study a separate experiment indicated that the TRYP–phenyl isocyanate reaction was found to be  $\geq 1 \times 10^7$  times faster than the water–phenyl isocyanate reaction. Any water collected in the impinger would thus have had no significant effect on the above findings. The study concluded that TRYP and 1,2-MP had similar reaction rates and *N*- $\omega$ -methyl-TRYP reacted about 3.7 times faster than TRYP. Compared to the TRYP reaction rate, the 1,2-PP and nitroreagent reaction rates were slower (0.5 and 0.004 times respectively).
- The fluorescence intensity of the tryptamine derivative was about 30 times greater than that of the fluorescence of the 1,2-MP derivative.

In 1994 NIOSH formally recommended this method by publishing it in their *Manual of Analytical Methods* as *Method No: 5522* (Key-Schwartz and Tucker, 1994).

## MAP

The reagent 1-(9-anthracenylmethyl)piperazine (MAP) was studied by NIOSH (Streicher *et al.*, 1996) as a potential reagent for TRIGs (Figure 5.7.20). Compared to the MAMA and TRYP reagents, MAP was found to have the highest rate of reaction with phenyl isocyanate and the greatest average UV and fluorescence responses per derivatized isocyanate group. The UV response was least dependent on isocyanate structure for MAP-derivatized ureas. The fluorescence response was found to be less dependent on isocyanate structure than that of MAMA derivatives, but more dependent than that of



**Figure 5.7.20** 1-(9-anthracenylmethyl)piperazine

TRYP derivatives. This method is being developed as an ISO standard (see Table 5.7.4).

#### HPLC methods for MDI and TDI in the presence of MDA and TDA

There are situations in which MDI or TDI coexist with their respective diamines, MDA or TDA. MDA and TDA are the respective precursors in the manufacture of MDI and TDI, and may be formed from the diisocyanates in the aqueous environment (but not in the vapour phase). Also, the diamines may be formed from the diisocyanates as artefacts in analytical procedures. There is, then, sometimes a need to analyse for MDI or TDI in the presence of MDA or TDA.

Dharmarajan *et al.* (1995) developed and validated a method to sample and determine MDI and MDA simultaneously in the same sampling medium. In this method, the air was sampled in  $2 \times 10^{-4}$  M solution of nitroreagent in toluene, which quantitatively collected both MDI and MDA. The MDI reacted with the nitroreagent to form the urea, and MDA was dissolved by the toluene solvent. Immediately after sampling in the field, the MDA was derivatized and stabilized by adding 0.25 ml of acetic anhydride to the absorber solution. In the laboratory, the toluene was evaporated to dryness, and the residue was redissolved in acetonitrile and analysed by HPLC with a UV detector at 254 nm. The acetylated MDA eluted early in the chromatogram and could be separated from the excess nitroreagent and the MDI urea. Both MDA and MDI could be quantitated from the same chromatogram.

#### Gas chromatographic methods

Most methods of gas chromatography (GC) for airborne organic chemicals are based on direct sampling onto charcoal or onto other sorbents such as Tenax<sup>TM</sup> or Amberlite<sup>TM</sup> XAD-2, followed by desorption of the organic chemicals from the sorbent with an organic solvent or by heat, then analysis of the desorbate using GC. However, diisocyanates react with the sorbents commonly used for GC, and can thus not be fully desorbed, indicating that GC is not an appropriate analytical approach. However, there are several publications describing GC methods for the sampling and analysis of diisocyanates in air. These methods tend to be research-oriented tools and are not used routinely, because governmental institutions, such as OSHA, have not officially

subscribed to them. One exception was the method developed by UK HSE (Hughes, 1990), which was based on the reaction of an organic isocyanate with propan-1-ol, followed by quantitative hydrolysis of the resultant urethane to the constituent alcohol; measurement of the alcohol level gave a direct measure of isocyanate concentration. Hydrolysis was effected after injection of the propanol derivatives into automatic thermal desorption (ATD) tubes packed with 2 % potassium hydroxide on ThermoTrap-TA (Chrompack™) in a heated ATD oven, volatiles being passed directly to a gas chromatograph via a heated transfer line.

Hanson *et al.* (1965) and Wheals and Thomson (1967) were probably the first investigators to report the use of GC for the sampling and analysis of airborne TDI. Wheals and Thomson used a 60 cm × 2.8 mm internal diameter glass column packed with 70 to 80 mesh, acid washed, and dimethyldichlorosilane-treated Chromosorb™ G, coated with Apiezon™ L and Epikote™ 1001. The column was operated at 100 °C with nitrogen carrier gas at 130 ml/min and an electron capture detector. Toluene solvent was used for preparation of the TDI standards for analysis.

Schanche and Hermann (1974) investigated the sampling of airborne TDI with an impinger containing toluene, and analysis by the method developed by Wheals and Thomson (1967). The moisture from air collected by the impinger reduced the recovery of TDI by this method. The direct sampling of isocyanates into impingers containing isooctane, and analysis by GC using electron-capture or nitrogen-selective detectors was reported by Skarping *et al.* (1985). They found the isocyanates to be more stable in isooctane than in toluene. None of these studies examined the interferences due to amines in the sampled air. If free amines are present in the air they interfere by reacting with isocyanates in toluene or isooctane, forming ureas.

Ebell *et al.* (1980) were the first to apply derivatization and GC to the sampling and analysis of diisocyanates. They reported a method where TDI and 4,4'-methylenebis(2-chloroaniline) (MOCA) were simultaneously sampled in an acidic absorbing solution. The TDA resulting from hydrolysis and the MOCA were derivatized using trifluoroacetic acid anhydride, and the acetylated derivatives were analysed by GC with an electron-capture detector.

Bishop *et al.* (1983) improved the method by Ebell *et al.* and adapted it for MDI and TDI. The diisocyanates were sampled in Marcali absorbing solution (3.5 % acetic and 2.5 % hydrochloric acid) to convert them to amine salts. The amines were freed by the addition of sodium hydroxide, and extracted into toluene. The amines were derivatized with hexafluorobutyric acid anhydride and heating for 1 h at 50 to 60 °C. The derivatized diisocyanates were analysed by GC with electron-capture detection.

Audunsson and Mathiasson (1983) developed a simultaneous sampling and analysis method for TDI and for amine catalysts commonly used in polyurethane processes. The method was based on impinger sampling with dilute sulphuric acid. The absorber solution hydrolysed the diisocyanates to amines and dissolved the catalyst amines. The amines were stabilized by forming the corresponding sulphate salt. After sampling, the absorber solution was treated with alkali and the liberated amines were extracted with toluene



### TLC of nitroreagent derivatives

Aliquots of 10  $\mu$ l of the sample and of the diisocyanate standards, treated similarly, were spotted onto a silica gel TLC plate. The spots were exposed to hydrochloric acid vapours in a glass chamber to convert all free amines in the sample to their corresponding hydrochloride salts. The excess nitroreagent was also converted to its salt. The plate was then developed by elution with methanol–water (10–90 v/v) solution for about 75 min (approximately 18 cm migration). The methanol–water elution washed off all of the amine and excess nitroreagent hydrochloride salts, leaving the diisocyanate urea intact at the spot. The plate was then dried to evaporate all of the water and methanol. The TLC plate was developed again using ethyl acetate–acetone–hexane (10–10–30 by volume) to elute and separate the diisocyanate ureas. After elution, the plate was dried and sprayed with a titanous chloride solution to reduce the nitro groups in the ureas to amino groups. The plate was dried and again exposed to hydrochloric acid vapour to form hydrochloride salts of the isocyanate–nitroreagent amine complex. The salts were then exposed to nitrous fumes to diazotize the isocyanate–amine–hydrochloride and sprayed with a 0.5 % aqueous solution of *N*-1-naphthylethylenediamine solution. The isocyanate–nitroreagent complexes developed a violet–red coloured spot. The  $R_f$  values of the isocyanates determined their identity, and the intensity of the coloured spots, measured either visually or with a scanning densitometer, was used to quantitate the isocyanate. This method was applicable to both aliphatic and aromatic isocyanates. The method was highly specific and, in contrast to the Marcali method, amines did not interfere in this method.

The first TLC method for aliphatic and aromatic isocyanates was developed by Keller *et al.* (1974) using *N*-(4-nitrobenzyl)-*N*-*n*-propylamine (nitroreagent) to react with the isocyanates forming the corresponding urea derivatives. The reaction of MDI with nitroreagent is shown in Figure 5.7.13.

The diisocyanates were sampled in impingers containing  $2 \times 10^{-4}$  M nitroreagent in toluene. The solution was concentrated to 1.0 ml by evaporating the toluene in a vacuum. The concentrated solution was then analysed by TLC. A detailed description of the TLC procedure gives the reader an idea of the complexity of this method.

Another TLC method for diisocyanates was developed by Ellwood *et al.* (1981) using 1-(2-pyridyl) piperazine (1,2-PP) as the reagent. In this high-performance TLC (HPTLC) method, the diisocyanates were sampled with an impinger containing  $2 \times 10^{-4}$  M 1,2-PP reagent in toluene. The diisocyanates reacted with 1,2-PP to

form the corresponding ureas.

The urea solution was concentrated to 100  $\mu$ l, of which 1.0  $\mu$ l was applied to the HPTLC plate, alongside aliquots of solutions of isocyanate standards. The spots were eluted with an aqueous solution of potassium iodoplatinate solution, which separated the various ureas, producing coloured spots on a pale pink background. The ureas formed various colours, which were used for qualitative identification and detection, and the intensity of the colour allowed semiquantitative measurements of diisocyanates.

Historic TLC methods were labour intensive and cumbersome, requiring skilled personnel to produce reliable results consistently. More recently, automated multidevelopment TLC has now made the TLC technique comparable to HPLC methods in ease and performance. However, the further rapid advances and high level of automation in HPLC instrumentation and technology have now largely led to the replacement of TLC methods by HPLC methods.

### Capillary electrophoresis

Capillary electrophoresis (CE) is a relatively recent development in chromatographic technique. It combines the separation technology of capillary gas chromatography, the high sensitivity detection of HPLC, and the separation modes of gel electrophoresis. Although the feasibility of the technique was indicated as early as 1965 by Hjertén for the separation of proteins, nucleic acids and inorganic ions, the first commercial instrument appeared only in 1988. The first application of this technique to isocyanate analysis was by Rudzinski

*et al.* (1994) for the sampling and analysis of 1,6-hexamethylenediisocyanate (HDI) in a spray painting operation. The atmosphere was sampled with 37 mm 1,2-PP coated filters, and the same samples were analysed by both conventional HPLC and CE techniques. The HDI analytical results by CE compared well with those of the HPLC technique. This method can also be applied to MDI and TDI.

## Piezoelectric methods

*Papers on monitoring TDI using piezoelectric crystal sensors*  
Alder and Isaac (1981);  
Fielden *et al.* (1984);  
Morrison and  
Guilbault (1985).

The piezoelectric crystal sensor technology is based on a change in frequency of oscillating crystals when foreign material is deposited onto them. Compact, portable monitoring devices have been developed for many substances. Several attempts have been made to develop sensitive and selective direct reading monitors for isocyanates based on piezoelectric crystal sensors.

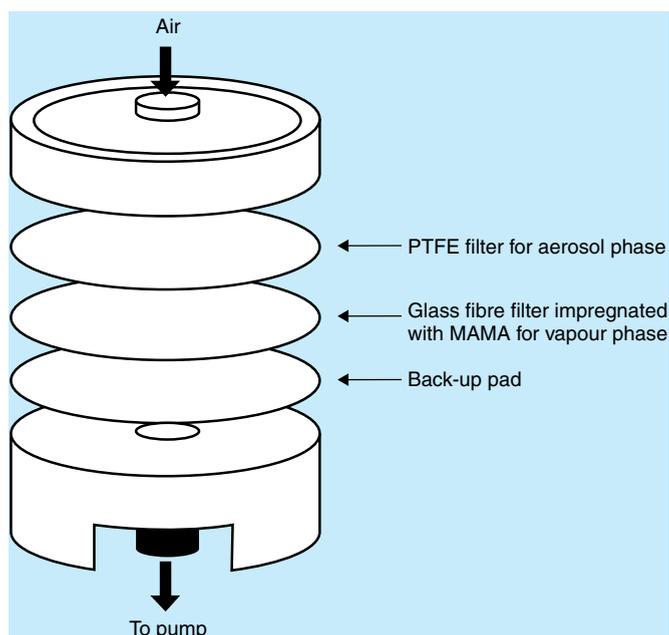
The main problem with these sensors is their lack of sensitivity. Long-term OEL values are usually about 5 ppb for TDI and the detection limit of these sensors is approximately 10 ppb in air. This technology is particularly well suited to the detection of gaseous pollutants: TDI has been investigated but not MDI.

## Other sampling methods

Iso-Chek™ is a double-filter sampling technique developed by Lesage *et al.* (Lesage and Perrault, 1990; Lesage *et al.*, 1992) for the sampling and analysis of isocyanates and is manufactured by the Omega Specialty Instrument Company. The method has been adopted by the ASTM as a standard method for TDI in air (ASTM Method D 5932-96). The sampler consists of a 5 µm PTFE filter and a glass-fibre filter loaded in tandem with a cellulose-ester back-up pad into a 37 mm filter cassette (Figure 5.7.22). The glass-fibre filter is coated with 9-(*N*-methylaminomethyl)anthracene (MAMA) reagent. Air is drawn through at up to 1 l/min. Aerosols containing nonvolatile isocyanate monomers and oligomers are collected on the PTFE filter while vapour phase diisocyanate monomers pass through, and are trapped by the MAMA-treated filter.

It was recommended that sampling times should be short (less than 30 min) and that the PTFE filter should be desorbed in the field immediately after sampling with 5 ml of 0.1 mg/ml solution of 1-(2-methoxyphenyl)piperazine in toluene. This step was essential because the diisocyanates collected on the PTFE filter were still not derivatized and could react with moisture and/or other reactive species in air and be lost for analysis. The desorbed PTFE filter samples and the MAMA filters were analysed by conventional HPLC methods. The limitations of this method were the short-term sampling and the potential loss of diisocyanates collected on the PTFE filters due to other reactions.

A study by the International Isocyanate Institute evaluated the performance of the commercial Iso-Chek device in laboratory generated atmospheres of TDI, MDI and polymeric MDI (Rando *et al.*, 2001). The authors concluded that, under the study conditions, the Iso-Chek significantly underestimated the TDI concentrations as compared with the OSHA 1-(2-pyridyl)piperazine method (OSHA Method 42) or the Tulane denuder sampler (Rando and Poovey, 1994): see below. The 15 min and 3 h sampling time comparisons for TDI showed that the Iso-Chek values were 55 and 38 % of those of the Tulane sampler and 66 and 60 % of those of the OSHA method, respectively. As noted above, the maximum recommended sampling time for the Iso-Chek is 30 min. The short-term performance of the Iso-Chek for MDI and polymeric MDI measured

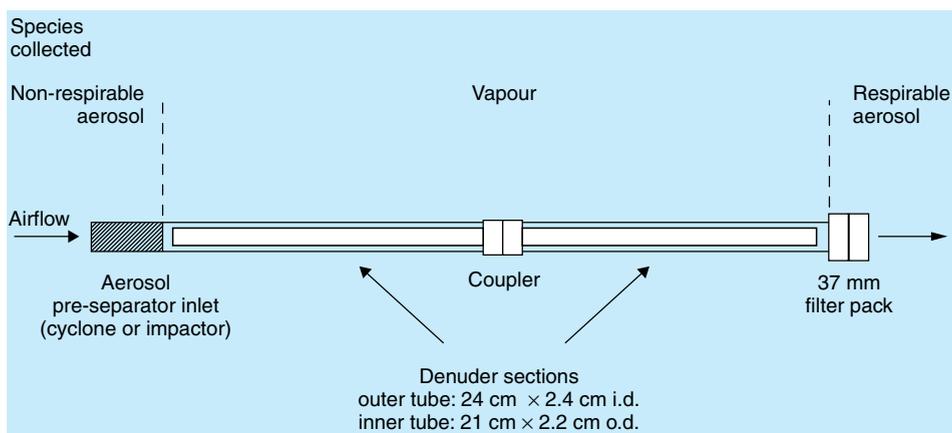


**Figure 5.7.22** Iso-Check™ diisocyanate sampling cassette. Figure reproduced from Lesage *et al.* (1992), Workers' exposure to isocyanates, by courtesy of the American Industrial Hygiene Association

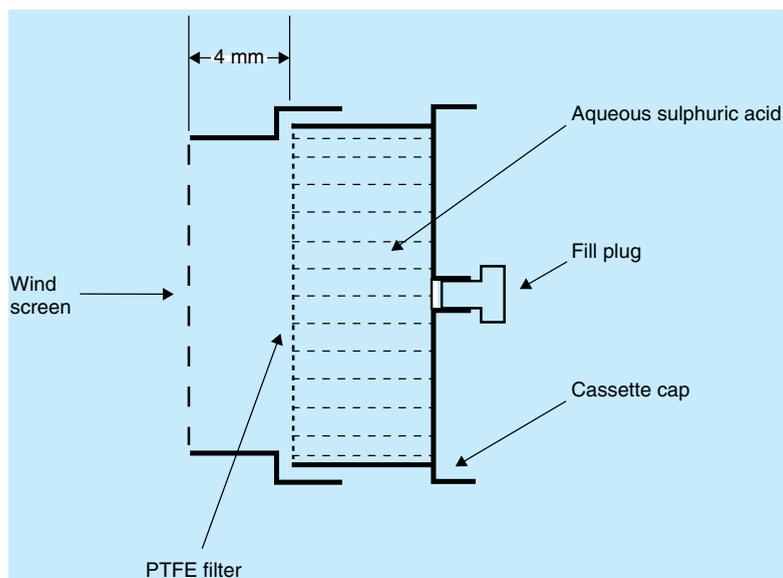
as total isocyanate groups was on average 84 and 94 % and the long-term samples were 64 and 52 % compared to the Tulane sampler respectively. Rando *et al.* also showed that the MAMA reagent was not coated uniformly on the glass-fibre filter and significant migration of the MAMA reagent to the cellulose back-up pad was observed. The TDI underestimation was attributed to the relatively low amount of MAMA reagent on the glass-fibre filter, to the nonuniform coating of the MAMA reagent and to the potential migration of the MAMA reagent to the cellulose back-up pad.

The design of the Tulane denuder sampler was based on the very large differences in the diffusivities of gases and submicron particles which effected a quantitative separation of the two (Figure 5.7.23). A mixture of MDI vapour and MDI aerosol was passed through an aluminium cyclone designed to provide separation of the nonrespirable fraction of the sampled aerosol. The cyclone was followed by an annular denuder section. This consisted of an inner and an outer cylinder with an annular spacing of 0.1 cm, the sampled air flowing between the cylinders at a nominal flow rate of 2 l/min. The denuder walls and the 37 mm filter pack (a PTFE holder containing a glass fibre filter) were coated with a mixture of MAMA reagent (1 mg) and tributylphosphate (20 mg). Immediately after sampling, the cyclone inlet was washed with 2 ml of a solution of MAMA in dimethylsulphoxide. The denuder and filter were then desorbed with 2 ml of dimethylsulphoxide, and the cyclone, denuder and filter samples analysed separately by HPLC.

Rando *et al.* (1989a, 1989b) developed a passive personal or area monitoring device for TDI, which combined the principle of diffusion through a microporous PTFE membrane with spectrophotometric analysis. The dosimeter



**Figure 5.7.23** Denuder for separating MDI vapour from MDI aerosol



**Figure 5.7.24** Diffusive sampler for TDI vapour. Figure reproduced from Rando *et al.* (1989), A diffusive sampler for personal monitoring of toluene diisocyanate (TDI) exposure; Part II: laboratory and field evaluation of the dosimeter, by courtesy of the American Industrial Hygiene Association

was constructed by welding a 37 mm, 0.5 µm pore size, Millipore™ type FH PTFE filter to a 37 mm Millipore™ polystyrene aerosol cassette-cap (see Figure 5.7.24). An aqueous solution of sulphuric acid (0.5% v/v) was placed inside the cap in contact with the PTFE membrane. The hydrophobicity of PTFE and the surface tension of water prevented leakage of the absorbing solution through the PTFE membrane and allowed free diffusion of TDI from the outside into the dosimeter. The TDI diffusing through the PTFE was absorbed by the sulphuric acid solution, hydrolysed to TDA and stabilized by forming a TDA sulphate salt. After the sampling

procedure, the sulphuric acid absorbing solution was analysed for TDA by the modified Marcali method (Rando and Hammad, 1985) or by a method using Fluram™ (4-phenylspiro[furan-2(3H),1'-phthalan]-3,3'-dione), a widely used fluorometric reagent for amines (Guthrie and McKinney, 1977).

The dosimeter was evaluated both in the laboratory and in the field. The laboratory evaluation indicated that the mass transfer rate of TDI was around 0.015 µg/ppb h and this rate was the same for both the 2,4- and 2,6-isomers of TDI. The collection rate of TDI was proportional to exposure doses from 10 ppb h to at least 300 ppb h, and the response was isomer independent. The TDI collection rate was independent of humidity and usual atmospheric pressure variations. However, the collection rate decreased with a decrease in temperature (around 1 % per degree). Field testing of the passive dosimeter showed excellent agreement with modified Marcali impinger samples at low concentrations (<30 ppb).

This passive dosimeter has not been popular among industrial hygienists for several reasons. It is not commercially available and there is potential for accidental membrane rupture and leakage of the sulphuric acid absorbing solution onto workers. Potential interferences from amines or other species have not been fully evaluated.

### **Spectrophotometric methods of detection**

In the early years of diisocyanate manufacture, the only reliable methods available for monitoring MDI and TDI were based on colorimetry or spectrophotometry. These methods were developed initially for the analysis of TDI in air and later the same methods were adapted for MDI.

Colorimetric methods are based on the direct relationship of the concentration to the intensity of the colour of a chemical or a coloured reaction product of the chemical. In the early stages of the development of colorimetric methods the intensity of the colour of the unknown sample was simply matched visually against a series of coloured standards. The methods evolved to become spectrophotometric methods, where the subjective colour comparison was replaced by the measurement of the absorption of light of known intensity passing through the coloured chemical. Further developments in spectroscopy led to measuring the absorption of UV or visible light of known wavelength. The UV and visible absorption spectra of chemicals could be routinely determined and the wavelength of optimum absorption used to maximize the sensitivity of measurement.

### **Marcali method**

#### *Early published methods for TDI*

Ehrlicher and Pilz (1956, 1957); Ehrlicher (1956).

The first published methods for TDI date back to 1956, when Ehrlicher and Pilz published a series of papers on the sampling and analysis of TDI. One method (Ehrlicher and Pilz, 1957) was essentially based on collection of TDI in a bubbler containing 1:1 dimethylformamide (DMF) and 1 N hydrochloric acid (HCl) as the absorbing solution. The TDI was hydrolysed, giving the toluene diamine dihydrochloride. The toluene diamine was diazotized by the addition of sodium nitrite, and the excess nitrite was removed by reduction to nitrogen by the addition of sulphamic acid. The diazotized toluene diamine was then coupled with *N*-1-naphthylethylenediamine to produce a blue-violet colour. This colour was the basis of the spectrophotometric method for TDI. The Ehrlicher and Pilz method was slightly modified by Marcali in 1957.

He suggested the use of a mixture of 0.4N HCl and 0.4N acetic acid as the absorbing medium, and in the sample preparation, the addition of sodium bromide to catalyse the diazotization of the amine.

The Marcali method became the method of choice for TDI and later for MDI until the development of thin layer chromatographic and gas-liquid chromatographic methods. The Marcali method was further refined by Reilly (1963), Grim and Linch (1964) and Meddle *et al.* (1969). The Marcali method with the aforementioned improvements (without the dual-impinger technique described below, Meddle and Wood 1970) was adopted as the recommended method for the sampling and analysis of 2,4-TDI and MDI in the US by NIOSH (NIOSH 1977a, 1977b), and by the UK Health and Safety Executive (HSE, 1985).

Several toxicological and epidemiological studies used the Marcali method as the basis for the exposure measurement. Various modifications of the Marcali method and field kits based on the method were developed in the 1960s. The sensitivity, 0.02 ppm, reported by Marcali, was improved to measure 0.007 ppm in air samples of 15 litres by 1970. However, some of the major limitations of the Marcali impinger method could not be overcome:

- (1) The Marcali method could not differentiate between 2,4- and 2,6-TDI, or between the 4,4'- and 2,4'-MDI isomers and the related higher molecular weight species.
- (2) The Marcali method had different sensitivities to 2,4- and 2,6-TDI. Two grades of TDI are commercially marketed, an 80 % 2,4- and 20 % 2,6-TDI (80/20 TDI) mixture, and a 65 % 2,4- and 35 % 2,6-TDI (65/35 TDI) mixture. Marcali standard solutions made with these materials are suitable for analysis if airborne TDI is also present in the same ratios. However, field studies (see Table 2.19) have shown that, in many applications, the ratio of concentrations of 2,4- and 2,6-TDI in the air may not be as expected. Rando *et al.* (1984) demonstrated that, in foaming operations, at the beginning of the foam line, the airborne TDI is predominantly 2,4-TDI, and, at the end of the line, the 2,6-TDI is the predominant species in the air. This effect can be attributed to the lower reactivity of 2,6-TDI. In such an application, use of the Marcali method could introduce significant errors in the measurement of airborne TDI. To overcome this difference in the sensitivity to 2,4- and 2,6-TDI, Rando and Hammad (1985) suggested simple modifications to the Marcali method. The modifications consisted of diazotization at 0 °C (previously 25 °C) for precisely 0.5 min (previously 2.0 min) before measuring the absorbance at 548 nm (previously 550 nm). Under these conditions, the responses from the two isomers were the same.
- (3) Degradation products of polyurethane foam interfere with the Marcali method. The method produces anomalous results when used in monitoring hot-wire polyurethane foam cutting operations, MDI-based metal cast moulding operations and in flame bonding processes. Nitrous fumes from the propane burner in flame bonding operations also interfere with the Marcali method.
- (4) Aromatic amines interfere positively with the original Marcali method.

Meddle and Wood in 1970 recommended a significant modification to the Marcali method based on sampling with dual samplers in parallel, to overcome

the interference due to the aromatic amines (primarily MDA and TDA). In this dual-impinger method, one impinger with an absorbing solution of dimethylformamide and hydrochloric acid collected all diisocyanates and aromatic diamines and hydrolysed the diisocyanates to diamines. Thus it measured the total concentration of diisocyanates plus diamines. The second impinger, containing dimethylformamide and 1,6-diaminohexane (without hydrochloric acid), collected and measured only the aromatic diamines, because the diisocyanates reacted with diaminohexane to form a urea which could not react with the Marcali reagents. The diisocyanate concentration was then calculated by subtracting the diamine concentration found in the second impinger from the total diamine + diisocyanate concentrations measured in the first impinger.

#### Marcali method: hints on use

- Know the limitations of the method (see above).
- Use the Rando and Hammad (1985) modification to eliminate the differences in the sensitivity of 2,4- and 2,6-TDI isomers.
- As a rule, impinger methods should not be used to sample MDI condensation aerosol atmospheres because of sampling losses.
- In the sample preparation step before spectrophotometric measurement, the unreacted sodium nitrite is destroyed by the addition of sulphamic acid according to the following reaction:



A considerable amount of nitrogen can be produced depending upon the amount of sodium nitrite present. If at this stage the test tube is not vigorously shaken to dispel all the nitrogen from the test tube, the nitrogen evolution can continue during the spectrophotometric measurement. Tiny bubbles of nitrogen then stick to the sides of the spectrophotometric cell causing errors in the absorbance measurement. In the NIOSH procedure for MDI (NIOSH, 1977a, 1977b) not only is nitrogen liberated, as above, but also considerable amounts of carbon dioxide. This is the result of adjusting the acidity of the absorbing solution by the addition of 1.5 ml of 16 % sodium carbonate solution.

- *N*-1-Naphthylethylenediamine solution must be prepared daily.
- Pure 4,4'-MDI degrades fairly rapidly when stored at ambient conditions of laboratory temperature and humidity. Therefore MDI should be purified before use in the preparation of standards. Dissolve the MDI flakes in hot hexane and filter hot. Discard the residue. Cool, and filter off the MDI. Redissolve the MDI in a minimum volume of methylene chloride and reprecipitate by the addition of cold hexane. Collect the precipitated pure MDI by filtration, wash with cold hexane, dry and use for standard preparation.
- Pure 4,4'-MDA can be used for making Marcali standards with appropriate molecular weight correction.

**Other spectrophotometric methods**

Keller and Vogel developed a spectrophotometric method using the sodium salt of 2-{3-(2-methoxy-4-nitrophenyl)-1-methyl-2-triazenyl}-ethanesulphonic acid to produce a diazonium chloride to couple the toluene diamines. The absorption maxima of this TDA-coupled dye were very similar to those of 2,4- and 2,6-TDI, and therefore, using this reagent, a colorimetric method independent of the isomer ratio problem was possible (Keller and Vogel 1992).

Latawiec (1991) reported an interesting and novel approach to the screening or quantitation of common aromatic diisocyanates in a variety of matrices. In this method a solution of 4-nitrobenzenediazonium tetrafluoroborate in dimethylsulphoxide was used to sample diisocyanates. This reagent reacted with MDI and TDI to form coloured complexes which could be used to quantitate the diisocyanates visually or spectrophotometrically. Latawiec reported use of this reagent to determine residual TDI in foams and adhesives. This method has not been critically evaluated but may be usable as a potential screening procedure in wipe tests.

All the popular spectrophotometric methods were based on acid hydrolysis of MDI and TDI to their corresponding diamines. Therefore, all other aromatic amines or isocyanates in the air interfered positively with these methods. These spectrophotometric methods for TDI vapour were widely used, without modification, for the sampling and analysis of MDI, based on the assumption that, at normal ambient temperature and pressure, MDI exists only in the vapour phase. However, Dharmarajan and Weill (1978) pointed out that MDI in workplace air may contain both aerosol and vapour, and that impingers do not collect aerosols efficiently in the size range of 0.1 to 1  $\mu\text{m}$ , typical of MDI condensation aerosols.

Several other spectrophotometric methods have been developed for MDI and TDI in air. However, in the mid-1970s, the spectrophotometric methods were gradually replaced with the more specific and sensitive HPLC methods for diisocyanates.

**Analysis of nonairborne MDI and TDI*****Sampling and analysis of MDI and TDI in soil and water***

The main reason for measuring the presence of MDI or TDI in water, or in soil or other solid media, is to check on contamination following spillages and clean-up operations. In such situations, detection without quantification is normally required. In controlled environmental studies, such as ecotoxicity tests, or in experiments on the fate of MDI or TDI in the environment, quantitative measurements are normally needed: here the media include water, soil and sediments, so water is always present in these studies. However, MDI and TDI are almost insoluble in water so the test methods used have to be appropriate for heterogeneous samples.

**Detection of MDI or TDI**

MDI or TDI may be detected in or above water or soil simply by using paper tape, as supplied by tape monitor manufacturers. This technique was used by Kiestler (1999) in checking the efficacies of various mixtures used for neutralizing diisocyanate spills.

### **Quantitative analysis of MDI or TDI**

MDI or TDI may be determined quantitatively in aqueous systems, including water, soil and sediment, by extraction with a suitable solvent followed by either GC or, more usually, derivatization and HPLC.

In studies carried out on the fate of TDI in water, Kitano *et al.* (1989) used solvent extraction and GC to determine TDI levels, whilst Yakabe *et al.* (1994b) derivatized the diisocyanate with dibutylamine followed by HPLC analysis. In a similar study on the fate of MDI in water, Yakabe *et al.* (1994a) also used these techniques with MDI. For all the studies, the corresponding diamines, MDA and TDA, were also quantitatively determined by HPLC.

Heimbach (1993) carried out a study, which investigated the effects arising from a simulated accidental spillage of polymeric MDI into a pond (see *Part 4, The environment*). MDI was quantitatively determined in water, sediment and fish. For all three systems, HPLC was carried out on the dibutylamine derivative. TLC, following addition of nitroreagent, was used to assess whether there was any MDI in the water phase. In addition, MDA was determined in the three systems by HPLC.

Studies were carried out by Brochhagen and Keller (1983) following a road tanker accident and spillage of TDI. Levels of TDI in soil and water were determined using either a photometric method (according to Marcali) or TLC after addition of nitroreagent. TLC was also used to determine the concentrations of TDA in soil and water.

### **Quantitative estimation of MDI or TDI in bulk samples**

Determination of the isocyanate content of samples of MDI or TDI, or one of their many modified forms, is usually carried out for quality assurance purposes. The usual method is to react a known quantity of the sample with excess di-*n*-butylamine, and to back-titrate the excess diamine with standard aqueous hydrochloric acid.

Methods which may be useful are described in: SPI and PURMAC, 1991; ASTM D5155-96 (ASTM, 1996); EN ISO 9369: 1997 (BSI, 1997).

### **Wipe sampling techniques for MDI and TDI**

Wipe sampling methods are qualitative techniques to detect surface contamination by chemical substances. The amount of diisocyanate collected on a wiping medium is dependent upon the properties of the surface. Different responses may be obtained when the same amount of MDI or TDI is placed on clean glass, porous concrete, or synthetic materials, then wiped with a given wiping medium. Many of the analytical techniques already described can be adapted for wipe testing of diisocyanates. For example, glass-fibre filters soaked in dilute sulphuric acid can be used to wipe diisocyanate-contaminated surfaces. The acid-hydrolysed amines on the filter can then be analysed by spectrophotometric, HPLC or GC methods. However, this type of wipe test does not provide immediate results. Immediate response or direct reading wipe tests are very useful in many situations, such as after a spill.

Colorimetric Laboratories Inc. (CLI) (Klingner, 1992) markets a proprietary direct-indicating aliphatic and aromatic isocyanate wipe-test kit called Swypes<sup>™</sup>. Preliminary tests indicate satisfactory performance. CLI markets two

different kinds of Swypes, for detecting skin contamination, and for surface contamination, respectively.

The skin test kit contains a cloth pad for wiping the skin. The skin is wiped with the pad which is then placed in a container of developing solution with the colour detection strip at the top. The developing solution in the container rises by capillary action through the cloth pad to the detection strip. A red colour develops if the skin is contaminated with MDI or TDI. The skin Swype™ will detect about 3 to 5 µg of MDI or TDI.

For surface detection, the area to be tested is first wetted by spraying a developing solution. After about 30 s the surface is wiped with an impregnated pad; a red colour indicates MDI or TDI contamination. The colour development takes about 2 to 3 min depending upon the amount of diisocyanate present on the surface.

### ***Sampling and analysis of MDI, TDI, MDA and TDA in flexible polyurethane foams***

There may be occasions when it is necessary to prove that foams are fully cured by demonstrating the absence of MDI or TDI and/or their corresponding diamines. In these circumstances, the following approaches can be used for TDI and TDA, and may be adapted for MDI and MDA.

SPI Polyurethane Division (SPI, 1990) published three methods for the determination of residual TDI and TDA in flexible polyurethane foams, for compliance with Proposition 65, a Californian state regulation in the USA. They are all adaptations of the HPLC methods described above. A brief description of the methods is given below.

#### **Method 1**

The foam (5 g sample) is extracted three times with 100 ml of a 0.025 % 1,2-MP solution in toluene. TDI in the foam reacts with the 1,2-MP to form the urea, and TDA is extracted by the toluene. Approximately 1 ml of acetic acid anhydride is added to the extract to derivatize and stabilize the TDA. The combined aliquots of toluene are evaporated to dryness and redissolved in 5 ml of methanol. The sample is divided for TDI and TDA analysis using two different HPLC methods.

#### **Method 2**

The foam (5 g sample) is extracted three times with methylene chloride containing 0.1 % diethylamine. TDI reacts with the amine to form the urea and TDA is extracted by methylene chloride. The extracts are combined to a known volume.

A 50 ml aliquot of the extract is evaporated to dryness and extracted with a 50/50 methanol/water solution, and analysed by HPLC for TDI. A 200 ml aliquot of the extract is extracted with a 50 ml portion of 0.3 N HCl. A 5 ml portion of the acidic extract is diluted to 50 ml with the mobile phase (water with 2.05 % sodium acetate, 0.01 % (v/v) triethylamine, and 0.01 % phosphoric acid) and analysed by HPLC for TDA.

### Method 3

The foam (2 to 3 g sample) is extracted three times with a solution of *N*-methyl-1-naphthylmethylamine solution in methylene chloride. The TDI reacts to form the urea and TDA is extracted unchanged by the methylene chloride. An aliquot of the leachate can be directly analysed for TDI by HPLC using fluorescence detection. The remaining methylene chloride leachate is extracted with 10 % HCl in water using a separating funnel to isolate all the TDA. The aqueous layer containing the TDA is adjusted to pH 9 with aqueous potassium hydroxide and derivatized with Fluram™ and analysed by HPLC using fluorescence detection.

Further methods, which can be used to determine both MDA and TDA in polyurethane foams, have been developed by III in cooperation with ISOPA. In these methods a 500 mg sample of foam is placed in a 5 ml syringe and extracted 20 times with 3 ml of 1 % acetic acid in water, to give an aqueous solution. The solution is analysed using reverse phase HPLC and UV detection. The use of a mass spectrometer or electrochemical detection increases confidence in identification of samples containing co-eluting peaks. Full details are given in Lunardon *et al.*, 2001.

### A critical review of exposure assessment techniques used in occupational health studies of MDI and TDI

Over the past 40 years, a wealth of information has been gained about the symptoms, etiology and mechanism of isocyanate toxicities, through systematic research studies and evaluations. Many *in vivo* and *in vitro* studies, and some longitudinal and cross-sectional epidemiological studies of workers in industries using isocyanates have been conducted. The exposures to airborne TDI and/or MDI have been assessed using the best available technology of the time. However, as technology has evolved, several limitations and problems associated with the older methods have been revealed. In this section the exposure assessment techniques used in several important occupational health studies are critically reviewed. The intention of this section is not to denigrate any of these studies, but to provide a better insight and appreciation of the exposure assessment issues.

*Modifications of the Marcali method*  
Reilly (1963); Grim and Linch (1964); Meddle *et al.* (1969).

Levine *et al.* (1995) and Garabrant and Levine (2000) critically reviewed the methods of exposure assessment and the pulmonary effects of MDI and TDI in 19 epidemiological studies, covering exposed populations totalling over 2400 subjects. Seventeen of these studies had populations exposed to TDI and four to MDI. The exposed populations worked in diisocyanate manufacturing plants, polyurethane foam production, and other operations such as sewing polyurethane fabric, parts manufacturing, spray painting, injection moulding and adhesive manufacturing. The exposure assessment method used in nine of these studies was based on the spectrophotometric method developed by Marcali (1957) or a modified version of the Marcali method (see marginal note).

Five of these studies used the chemically impregnated paper tape monitors for both area and personal exposures (Model 7000 area and MCM personal monitors manufactured by MDA Inc.). Two studies used HPLC based methods and the remaining studies either did not monitor exposure or did not specify the monitoring methods used.

A critical review of the exposure assessment methods used in these studies revealed deficiencies and a discussion of these drawbacks could improve the design and reporting of future studies. The following are some of the exposure assessment deficiencies in these studies:

- Several studies did not report the limit of detection (LOD), the limit of quantitation (LOQ) and the acceptable measurement range of the monitoring techniques. The limit of detection is the level at which the analyst can be certain that he has detected the analyte (the analyte signal should be a minimum of three times the standard deviation of the blank signal) and the limit of quantitation is the amount of the analyte which can be quantified with an acceptable precision.
- There were studies which reported analyte concentration values below the range of what is generally considered possible by the method. These numbers could be false positives or have very large errors and bias built into them. As a general rule, the errors in measurement at the limit of detection levels are very high.
- The deficiencies of the Marcali method have already been described. This method can underestimate MDI and TDI concentrations depending upon the ratio of the isomers in the standards compared with the ratio in the environment sampled (Rando *et al.*, 1984).
- Impinger sampling, used in the Marcali and some HPLC methods, has been shown to significantly underestimate MDI, because of the poor aerosol collection efficiency of the impinger (Dharmarajan and Weill, 1978; Booth *et al.*, 1983; Hext, 1996).
- The Marcali method cannot differentiate between isocyanates and their corresponding amines and can therefore overestimate diisocyanate concentrations because of interferences from primary aromatic amines (Reilly, 1963; Grim and Linch, 1964; Meddle *et al.*, 1969).
- The Marcali method or the HPLC method can only provide one time-weighted average exposure and can thus miss peak exposures.
- The Model 7000 (area) and the MCM (personal) paper tape monitors were critically evaluated for the measurement of TDI and their limitations summarized (Dharmarajan and Rando, 1980). The minimum time required to resolve consecutive exposure peaks was 5 to 6 min for the Model 7000 monitor and 9 to 10 min for the MCM. Thus, spikes in concentrations over shorter time periods would have had their maxima underestimated. The LODs of these instruments were somewhere between 1 and 5 ppb for TDI. The LOQs were greater than 5 ppb. The error curve for the determination of TDI showed greater than 30 % noise at concentrations less than 10 ppb or greater than 60 ppb. Oxides of nitrogen, and chlorine interfered positively and sulphur dioxide showed negative interferences. At greater than 10 ppb TDI concentration, the calibration curves for 2,4- and 2,6-TDI differed, with 2,6-TDI having a lower response. Later studies (Hext, 1996) with newer tape monitors specifically designed for MDI showed that MDI aerosol concentrations were significantly underestimated by these paper tape monitors.
- Many of these studies used area monitoring results for determining personal exposures. However, several industrial hygiene studies have shown that area monitoring does not correlate with personal monitoring data.

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