

## VIII. APPENDIX I - Sampling and Calibration Methods

### (a) Sampling

The sample is drawn through an all-glass midget impinger containing 15 ml of absorbing solution (Appendix II). Sampling is performed for 20 minutes at a rate of 2 liters per minute, using a personal sampling pump or other satisfactory source of suction. The flow rate, with an impinger on line, should be checked before and after the sample is taken.

Care should be taken to prevent any loss of the sample due to spillage, leakage or evaporation during transfer or shipment to the laboratory. If the impingers are to be shipped intact, then the tips of the stem should be securely capped with parafilm or a polytetrafluoroethylene sleeve. If the stem is to be removed, be sure to allow all of the absorbing solution to run out of the tube before removing; complete drainage must be provided by touching the tip against the inner surface of the cylinder, by careful blowout into the cylinder or by gently tapping the tube against the inside cylinder wall. After the stem has been removed, stopper the cylinder with a clean polyethylene stopper. Do not use rubber stoppers. The cylinders should be shipped in an upright position in a hand-carrying case after careful and secure packing with cushioning materials. The TDI reaction product in the absorbing solution is stable for at least 2 weeks.

(b) Calibration

Since the accuracy of an analysis can be no greater than the accuracy of the volume of air which is measured, the accurate calibration of a sampling device is essential to the correct interpretation of an instrument's indication. The frequency of calibration is dependent on the use, care, and handling to which the pump is subjected. Pumps should be calibrated if they have been subjected to misuse or if they have just been repaired or received from a manufacturer. If the instrument receives hard usage, more frequent calibration may be necessary.

Ordinarily, pumps should be calibrated in the laboratory both before they are used in the field and after they have been used to collect a large number of field samples. The accuracy of calibration is dependent on the type of instrument used as a reference. The choice of calibration instrument will depend largely upon where the calibration is to be performed. For laboratory testing, a 1-liter burette or wet-test meter is recommended, although other standard calibrating instruments such as spirometer, Marriott's bottle, or dry-gas meter can be used. The actual set-up will be the same for either instrument. The calibration instrument will be connected in sequence to the impinger unit which will be followed by the sampler pump. In this way, the calibration instrument will be at atmospheric pressure. If the personal sampler pump is used, each pump must be calibrated separately. If the burette is used, it should be set up so that the flow is toward the narrow end of the unit.

Care must be exercised in the assembly procedure to ensure that seals at the joints are airtight and that the length of connecting tubing is kept at a minimum. Calibration should be performed under the same conditions of pressure and temperature as those encountered in use. The calibrated pump rotameter should be used to set the flow rate in the field.

The microimpinger tip inside diameter tolerance must be maintained at  $1.000 \pm 0.025$  mm, and a calibration must be provided with each impinger used to maintain volumetric accuracy within 5% to compensate for differences in pressure drop caused by orifice diameters outside this tolerance range. Calibration should be performed under the same conditions of pressure and temperature as will be encountered in use.

## IX. APPENDIX II - Analytical Methods

Toluene diisocyanate in air: The Marcali method [58], incorporating modifications by Grim and Linch [64] and Larkin and Kupel, [71] is recommended.

### Principle

TDI is hydrolyzed by the absorbing solution to the corresponding toluene diamine derivative.

The diamine is diazotized by the sodium nitrite-sodium bromide solution.

The diazo compound is coupled with N-(1-Naphthyl)ethylene-diamine to form a colored complex.

The amount of colored complex formed is in direct proportion to the amount of TDI present. The amount of colored complex is determined by reading the absorbance of the solution at 550 nm.

Toluene diamine is formed on a mole for mole basis from TDI. This amine is used in place of TDI for standards. This accomplishes two things. First, the amine is not as toxic as TDI. Second, TDI is semi-solid at room temperature. Weighing the semi-solid is more difficult than weighing the dry amine. Both compounds have been tested by this method and the results compare favorably.

### Range and Sensitivity

The range of the standards used is equivalent to 1.0 - 20.0  $\mu\text{g}$  TDI. In a 40-liter air sample, this range converts to 0.0035 - 0.070 ppm. The sensitivity can be increased by using longer path length spectrophotometer cells.

If the sample is so concentrated its absorbance is greater than the limits of the standard curve, it can be diluted with absorber solution and the absorbance reread. This extends the upper limit of the range. The upper limit can also be extended by taking a smaller air sample.

A single bubbler absorbs 95% of the diisocyanate if the concentration is below 2 ppm. Above 2 ppm, about 90% is recovered.

#### Interferences

Any free organic amine will interfere, including any that may be present in detergents.

Methylene-di-(4-phenylisocyanate) (MDI) will form a colored complex in this reaction. However, its color development time is about 1 - 2 hours compared with 5 minutes for TDI. Therefore MDI is not a serious problem, if color density is determined within 10 minutes of the addition of coupling reagent.

#### Apparatus

Beckman Model B spectrophotometer or equivalent

Cells, 1-cm, 4-cm, 5-cm, or 10-cm matched cells

Several (each) volumetric flasks: 50 ml, 100 ml, 1-liter,  
glass-stoppered

Balance capable of weighing to at least three decimal places

Pipettes: 0.5 ml, 1 ml, 15 ml

Graduated cylinders: 25 ml, 50 ml

#### Reagents

All reagents must be ACS reagent grade or better

Double distilled water

2, 4-diaminotoluene

Hydrochloric acid, concentrated, 11.7 N

Glacial acetic acid, concentrated, 17.6 N

Sodium bromide

Sodium nitrite solution: Dissolve 3.0 g sodium nitrite and 5.0 g sodium bromide in about 80 ml double distilled water. Adjust volume to 100 ml with double distilled water.

Sulfamic acid

Sulfamic acid solution, 10% w/v: dissolve 10 g sulfamic acid in 100 ml double distilled water.

N-(1-Naphthyl)ethylenediamine dihydrochloride

N-(1-Naphthyl)ethylenediamine solution: Dissolve 50 mg in about 25 ml double distilled water. Add 1 ml concentrated hydrochloric acid and dilute to 50 ml with double distilled water. Solution should be clear; any coloring is due to contamination by free amines, and if the solution is colored it should not be used.

Absorber solution: Add 35 ml concentrated hydrochloric acid and 22 ml glacial acetic acid to approximately 600 ml double distilled water. Dilute the solution to 1 liter with double distilled water. Use 15 ml in each sample-collecting impinger.

Standard solution A: Weigh out 140 mg of 2,4-toluenediamine (equivalent to 200 mg of 2,4-toluene diisocyanate). Dissolve in 660 ml of glacial acetic acid, transfer to a 1-liter glass-stoppered volumetric flask, and make up to volume with double distilled water.

Standard solution B: Transfer 10 ml of standard solution A to a glass-stoppered 1-liter volumetric flask. Add 27.8 ml of glacial acetic acid so that when solution B is diluted to 1 liter with double distilled water, it will be 0.6N with respect to acetic acid.

#### Procedure

##### Cleaning Equipment:

Wash all glassware in a hot amine-free detergent solution, or soak in a 1% aqueous trisodium phosphate (analytical reagent) solution at room temperature, preferably overnight, to remove any oil.

Rinse well with hot tap water.

Rinse well with double distilled water. Repeat this rinse several times. Any amines from organic detergents must be removed to prevent interferences.

##### Analysis of Samples:

Remove impinger tube taking care not to lose any absorber solution.

Start blank at this point by adding 15 ml fresh absorber solution to a clean impinger cylinder. To each bubbler add 0.5ml of 3% sodium nitrite solution, gently agitate, and allow solution to stand for 2 minutes.

Add 1 ml of 10% sulfamic acid solution, agitate and allow solution to stand about 2 minutes to destroy all the excess nitrous acid present.

Add 1 ml of 0.1% N-(1-Naphthyl)ethylenediamine solution. Agitate and allow color to develop. Color will be developed in 5 minutes. A reddish-blue color indicates the presence of TDI.

Add double distilled water to adjust the final volume to 20 ml in the cylinder. Mix.

Transfer each sample and blank to 1-cm or longer spectrophotometer cell.

Using the blank, adjust the spectrophotometer to 0 absorbance

Determine the absorbance of each sample at 550 nm.

From the previously prepared calibration curve (see below) read the micrograms TDI corresponding to the absorbance of the sample and calculate the parts per million TDI.

#### Calibration and Standards

To each of a series of eight 25-ml graduated cylinders add 5 ml of 1.2N hydrochloric acid.

To these cylinders add the following amounts of 0.6N acetic acid: 10.0, 9.5, 9.0, 8.0, 7.0, 6.0, 5.0, and 0.0 ml, respectively.

To these cylinders add standard solution B in the same order as the acetic acid is added: 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 10.0 ml, so that the final volume is 10 ml. None (0.0 ml) of the standard is added to the 10 ml acetic acid; 0.5 ml of the standard is added to the 9.5 ml acid; and so on. The cylinders now contain the equivalent of 0.0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, and 20.0  $\mu\text{g}$  TDI, respectively. The standard containing none of the standard solution is the blank.



Add 0.5 ml of the 3.0% sodium nitrite reagent to each cylinder.  
Mix. Allow to stand 2 minutes.

Add 1 ml of the 10% sulfamic acid solution. Mix. Allow to stand for 2 minutes.

Add 1 ml of the N-(1-Naphthyl)ethylenediamine solution. Mix. Let stand for 15 minutes.

Make up to exactly 20 ml with double distilled water.

Transfer each solution to 1-cm or longer spectrophotometer cell. (At the lower end of the calibration curve, 5-cm cells give an 11% relative instrumental error for the 1.0 µg TDI standard. For smaller path lengths, the error is greater.)

Using the blank, adjust the spectrophotometer to 0 absorbance at 550 nm.

Determine the absorbance of each standard at 550 nm.

A standard curve is constructed by plotting the absorbance against micrograms TDI.

#### Calculations

$$\text{ppm} = \frac{\text{micrograms} \times 24.45}{174.15 \times 40} = \text{micrograms} \times 0.00351$$

micrograms - micrograms TDI taken from standard curve

mol wt = wt TDI = 174.15

V = volume of air sample in liters (40 liters)

X. APPENDIX III - MATERIAL SAFETY DATA SHEET

The following items of information which are applicable to any specific product or material containing toluene diisocyanate shall be provided in the appropriate section of the Material Safety Data Sheet or approved form. If a specific item of information is inapplicable (ie, flash point) initials "n.a." (not applicable) should be inserted.

(i) The product designation in the upper left hand corner of both front and back to facilitate filing and retrieval. Print in upper case letters in as large print as possible.

(ii) Section I. Name and Source.

(A) The name, address, and telephone number of the manufacturer or supplier of the product.

(B) The trade name and synonyms for a mixture of chemicals, a basic structural material, or for a process material; and the trade name and synonyms, chemical name and synonyms, chemical family, and formula for a single chemical.

(iii) Section II. Hazardous Ingredients.

(A) Chemical or widely recognized common name of all hazardous ingredients.

(B) The approximate percentage by weight or volume (indicate basis) which each hazardous ingredient of the mixture bears to the whole mixture. This may be indicated as a range of maximum amount, ie, 10-20% V; 10% max. W.

(C) Basis for toxicity of each hazardous material such as established OSHA standard in appropriate units and/or LD50 showing

amount and mode of exposure and species, or LC50 showing concentration, duration of exposure, and species.

(iv) Section III. Physical Data.

(A) Physical properties of the total product including boiling point and melting point in degrees Fahrenheit; vapor pressure, in millimeters of mercury; vapor density of gas or vapor (air = 1); solubility in water, in parts per hundred parts of water by weight; specific gravity (water = 1); percentage volatile (indicate if by weight or volume) at 70 Fahrenheit; evaporation rate for liquids (indicate whether butyl acetate or ether = 1); and appearance and odor.

(v) Section IV. Fire and Explosion Hazard Data.

(A) Fire and explosion hazard data about a single chemical or a mixture of chemicals, including flash point, in degrees Fahrenheit; flammable limits, in percent by volume in air; suitable extinguishing media or agents; special fire-fighting procedures; and unusual fire and explosion hazard information.

(vi) Section V. Health Hazard Data.

(A) Toxic level for total compound or mixture, relevant symptoms of exposure, skin and eye irritation properties, principal routes of absorption, effects of chronic (long-term) exposure and emergency and first-aid procedures.

(vii) Section VI. Reactivity Data.

(A) Chemical stability, incompatibility, hazardous decomposition products, and hazardous polymerization.

(viii) Section VII. Spill or Leak Procedures.

(A) Detailed procedures to be followed with emphasis on precautions to be taken in cleaning up and safe disposal of materials leaked or spilled. This includes proper labeling and disposal of containers containing residues, contaminated absorbants, etc.

(ix) Section VIII. Special Protection Information.

(A) Requirements for personal protective equipment, such as respirators, eye protection and protective clothing, and ventilation, such as local exhaust (at site of product use or application), general, or other special types.

(x) Section IX. Special Precautions.

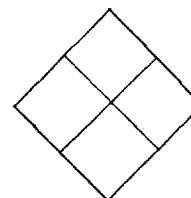
(A) Any other general precautionary information, such as personal protective equipment for exposure to the thermal decomposition products listed in Section VI, and to particulates formed by abrading a dry coating, such as by a power sanding disc.

(xi) The signature of the responsible person filling out the data sheet, his address, and the date on which it is filled out.

PRODUCT DESIGNATION

**MATERIAL SAFETY  
DATA SHEET**

Form Approved  
Budget Bureau No.  
Approval Expires  
Form No. OSHA



**SECTION I SOURCE AND NOMENCLATURE**

MANUFACTURER'S NAME	EMERGENCY TELEPHONE NO.
ADDRESS (Number, Street, City, State, ZIP Code)	
TRADE NAME AND SYNONYMS	CHEMICAL FAMILY
CHEMICAL NAME AND SYNONYMS	FORMULA

**SECTION II HAZARDOUS INGREDIENTS**

BASIC MATERIAL	APPROXIMATE OR MAXIMUM % WT. OR VOL.	ESTABLISHED OSHA STANDARD	LD 50		LC 50	
			ORAL	PERCUT.	SPECIES	CONC.

**SECTION III PHYSICAL DATA**

BOILING POINT	°F.	VAPOR PRESSURE	mm Hg.
MELTING POINT	°F.	VAPOR DENSITY (Air=1)	
SPECIFIC GRAVITY (H <sub>2</sub> O=1)		EVAPORATION RATE ( _____ =1)	
SOLUBILITY IN WATER	Pts/100 pts H <sub>2</sub> O	VOLATILE	% Vol.                      % Wt.
APPEARANCE AND ODOR			

**SECTION IV FIRE AND EXPLOSION HAZARD DATA**

FLASH POINT	FLAMMABLE (EXPLOSIVE) LIMITS	UPPER
METHOD USED		LOWER
EXTINGUISHING MEDIA		
SPECIAL FIRE FIGHTING PROCEDURES		
UNUSUAL FIRE AND EXPLOSION HAZARDS		

PRODUCT DESIGNATION

**SECTION V HEALTH HAZARD DATA**

TOXIC LEVEL

CARCINOGENIC

PRINCIPAL ROUTES OF ABSORPTION

SKIN AND EYE IRRITATION

RELEVANT SYMPTOMS OF EXPOSURE

EFFECTS OF CHRONIC EXPOSURE

EMERGENCY AND FIRST AID PROCEDURES

**SECTION VI REACTIVITY DATA**

CONDITIONS CONTRIBUTING TO INSTABILITY

CONDITIONS CONTRIBUTING TO HAZARDOUS POLYMERIZATION

INCOMPATIBILITY (Materials to Avoid)

HAZARDOUS DECOMPOSITION PRODUCTS

**SECTION VII SPILL OR LEAK PROCEDURES**

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED

WASTE DISPOSAL METHOD

**SECTION VIII SPECIAL PROTECTION INFORMATION**

VENTILATION REQUIREMENTS LOCAL EXHAUST

PROTECTIVE EQUIPMENT (Specify Types) EYE

MECHANICAL (General)

GLOVES

SPECIAL

RESPIRATOR

OTHER PROTECTIVE EQUIPMENT

**SECTION IX SPECIAL PRECAUTIONS**

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORAGE

OTHER PRECAUTIONS

Signature \_\_\_\_\_

Address \_\_\_\_\_

Date \_\_\_\_\_

XI. APPENDIX IV - DEFINITION OF TERMS AND ABBREVIATIONS

FEV 1.0 - Forced expiratory volume in 1 second. (The volume of air expired during the first one second of a maximally forced expiration.)

FR 75% - Flow rate at 75% (etc.) of vital capacity.

FVC - Forced vital capacity.

PFR - Peak Flow rate.

TLV - Threshold Limit Value, an occupational health guide recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) as a safe limit for long-term exposures of workers for an 8-hour day, 40-hour week work schedule.

XII. APPENDIX V

British Rubber Manufacturers' Association Questionnaire

Use the actual wording of each question. Put x in the appropriate space after each question. When in doubt record 'NO'.

PREAMBLE I am going to ask you some questions mainly about your chest.  
I should like you to answer 'YES' or 'NO' whenever possible.

- |   | YES | NO  | N/A |
|---|-----|-----|-----|
| 1. Do you usually cough first thing in the morning or on getting up?  | ___ | ___ |     |
| (Count a cough with first smoke or on first going out of doors. Exclude throat clearing or a single cough.)               |     |     |     |
| 2. Do you cough like this on most days for as much as three months each year?   | ___ | ___ | ___ |
| 3. Do you cough at work?  | ___ | ___ |     |
| 4. Do you usually bring up any phlegm from your chest first thing in the morning or on getting up?                        | ___ | ___ |     |
| (Count phlegm with the first smoke or on first going out of doors. Exclude phlegm from the nose. Count swallowed phlegm.) |     |     |     |
| 5. Do you bring up phlegm like this on most days for as much as three months each year?                                   | ___ | ___ | ___ |
| 6. In the past three years, have you had a period of (increased) cough and phlegm lasting 3 weeks or more?                | ___ | ___ |     |
| 7. Have you had more than one such period?  | ___ | ___ |     |
| 8. Does your chest ever feel tight or your breathing become difficult?  | ___ | ___ |     |
| 9. Do you get this apart from colds?  | ___ | ___ |     |
| If YES: specify.....(Interviewer to code:)  |     |     |     |
| (a) With exercise   | ___ | ___ |     |
| (b) At work   | ___ | ___ |     |



(c) Any other time

If disabled from walking by skeletal or other physical disability put 'X' here.

10. Are you troubled by shortness of breath, when hurrying on the level or walking up a slight hill?

(If 'No' omit questions 11 and 12)

11. Do you get short of breath walking with other people of your own age on level ground?

(If 'No' omit question 12)

12. Do you have to stop for breath when walking at your own pace on level ground?

13. Do you usually have a stuffy nose or catarrh at the back of your nose in the winter?

14. Do you have this in the summer?

(If 'No' to both questions 13 and 14, go to question 16)

15. Do you have this on most days for as much as three months each year?

16. During the past 3 years have you had any chest illness which has kept you off work or from your usual activities for as much as a week?

17. Did you bring up more phlegm than usual in any of these illnesses?

18. Have you had more than one illness with phlegm like this in the last 3 years?

HAVE YOU EVER HAD:

19. An injury or operation affecting your chest?

20. Heart trouble?

21. Bronchitis?

22. Pneumonia? \_\_\_\_\_
23. Pleurisy? \_\_\_\_\_
24. Pulmonary tuberculosis? \_\_\_\_\_
25. Bronchial asthma? \_\_\_\_\_
26. Eczema? \_\_\_\_\_
27. Dermatitis? \_\_\_\_\_
28. Pneumoconiosis? \_\_\_\_\_
29. Byssinosis? \_\_\_\_\_
30. Other chest trouble? \_\_\_\_\_

Give relevant details after each positive answer.

31. Do you smoke? \_\_\_\_\_
- (Record 'Yes' if regular smoker up to one month ago)  
If 'No' to 31:
32. Have you ever smoked? \_\_\_\_\_
- (Record 'No' if subject has never smoked as much as one cigarette a day, or 1 oz. tobacco a month, for as long as one year)
33. Age when stopped \_\_\_\_\_ years. Was this in last month? \_\_\_\_\_

If 'Yes' to 31 or 32: Fill in figures below:

	Amount smoked	
	Now	Before stopping
Cigarettes/day (Average including weekends) .. .. .	...	.....
Oz. tobacco/week (handrolled) ..	...	.....
Oz. tobacco/week (pipe) .. ..	...	.....
Cigars/week (large) .. .. .	...	.....
Cigars/week (small) .. .. .	...	.....

OCCUPATION (1st interview only)

(Record on dotted lines the years in which subject has worked in any of these industries, e.g. 1960-63)

- |  | YES   | NO    |
|--|-------|-------|
| 34. Have you ever worked in a dusty job? _____                                 | _____ | _____ |
| 35. In a coal mine? _____  | _____ | _____ |
| 36. In any other mine? _____   | _____ | _____ |
| 37. In a quarry? _____   | _____ | _____ |
| 38. In a foundry? _____  | _____ | _____ |
| 39. In a pottery? _____  | _____ | _____ |
| 40. In a cotton, flax or hemp mill? _____                                      | _____ | _____ |
| 41. With asbestos? _____   | _____ | _____ |
| 42. In any other dusty job? _____  | _____ | _____ |
| If 'Yes', specify _____  |       |       |
| _____  |       |       |
| 43. Have you been exposed regularly to irritating gas or chemical fumes? _____ | _____ | _____ |

If 'Yes' give details of nature and duration \_\_\_\_\_  
\_\_\_\_\_

OCCUPATION (Follow-up only)

44. What is your present job? \_\_\_\_\_

45. How long have you been doing it? \_\_\_\_\_

46. What was your previous job in the factory? \_\_\_\_\_

Taken with minor changes from Operating and Medical Codes of Practice for Safe Working with Toluene Di-isocyanate, Health Advisory Committee, British Rubber Manufacturers' Association Ltd. [81]

Table XIII-1

Properties of Commercial Samples of 80% 2,4:20% 2,6 Toluene Diisocyanate\*

Molecular Weight	174.16		
Flash Point	275 F		(135 C)
Specific Gravity of Liquid	1.22 at 77 F (25 C)		
Boiling Point	482 F		(250 C)
Freezing Point	68-72 F		(20-22C)
Vapor Pressure	Temp. F	Temp. C	mm Hg
	50	10	.02
	77	20	.05
	100	38	.10
	150	66	.43
	200	93	1.90
	250	121	10.0
	300	149	36.0

\*Taken from Upjohn Technical Bulletin 105. [3]

Table XIII-2

## Summary of TDI Concentrations in Air and Cases of TDI Intoxication at 14 Plants

Plant	Year(s)	Air Analyses		Workers Exposed	Number of Cases	
		Number of Tests	Av. TDI Conc. ppm		Accepted or Established	Questionable or Disputed
1	1957	--	---	2	1	1
2	1957-58	14	0.005	50	3	28
	1960	33	0.028	100	14	25
	1961-62	55	0.015	50	3	2
3	1958-60	12	0.009	25	0	0
4	1958-62	21	0.004	40	5	15
5	1958-61	11	0.008	6	1	?
6	1958-61	28	0.015	40	8	0
7	1961	4	<0.001	4	0	0
8	1961	5	<0.001*	5	1	0
9	1961	3	0.006	4	0	0
10	1961	14	0.002**	3	2	0
11	1961	14	0.54**	4	4	0
12	1962	6	0.009	6	0	1
13	1962	4	Nil	20	0	1
14	1962	6	0.000	20	0	0
Total		230		379	42	73

\*Probably not representative of exposure.

\*\*Not representative of exposure.

From Elkins et al. [49]

73-11022