Method number:	PV2046
Target Concentration:	0.02 ppm (170 µg/m^3) (arbitrary). There is no OSHA permissible exposure level (PEL) or ACGIH threshold limit value (TLV) for NDI.
Procedure:	Samples are collected by drawing a known volume of air through a glass fiber filter (GFF) coated with 1.0 mg of 1-(2-pyridyl) piperazine (1-2PP) which is contained in an open-face cassette. The samples are extracted with 90/10 (V/V) acetonitrile/dimethyl sulfoxide (ACN/DMSO) and analyzed by high performance liquid chromatography (HPLC) using an ultraviolet (UV) or fluorescence detector.
Recommended air volume and sampling rate:	60 minutes at 1.0 L/min (60 L)
Detection limit of the overall procedure	8.0 µg/m^3 (based on the recommended air volume and the analytical detection limit).
Special precautions:	The 1-2PP coated glass fiber filter should be stored at reduced temperature until use.
Status of method:	Partially validated method. This method is presented for information and trial use only.

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1 General Discussion

1.1 Background

1.1.1 History of procedure

This evaluation was undertaken to determine the effectiveness of a 1-2PP coated glass fiber filter as a sampling device for NDI. It follows the procedure developed for methylene bisphenyl isocyanate (MDI) (Ref. 5.1).

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

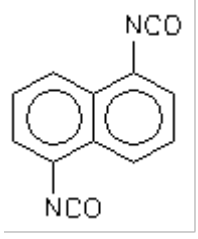
Inhalation of NDI vapors or mists can cause irritation of the mucous membranes in the respiratory tract, running nose, sore throat, productive cough, and shortness of breath or asthma, as has been reported with other isocyanates (e.g. TDI and MDI) (Ref. 5.2).

From the available information on NDI, it appears that its toxicological action is similar to other isocyanates (e.g. TDI and MDI). For this reason, the target concentration adopted 0.02 ppm, the same as MDI. (Ref. 5.1)

1.1.3 Potential workplace exposure

NDI is used in making high-grade urethane cast elastomers (Ref. 5.2). No information was available on the number of workers potentially exposed to NDI.

1.1.4 Physical properties (Ref. 5.2)

CAS number:	3173-72-6
Chemical name:	naphthalene, 1,5-diisocyanato-
Synonyms name:	1,5-naphthalene diisocyanate (NDI)
Molecular formula:	$C_{12}H_6N_2O_2$
Molecular weight:	210.2
Boiling point:	244 °C at 13.3 kPa (100 mmHg)
Melting point:	127 °C
Specific gravity:	1.45 at 20 °C
Solubility:	Soluble in water.
Appearance:	White to pale yellow flakes
Structural formula:	

1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure (based on fluorescence detector)

The detection limit of the analytical procedure is 1.63 ng as NDI per injection. Usually this is the amount of analyte which gives a peak whose height is approximately five times the baseline noise. Because of the interference from 1-2PP and the coated GFF, the higher detection limit was used here.

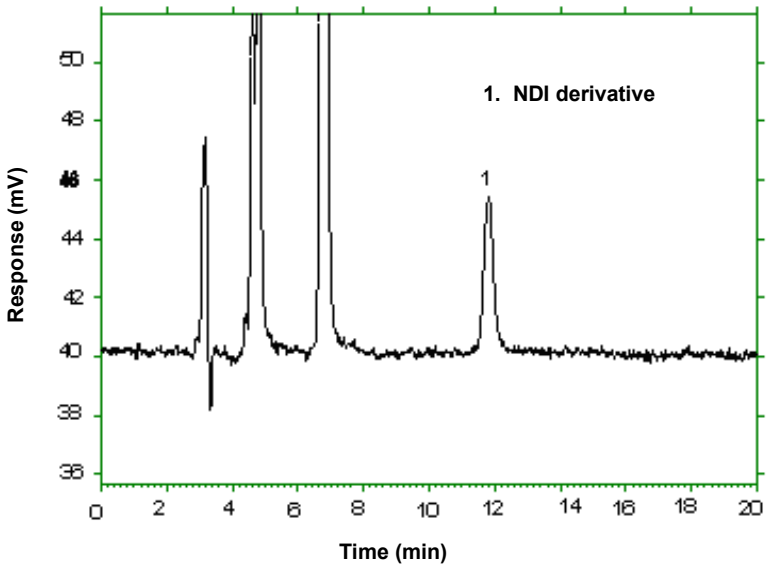


Figure 1.2.1 Chromatogram of the analytical detection limit.

1.2.2 Detection limit of the overall procedure (based on fluorescence detector)

The detection limit of the overall procedure is 0.49 µg as NDI per sample. This is the amount of analyte spiked on a glass fiber filter that, upon analysis, produces a peak similar in size to that of the detection limit of the analytical procedure.

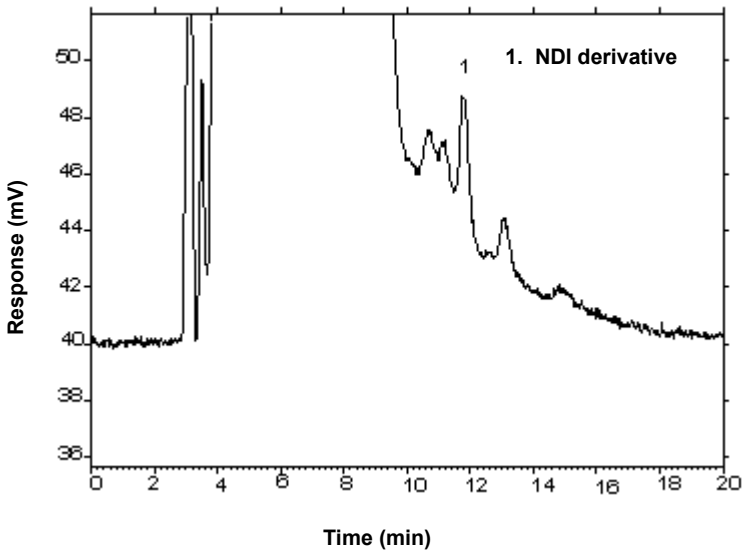


Figure 1.2.2. Chromatogram of the detection limit of the overall procedure.

2 Sampling Procedure

2.1 Apparatus

2.1.1 Samples are collected using a personal sampling pump that can be calibrated within ±5% of the recommended flow rate with the sampling device attached.

2.1.2 A three-piece polystyrene cassette containing a glass fiber filter coated with 1.0 mg of 1-2PP and an untreated backup pad (figure 2.1.2.). These cassettes are commercially available from Millipore Corporation.

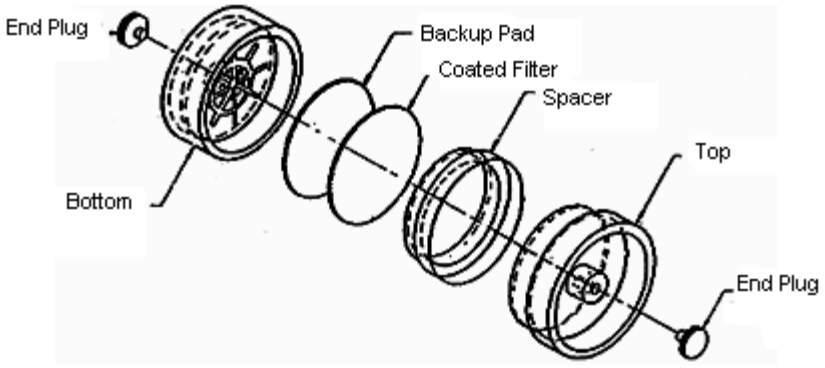


Figure 2.1.2 Sample cassette.

2.2 Glass fiber filter coating procedure

Prepare a solution of 2 mg/mL of 1-2PP in methylene chloride. Spike the glass fiber filters with 0.5 mL of this solution. Allow the filters to air dry, and then dry them in a 40 °C vacuum oven for an additional 2 hours.

Store coated glass fiber filters in a closed jar at reduced temperature as a precaution to prevent decomposition of the 1-2PP. Avoid exposure to strong sunlight.

2.3 Sampling technique

2.3.1 Open-face sampling is performed by removing the top cover from the three-piece cassette and the small plug from the exit port.

2.3.2 Attach the sampler to the sampling pump with a piece of flexible tubing and place it in the worker's breathing zone.

2.3.3 After sampling for the appropriate time, remove the tube and reseal the cassette with the plastic plugs. Wrap each sample end-to-end with a Form OSHA-21 seal.

2.3.4 Record the air volume for each sample and list any possible interference.

2.3.5 Submit at least one blank for each set of samples. The blank is handled in the same manner as the samples except no air is drawn through it.

2.3.6 Submit bulk samples for analysis in a separate container from the air samples.

2.4 Extraction efficiency

Three groups of four 1-2PP coated GFFs were each liquid spiked with 5 µL, 10 µL, and 20 µL of a DMSO solution of NDI 1-2PP derivative equivalent to 0.975 µg/µL NDI. These amounts represent 0.5, 1.0, and 2.0 times the target concentration respectively. They were transferred to 4-mL vials, and sealed with polytetrafluoroethylene PTFE-lined caps and allowed to equilibrate overnight in a drawer at room temperature. The next day the samples were analyzed as per Section 3. The results are listed in Tables 2.4.1., 2.4.2., and 2.4.3. The average extraction efficiencies at 0.5, 1.0, and 2.0 times the target concentration are 0.944, 0.976, and 0.982 respectively.

Table 2.4.1
Extraction Efficiency of NDI
at 0.5x Target Concentration

sample i.d.	µg spiked	µg recovered	recovery (decimal)
D1	4.875	4.623	0.948
D2	4.875	4.541	0.931
D3	4.875	4.638	0.951
D4	4.875	4.609	0.945

Table 2.4.2
Extraction Efficiency of NDI
at 1x Target Concentration

sample i.d.	µg spiked	µg recovered	recovery (decimal)
D5	9.750	9.582	0.983
D6	9.750	9.497	0.974
D7	9.750	9.524	0.977
D8	9.750	9.443	0.969

Table 2.4.3
Extraction Efficiency of NDI
at 2x Target Concentration

sample i.d.	µg spiked	µg recovered	recovery (decimal)
D9	19.50	18.99	0.974
D10	19.50	19.26	0.988
D11	19.50	19.07	0.978
D12	19.50	19.27	0.988

2.5 Retention efficiency

Five 1-2PP coated GFFs were each liquid spiked with 10 µL of a DMSO solution of NDI 1-2PP derivative equivalent to 0.975 µg/µL NDI. All cassettes were sealed with end-plug and allowed to equilibrate overnight in a drawer at room temperature. The next day 60 L of humid air (80% relative humidity) were drawn through each of the samples at 1.0 L/min. The samples were analyzed as per section 3. The results are listed in Table 2.5. The average retention efficiency from the five samplers was 0.978.

Table 2.5
Retention Efficiency of NDI
at 1x Target Concentration

sample i.d.	µg spiked	µg recovered	recovery (decimal)
RE-1	9.750	9.424	0.967
RE-2	9.750	9.693	0.994
RE-3	9.750	9.583	0.983
RE-4	9.750	9.477	0.972
RE-5	9.750	9.473	0.972

2.6 Sample storage

Ten 1-2PP coated GFFs were each liquid spiked with 10 µL of a DMSO solution of NDI 1-2PP derivative equivalent to 0.975 µg/µL NDI. All cassettes were sealed with end-plugs and allowed to equilibrate overnight in a drawer at room temperature. The next day 60 L of humid air (80% relative humidity) were drawn through each of the sample cassettes at 1.0 L/min. The ten samples were divided into two groups of five cassettes each. The first group was stored in a refrigerator (0 °C); the second group was stored in a drawer at ambient temperature. After eight days, they were extracted and analyzed as in Section 3. The results are listed in Table 2.6.1. and 2.6.2. The average recoveries for the refrigerator and ambient temperature storage studies were 0.974 and 0.954, respectively.

Table 2.6.1
Refrigerated Storage

days stored	µg spiked	µg recovered	recovery (decimal)
8	9.750	9.640	0.989
8	9.750	9.639	0.989
8	9.750	9.420	0.966
8	9.750	9.465	0.971
8	9.750	9.288	0.953

Table 2.6.2
Ambient Storage

days stored	µg spiked	µg recovered	recovery (decimal)
8	9.750	9.385	0.963
8	9.750	9.348	0.959
8	9.750	9.205	0.944
8	9.750	9.273	0.951
8	9.750	9.289	0.953

2.7 Recommended air volume and sampling rate

2.7.1 The recommended air volume is 60 L.

2.7.2 The recommended flow rate is 1.0 L/min.

2.8 Interferences (sampling)

It is not known if any compounds will interfere with the collection of NDI. Any suspected interferences should be reported to the laboratory.

2.9 Safety precautions (sampling)

2.9.1 Attach the sampling equipment in such a manner that it will not interfere with work performance or employee safety.

2.9.2 Follow all safety practices that apply to the work area being sampled.

3 Analytical Procedure

3.1 Apparatus

3.1.1 A balance capable of weighing to the nearest one hundredth of a milligram. A Mettler AE240 balance was used in this evaluation to prepare the concentrated standards.

3.1.2 Volumetric flasks, pipets, and syringes of various convenient sizes for preparing standards, making dilutions and making injections.

3.1.3 Glass vials 4-mL with PTFE-lined caps.

3.1.4 An HPLC equipped with a UV detector, and a WISP auto-sampler was used in this evaluation.

3.1.5 An HPLC column capable of separating NDI from any interference. An Econosphere CN column (250-mm x 4.6-mm) was used in this evaluation.

3.1.6 An electronic integrator or some other suitable means for measuring detector response. The Waters 860 Data System was used in this evaluation.

3.2 Reagents

3.2.1 Acetonitrile (ACN), HPLC grade. The solvent used in this evaluation was obtained from Burdick and Jackson, Baxter Healthcare Co.

3.2.2 Dimethyl sulfoxide (DMSO), HPLC grade. The solvent used in this evaluation was obtained from Burdick and Jackson, Baxter Healthcare Co.

3.2.3 Water, HPLC grade. A Millipore Milli-Q system was used to prepare the water in this evaluation.

3.2.4 1-(2-pyridyl) piperazine. 1-2PP, 98% purity, was obtained from Aldrich.

3.2.5 NDI. 100% purity was obtained from Bayer USA Inc.

3.2.6 Extraction solution: 90/10 (V/V) ACN/DMSO.

3.3 Standard preparation

3.3.1 Prepare stock standards by weighing 10 mg of NDI in 10-mL volumetric flasks and diluting to volume with DMSO containing excess 1-2PP (two large drops about 62 mg) solution.

3.3.2 Prepare analytical standard by diluting the stock standards with 90/10 (V/V) ACN/DMSO. A 3.4 µg/mL standard solution corresponds to the target concentration.

3.3.3 Prepare a sufficient number of analytical standards to generate a calibration curve. Analytical standard concentrations must bracket sample concentrations.

3.4 Sample preparation

3.4.1 Transfer the 1-2PP coated GFF to a 4-mL vial.

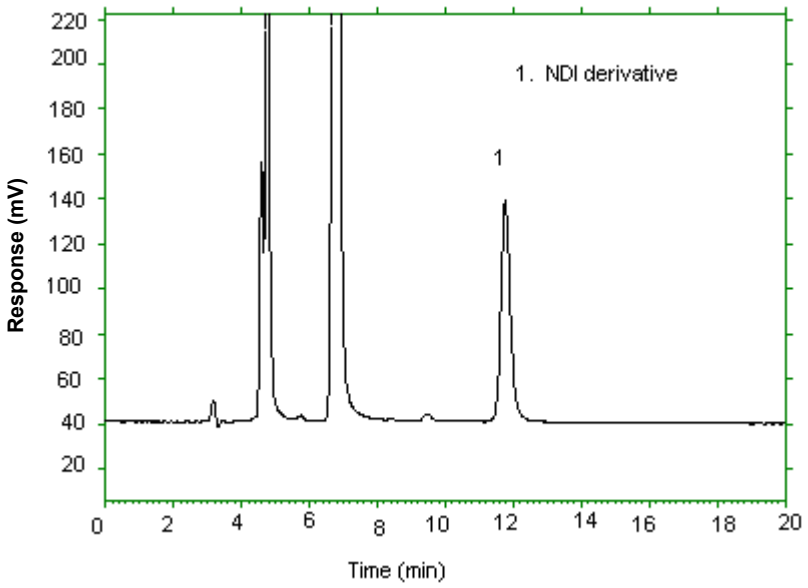
3.4.2 Add 3.0 mL of extracting solution to each vial.

3.4.3 Cap the vials and shake them on a mechanical shaker for 30 min.

3.5 Analysis

3.5.1 Instrument conditions

Column:	Econosphere CN
Eluent:	42.5/57.5 (V/V) ACN/Water, 0.075M Ammonium acetate, pH = 5.9
Flow rate:	1.0 mL/min
Injection volume:	10 µL
Retention time:	11.8 min
UV detector:	254 nm
Fluorescence detector:	excitation 240 nm, emission 370 nm
Chromatogram:	based on fluorescence



Chromatogram at the target concentration.

3.6 Interferences (analytical)

3.6.1 Any compound that responds to fluorescence or UV detector under the analytical conditions and has a similar retention time as the analyte is a potential interference. Generally, chromatographic conditions can be altered to separate an interference from the analyte.

3.6.2 Retention time on a single column is not considered proof of chemical identity. Additional means of identification include using an alternate HPLC column or detection at another wavelength (peak ratioing) or detector ratioing (fluorescene/UV).

3.7 Calculations

3.7.1 Construct a calibration curve by plotting detector response versus concentration (µg/mL) of NDI.

3.7.2 Determine the µg/mL of NDI in samples and blank from the calibration curve.

3.7.3 Blank correct each sample by subtracting the µg/mL found in the blank from the µg/mL found in the corresponding samples.

3.7.4 Determine the air concentration by using the following formulae.

$$mg/m^3 = \frac{(\mu g/mL,\ blank\ corrected)(desorption\ volume,\ mL)}{(air\ volume,\ L)(desorption\ efficiency,\ decimal)}$$

$$ppm = \frac{(mg/m^3)(24.46)}{(210.2)}$$

Where:

24.46 = molar volume (Liters/mole) at 101.3 kPa (760 mmHg) and 25 °C
210.2 = molecular weight of NDI

3.8 Safety precautions (analytical)

3.8.1 Avoid skin contact and air exposure to NDI.

3.8.2 Avoid skin contact and air exposure to all solvents.

3.8.3 Wear safety glasses at all times in the laboratory.

4 Recommendation for Further Study

This method needs to be fully validated.

5 References

5.1 "OSHA Analytical Methods Manual," U.S. Department of Labor, Occupational Safety and Health Administration, OSHA Analytical Laboratory: Salt Lake City, UT, Method 47, American Conference of Governmental Industrial Hygienists (ACGIH): Cincinnati, OH, 1985, ISBN: 0-936712-66-x.

5.2 "Material Safety Data Sheet", Mobay Corporation, polyurethane division, Bayer USA Inc. 1993