HDI BIURET (BIURET OF HEXAMETHYLENEDIISOCYANATE)

Method number:	PV2030
Matrix:	Air
Target Concentration:	0.43 mg/m^3 or 0.02 ppm (arbitrary). There is no OSHA PEL or ACGIH TLV for HDI biuret.
Procedure:	Samples are collected by drawing a known volume of air through glass fiber filters coated with 1 mg of 1-(2-pyridyl)piperazine (l-2PP) in open-faced cassettes. Samples are extracted with 90/10 (v/v) acetonitrile/di-methyl sulfoxide (ACN/DMSO) and analyzed by high performance liquid chromatography (HPLC) using a UV or a fluorescence detector.
Recommended air volume and sampling rate:	15 L at a flow of 1 L/min
Detection limit of the overall procedure (based on the recommended air volume):	0.02 mg/m^3
Status of method:	Stopgap method. This method has been only partially evaluated and is presented for information and trial use.

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Chemists: David B. Armitage
Yihlin Chan
George F. Lewis

Carcinogen and Pesticide Branch
OSHA Analytical Laboratory
Salt Lake City Utah

1. General discussion

1.1. Background

The growing concern with workers' exposure to a variety of isocyanates has spurred a demand for the analysis of work site atmosphere for HDI biuret. OSHA Analytical Laboratory had so far validated the sampling and analytical methods for MDI, 2,4-TDI, 2,6-TDI, and HDI. In all cases, l-(2PP) treated glass fiber filters were selected for the collection. Therefore, this sampling medium was tested for HDI biuret. This report describes the preliminary validation of the sampling method as well as the analytical method developed.

HDI biuret is manufactured by treating HDI with water under controlled conditions. Pure HDI biuret is not commercially available. Mobay's Desmodur 100 is a mixture of homo-polymers, one of which being HDI biuret, comprising usually from 30 to 40% by weight. In this report, the commercial HDI biuret was first derivatized with l-(2PP) then purified via preparative HPLC, and the obtained pure HDI biuret l-(2PP) derivative was used as the analytical standard.

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

No toxicity data of HDI biuret was found in TOXNET or TOXLINE data bases. NIOSH reported increase in symptoms of eye irritation, nasal irritation, throat irritation and chest discomfort among workers engaged in spray painting. These workers were found to be exposed to significant concentrations of organic solvents and isocyanates compound (HDI and HDI biuret). (Ref. 5.1.)

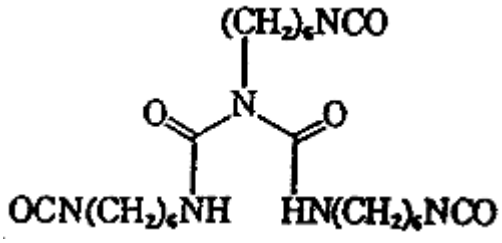
1.3. Potential workplace exposure

No data on the extent of worker exposure to AD1 biuret could be found. The type of work most liable to HDI biuret exposure is spray painting with polyurethane paints -- for example, of airplanes (Ref. 5.1.) and of cars (Ref. 5.2.).

1.4. Physical properties (Ref. 5.4.)

Chemical name:	N,N',2-Tris(6-isocyanatohexyl)imidodicarbonic diamide
Synonyms:	HDI biuret; biuret of 1,6-hexamethylene diisocyanate; Desmodur 100
CAS no.:	4035-89-6
Molecular formula:	C23H38N6O5
Molecular weight:	478
Melting point:	-19 ℃
Density:	1.114(40/4)

Structure:



1.5. Detection limit of the analytical procedure

The detection limit of the analytical procedure is 0.47 ng per injection. This is the amount of analyte which will give a peak whose height is approximately 5 times the baseline noise.

2. Sampling procedure

2.1. Apparatus and reagents

2.1.1. A personal sampling pump that can be calibrated to within 5% of the recommended flow rate

2.1.2 1-(2-Pyridyl)piperazine (1-2PP) treated glass fiber filter. Coated filters are prepared by applying 0.5 mL of a solution of 2 mg/mL l-2PP in methylene chloride to each filter, and drying the filter.

2.1.3. Filter holder (cassette) for 37-mm filters

2.2. Sampling procedure (Ref. 5.5.)

2.2.1. Calibrate pump. Remove the inlet cover from the three-piece cassette in order to sample open face. Save it for installation after sampling.

2.2.2. Attach the collection device to the shirt within the breathing zone. Position the excess tubing so as not to interfere with the work of the employee.

2.2.3. Turn on pump and record the starting time.

2.2.4. Check the pump flow periodically.

2.2.5. Prepare a blank. The blank should be treated the same way as the samples except no air was drawn through it.

2.2.6. At the end of the sampling period, turn off the pump and record the ending time.

2.2.7. Replace the cover and seal the casette with an OSHA-21.

2.3. Recommended air volume and sampling rate

2.3.1. The recommended air volume is 15 L.

2.3.2. The recommended sampling rate is 1 L/min.

2.4. Extraction efficiency

Three 1-(2PP)-treated glass fiber filters were each spiked with 1.920 µg of derivatized HDI biuret. The filters were extracted with 5.0 mL of 90/10 (v/v) ACN/DMSO and analyzed. The average recovery was 102.0%.

Derivatized HDI Biuret		
sample	recovered (µg)	recovery (%)
YC13	1.863	97.0
YC14	1.934	100.7
YC15	2.080	108.3
	average	102.0

2.5. Retention efficiency

Three 1-2PP-treated glass fiber filters were each spiked with 1.920 µg of derivatized HDI biuret. Humid air (70% RH, 15 L at 1 L/min) was drawn through the filters. The filters were extracted with 5.0 mL of 90/10 (v/v) ACN/DMSO and analyzed. The average recovery was 104.5%.

Derivatized HDI Biuret		
sample	recovered (µg)	recovery (%)
YC16	1.894	98.6
YC17	2.104	109.6
YC18	2.019	105.2
	average	104.5

2.6. Storage

Three 1-(2PP)-treated glass fiber filters were each spiked with: 1.920 ug of derivatized HDI biuret. Humid air (70% RH, 15 L @ 1 L/min) was drawn through the filters. The filters were stored at room temperature in the dark for 7 days, extracted with 90/10 (v/v) ACN/DMSO and analyzed. The average recovery was 96.7%.

Derivatized HDI Biuret		
sample	recovered (µg)	recovery (%)
YC19	1.908	99.4
YC20	1.843	96.0
YC21	1.817	94.6
	average	96.7

2.7. Interferences

Compounds such as anhydrides, acid chlorides, and other isocyanates that react with 1-(2-pyridyl)piperazine may compete for the derivatizing agent on the filter and diminish the latter's collection efficiency.

3. Analytical method

3.1. Apparatus

3.1.1. High performance liquid chromatograph

3.1.2. Nucleosil CI8 column or equivalent

3.1.3. UV or fluorescence detector

3.1.4. Stripchart recorder

3.2. Reagents

3.2.1. Water, HPLC grade

3.2.2. Acetonitrile, HPLC grade

3.2.3. Dimethyl sulfoxide, reagent grade

3.2.4. HDI biuret, purified (see below)

3.2.5. 1-(2-Pyridyl)piperazine, reagent grade

3.2.6. Di-n-butylamine, reagent grade

3.2.7. Phosphoric acid, reagent grade

3.3. Standard preparation

3.3.1. Preparation and purification of the 1-(2-pyridyl)-piperazine derivative of HDI biuret

Desmodur 100 1.17 g was dissolved in 30 mL of DMSO. 1-(2 Pyridyl) piperazine 1.17 g was added. The mixture was stirred for 1 hour and then poured into 2000 mL of distilled water. The white, soft, sticky mass that separated was collected and dried in a vacuum oven at 45°C, yielding glassy, brittle solid. The major peak of the product above was collected through Solvent was evaporated under a stream of residue was dried in a vacuum oven at 45°C. At tempted recrystallization of the residue failed. Reverse phase HPLC with diode array detector indicated it to be pure (See Figure 3).

3.3.2. Preparation of standard solution

Weigh 3 to 5 mg of the purified HDI biuret l-(2PP) derivative in a 10-mL volumetric flask. Add dimethyl sulfoxide to the mark. Dilute with acetonitrile to a suitable working range. Apply a correction factor of 0.4943 (F.W. of HDI biuret 478/F.W. of the derivative 967) to express the concentrations in terms of HDI biuret.

3.4. Sample preparation

Samples were extracted with 4.0 mL of 90/10 (v/v) ACN/DMSO by shaking for 30 minutes on a mechanical shaker.

3.5. Analysis

3.5.1. Instrument conditions

Column:	Nucleosil C18 10 um
Eluent:	57% acetonitrile, 43% water, 0.01 M di-n-butylamine, phosphoric acid to pH 5.3
Flow rate:	1.6 mL/min
Detectors:	
Fluorescence:	excitation 240 nm, emission 370 nm
UV:	254 nm
Injection size:	10 µL
Retention time:	9.2 min

3.5.2. Chromatograms (See Figure 2)

3.6. Interferences

3.6.1. Any collected compound that has the same retention time as HDI biuret and responds to the detector is a potential interference. Generally, chromatographic conditions can be varied to separate an interference from the analyte.

3.6.2. Retention time alone is not proof of a chemical identity. Confirmation by other means should be sought whenever possible.

3.7. Calculations

3.7.1. A calibration curve for HDI biuret is constructed by plotting standard concentrations versus detector response (see Figure 4).

3.7.2. The concentration of HDI biuret for a sample is determined from the calibration curve.

3.7.3. The air concentration is determined by the formula:

$$\frac{mg}{m^3} = \frac{(\frac{\mu g}{mL}) \times (4\,mL)}{(\text{air volume, L}) \times (\text{extraction efficiency})}$$

4. Recommendations for further study

4.1. The method should be fully validated.

4.2. Validation should also be conducted at the levels of the field samples.

4.3. Alternative methods of establishing the purity of HDI biuret should be investigated.

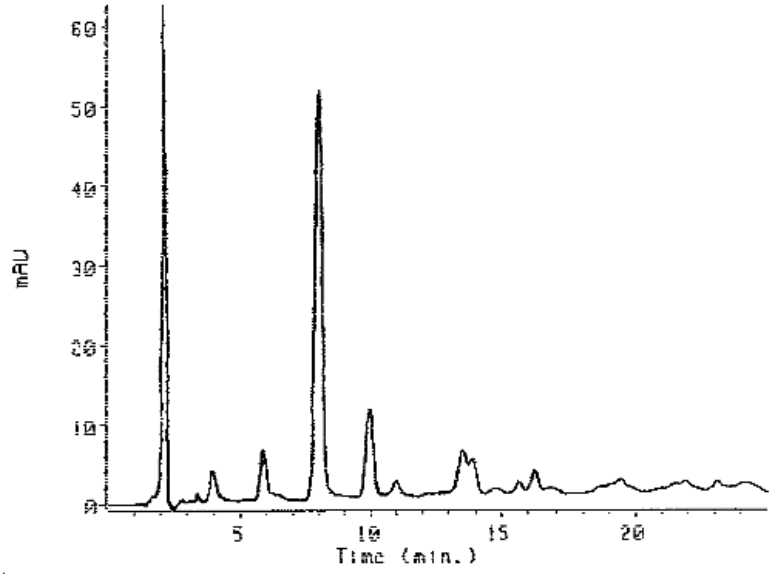


Figure 1. Chromatogram of the Derivatized Desmodur 100

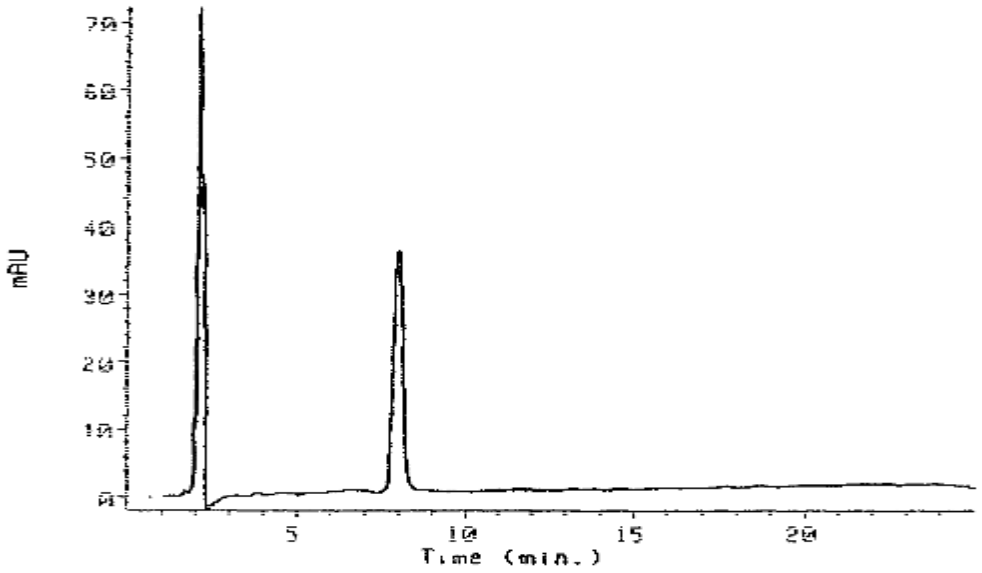


Figure 2. Chromatogram of the Purified HDI Biuret Derivative

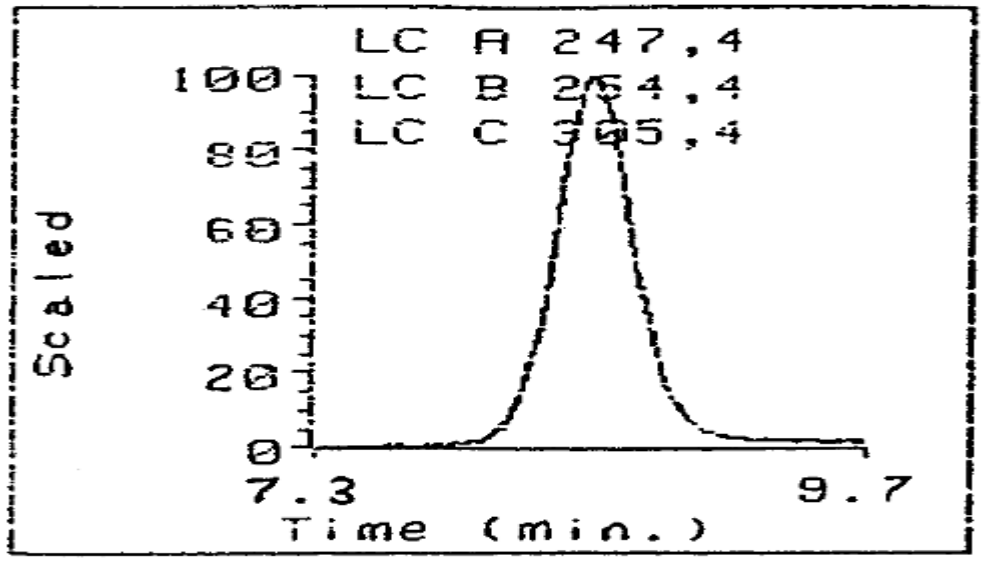


Figure 3. Three Wavelengths Monitoring on a Diode Array Detector of the Purity of the Purified HDI Biuret Derivative. (Note the three traces superimpose perfectly indicating high purity.)

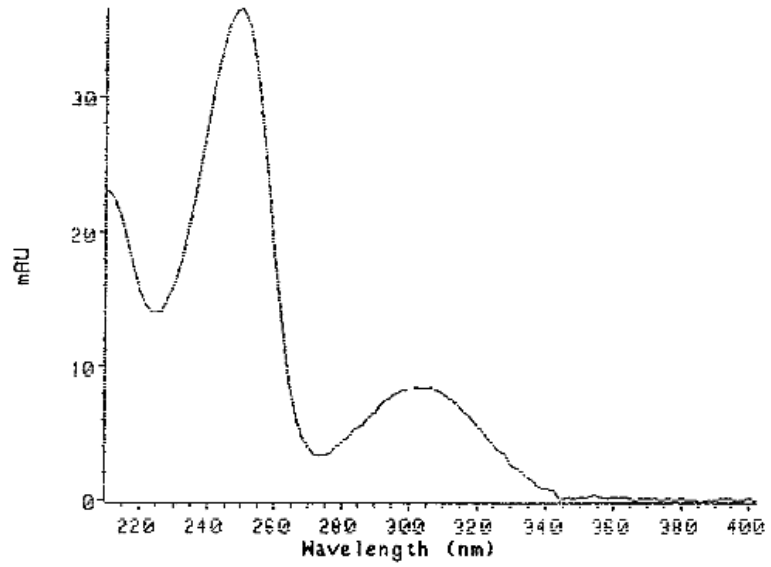


Figure 4. UV Scan of the Pure HDI Biuret Derivative

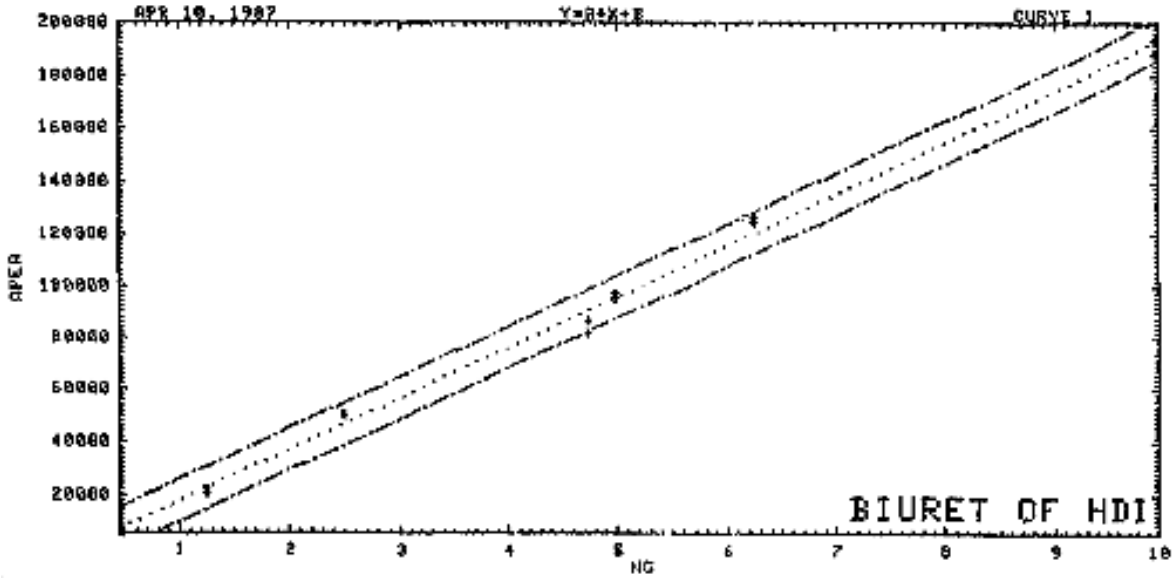


Figure 5. Calibration Curve of HDI Biuret

5. References

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