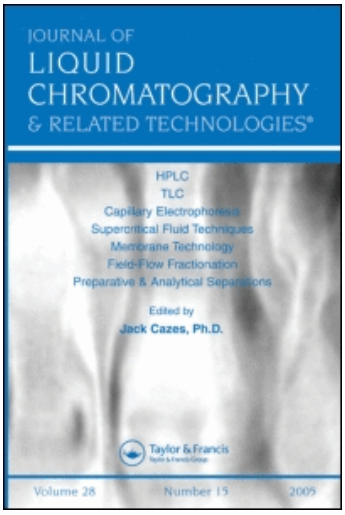

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Determination of Isocyanic Acid in Air by High Performance Liquid Chromatography

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DETERMINATION OF ISOCYANIC ACID IN AIR BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

Isocyanic acid in air is determined quantitatively by collection in a scrubber solution of N-4-nitrobenzyl-N-n-propylamine. The urea derivative, which is formed, is determined by using reverse phase high performance liquid chromatography.

INTRODUCTION

Low levels of airborne isocyanates have been measured by a variety of techniques such as colorimetry (1), gas chromatography (2,3,4) and high performance liquid chromatography (HPLC), (5,6). The colorimetric approach to the detection of isocyanate is limited to aromatic isocyanates, and therefore cannot be used for the determination of isocyanic acid (HNCO). Gas chromatography can be used to determine HNCO in the gas phase (7). However, this approach is not attractive in situations where isocyanic acid must be collected at a remote (e.g., plant) site and measured at a later date because HNCO may decompose before it can be analyzed. The gas chromatographic approach also requires the availability of a standard solution of HNCO for calibration.

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The most attractive approach to the measurement of low levels of HNCO in air is a method in which the HNCO is trapped and stabilized. Such an approach is offered by a method in which HNCO is reacted with a secondary amine to form a stable urea derivative. The urea is subsequently measured by HPLC with UV detection. This approach was described for the measurement of several aromatic isocyanates (5,6). This paper describes the use of a derivatization - high performance liquid chromatographic method for the measurement of HNCO in air at concentrations over a range from 0.05 to 25 ppm (v/v). The effect of humidity has also been studied. The preparation of a stable urea derivative for instrument calibration is also described.

MATERIALS

Apparatus

A Spectra-Physics SP-8000B High Performance Liquid Chromatograph with SP-8310 UV/Visible Detector (254 nm) and a Micromeritics Autoinjector with a 100-µL sample loop was used. The column was a 4.6-mm ID x 250 mm stainless-steel column packed with Partisil-5 ODS, 5 micron (Whatman Cat. No. 4220-104). Scrubbers (30-mL capacity) were obtained from Ace Glass (Part No. 7530-05). A Mine Safety Appliances Pump, Model S, was used for sample collection.

Reagents

The nitro reagent (N-4-nitrobenzyl-N-n-propylamine) was obtained as the hydrochloride salt from Aldrich (Catalog No. 22,191-0). Sodium hydroxide, sodium sulfate, toluene, triethylamine, HPLC grade acetonitrile, Type 3A Molecular Sieves, and phosphoric acid were Baker Reagent Grade materials.

Milli-Q purified (Millipore) water was used. Isocyanic acid solutions were made by dilution from a concentrated (17%) solution of isocyanic acid in toluene (U.S. Pat #4,364,913, American Cyanamid Co., December 1982).

METHODS

Preparation of Nitro Reagent

Approximately 240 mg of the nitro reagent hydrochloride were dissolved in 20 mL of distilled water. 25 mL of 1N NaOH were added to precipitate the nitro reagent which was then extracted with 50 mL of toluene. The toluene extraction was dried with ~10 g Na_2SO_4. The toluene was removed by evaporation and the free base was diluted to 500 mL with HPLC grade acetonitrile which had been dried overnight with ~25 g of molecular sieves. The nitro reagent should be stored in the dark and used no more than three weeks.

Preparation of N-4-nitrobenzyl-N-n-propylurea

Dissolve 5.0 g of N-4-nitrobenzyl-N-n-propylamine hydrochloride (Aldrich Chemical #22191-0, 98%) in 50 mL of water in a 250 mL separatory funnel and add 25 mL of 5% NaOH. The free base will separate as a yellow oil. Add 50 mL toluene and agitate gently until the oil dissolves. Draw off the aqueous layer and extract it again with 50 mL of toluene. Combine the toluene layers which contain the free base and filter off the insoluble white solid through Whatman #40 filter paper. Collect the toluene filtrate in a 4-ounce bottle containing 10 g of anhydrous Na_2SO_4. Cap the bottle, shake gently and allow to stand overnight. The theoretical amount of free nitroamine in the toluene solution is 4.13 g. This amount of amine will react theoretically with 0.91 g isocyanic acid. Decant the clear yellow-colored toluene solution into a 250-mL separatory funnel. Add slowly a measured volume of a toluene solution of isocyanic acid (16 mL of solution containing 7.7% HNCO was used which is equivalent to about 1.07 g HNCO). The solution becomes turbid and slightly warm during addition of the isocyanic acid solution, but after mixing, it changes to a clear yellow. Allow the solution to stand for an hour and then extract it twice with 50 mL of aqueous 0.1 N NaOH, once with 50 mL of 0.1N HCl and once with 50 mL H_2O. During the extractions a small amount

of waxy white solid will precipitate out. The solids were kept with the toluene layer. Dilute the toluene layer to 200 mL with toluene and warm gently. The waxy solid will dissolve to give a clear solution. Cool the toluene solution in an ice bath for 1 hour. White crystals will form on the walls of the separatory funnel. Pour off the toluene and dissolve the crystals in the separatory funnel in 60 mL warm toluene. Transfer the solution to a 150-mL beaker and cool in an ice bath. Crystals will form on the walls and bottom of the beaker. Pour off the toluene and dry the crystals in a vacuum desiccator over Drierite. Remove the dried crystals from the beaker and pulverize them with a mortar and pestle. The yield is 1.56 g (31%) and the product has a melting point of 92-95°C.

The following C, H, N values were obtained for the product:

	C	H	N
Found	56.59	6.33	17.64
Theory	55.68	5.95	17.71

The proposed structure of the material was confirmed by proton NMR spectrometry.

Preparation of N-4-Nitrobenzyl-N-n-Propylurea Standard Solution

Approximately 15 mg (to the nearest 0.05 mg) of the urea derivative standard were weighed into a 100 mL volumetric flask and diluted to volume with HPLC grade acetonitrile (15 mg of urea derivative/100 mL corresponds to 27.2 µg/mL HNCO). The standard solution should be stored in the dark and used within two weeks.

Preparation of Mobile Phase

Ten mL of triethylamine were added to 990 mL of Milli-Q purified water. The pH was adjusted to 3.0 with phosphoric acid. 700 mL of this solution were mixed with 300 mL of acetonitrile, filtered through a 0.3 micron pore size glass fiber filter and degassed by sonication before use.

Collection and Treatment of Air Samples Which Contains HNCO

20 mL of ~2 x 10^{-3} M nitro reagent were added to each of two scrubbers. The two scrubbers were then connected in series. A calibrated air pump was connected to the scrubber train and air was drawn through the system at a rate of 0.5 L/min. The scrubber should be wrapped with aluminum foil in order to minimize exposure of the solution to light. Recommended sampling times are shown in Table 1. A blank should be collected from an HNCO-free atmosphere for the same period of time that the sample was collected.

The scrubbers were then removed from the system and the contents of the second scrubber was discarded. The second scrubber was used to prevent small amounts of HNCO from getting into the pump. The first scrubber traps most of the HNCO (see Table 3). The solution from the first scrubber was treated as described in Table 2. After treatment, the solution is ready for measurement by HPLC.

Chromatographic Measurements

The column was equilibrated with the mobile phase at 40°C (ambient conditions can be used) until a steady baseline was achieved. A flow rate of 1.5 mL per minute was used. Linearity of response of the HPLC system was demonstrated by injection of

TABLE 1

Recommended Air Sampling Times

Air Conc of HNCO	Air Conc. of HNCO	Collection time at 0.5 L/min.	Liters Collected	µg HNCO expected
50 ppm	≈0.1 g/m^3	4 min.	2	200
5 ppm	10 mg/m^3	20 min.	10	100
0.5 ppm	1 mg/m^3	1 hour	30	30
50 ppb	0.1 mg/m^3	1 hour	30	3
	Blank	4 min.- 1 hr.	2-30	---

TABLE 2

Treatment of Scrubber Samples for Chromatographic Measurement

HNCO Air Conc.		Scrubber Solution Treatment	µg HNCO expected in 5 mL flask
50 ppm	≈0.1 g/m^3	Dilute to 25 mL with acetonitrile, add 1 mL (from 25-mL flask) and 1 mL acetonitrile to a 5-mL flask, dilute to mark with the aqueous component of the eluting solvent.	8
5 ppm	10 mg/m^3	Dilute to 25 mL with acetonitrile, dilute 2 mL (from the 25-mL flask) to 5 mL with the aqueous component of the eluting solvent.	8
0.5 ppm	1 mg/m^3	Evaporate to ~2 mL, dilute to 5 mL with the aqueous component of the eluting solvent.	6
50 ppb	0.1 mg/m^3	Evaporate to dryness, dissolve in 0.5 mL acetonitrile, dilute to 5 mL with eluting solvent.	3
Blank	Blank	Evaporate to dryness, dissolve in 0.5 mL acetonitrile, dilute to 5 mL with eluting solvent.	<0.5

solutions which contained 3, 6 and 9 µg of HNCO moved (as the urea derivative) in 5 mL of the eluting solvent. These values correspond to 16.5, 33.1, and 49.6 µg of urea derivative/5 mL. The urea derivative elutes at approximately 8.5 minutes. A linearity plot (with additional concentrations) is shown in Figure 1. Typical chromatograms for the standard and sample are shown in Figures 2 and 3, respectively. The sample measurement was carried out by injecting a sample and then a standard which gave a peak with

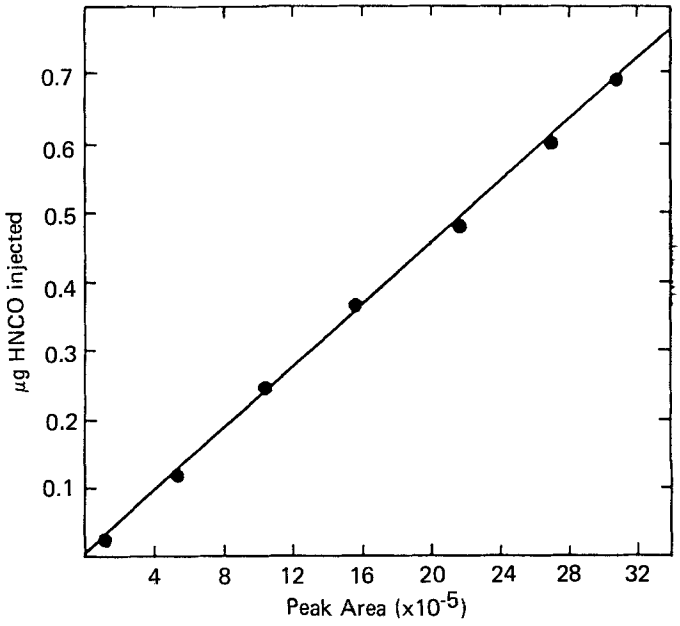

FIGURE 1. Micrograms of isocyanic acid vs peak area

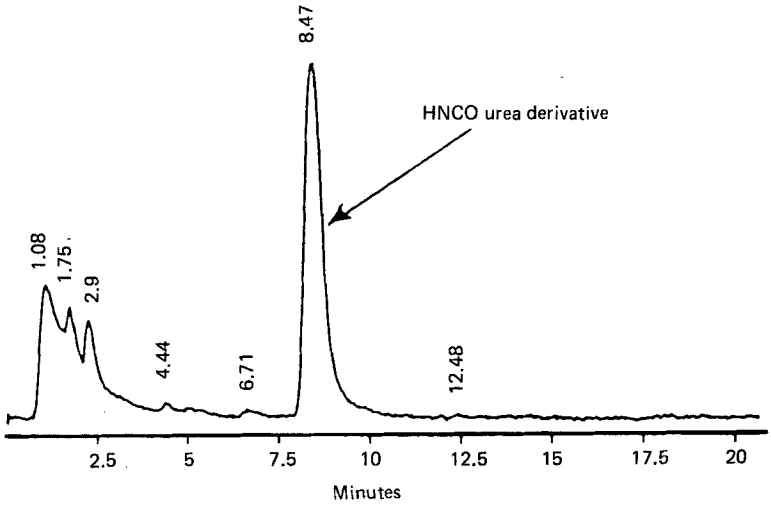

FIGURE 2. Chromatogram of standard urea derivative. 13.6 µg (HNCO basis) in 4 mL. 1 mL diluted to 10 mL. 100 µL (0.0340 µg) injected.

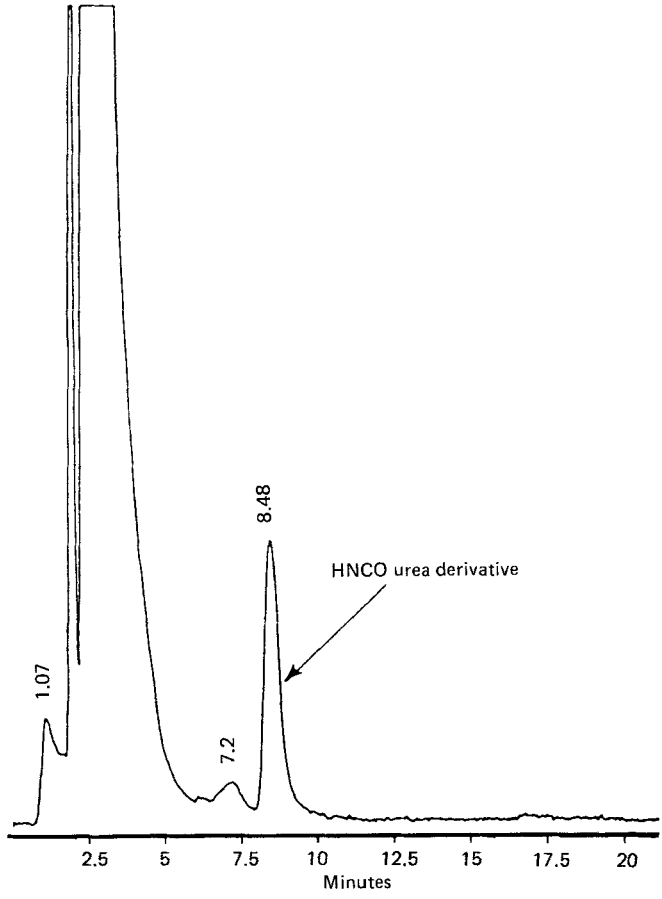

FIGURE 3 Chromatogram of a sample. Total residue dissolved in 4 mL. 1 mL diluted to 10 mL, 100 µL injected, 0.0289 µg found (as HNCO) or 11.6 µg HNCO found in sample.

approximately the same area as the sample. A blank was measured in a similar manner.

Calculations

Case 1: total sample (after complete or partial evaporation of acetonitrile) is in a 5-mL flask. The standard is in a 5-mL flask. (Spl refers to the scrubber solution).

$$\mu g\ HNCO\ spl = \left[\frac{\mu g\ std\ (in\ 5\ mL)}{peak\ area\ std} \times peak\ area\ spl\right] - \mu g\ blank$$

Case 2: the scrubber solution has been diluted to 25 mL. An aliquot of the scrubber solution (from the 25-mL flask) is diluted to 5 mL (see Table II). The standard is in a 5-mL flask.

$$\mu g\ HNCO\ spl = \left[\frac{\mu g\ std\ (in\ 5\ mL)}{peak\ area\ std} \times peak\ area\ spl \times \frac{25}{A}\right] - \mu g\ blank$$

where A is the aliquot volume in mL.

Blank

Blank and standard are in 5-mL flasks

$$\mu g\ \text{"HNCO"}\ blank = \frac{\mu g\ std}{peak\ area\ std} \times peak\ area\ blank$$

Concentration in Actual Atmospheres Tested

$$ppm\ HNCO\ (v/v) = \frac{A(62.36)\ (273 + °C)}{43\ (V)\ (Torr)}$$

where A = μg HNCO collected in trap (from Case 1 or Case 2)
62.36 = Gas constant
°C = Collection temperature
43 = mol. wt. of HNCO
V = Total volume of air (liters) sampled
Torr = Barometric pressure

RESULTS AND DISCUSSION

Recovery Values

The efficiency of the nitro reagent scrubber system for trapping HNCO was determined by drawing known atmospheres of HNCO through the scrubber for a fixed time. Known air concentrations of HNCO were generated by continuous (syringe) injection of a toluene solution of HNCO into a stream of air which was being pulled through the scrubber system. A Sage pump was used to drive the syringe at a constant rate. The pump-syringe system was cali-

TABLE 3

Recovery Data

Air Conc. of HNCO (v/v)	Collection time at 0.5 L/min.	Collection Volume, Liters	Relative Humidity	µg HNCO Expected	µg HNCO found		Recovery (%)
					First Scrubber	Second Scrubber	
24 ppm	8 min.	4		194.2	160	2.4	82
12 ppm	15 min.	7.5		182	147		81
4.65 ppm	30 min.	15		121	114	1.7	94
3.37 ppm	30 min.	15	16%	87.5	92.8	0.16	106
427 ppb	1 hour	30	60%	22.2	18.7	0.96	84
407 ppb	1 hour	30	90%	21.0	21.3	0.66	101
397 ppb	1 hour	30	60%	20.65	14.5	0.36	70
387 ppb	1.5 hour	45	60%	30.7	32.4	0.8	106
350 ppb	1 hour	30	16%	18.2	15.6	0.0	86
338 ppb	1 hour	30		17.6	20.5	0.0	116
295 ppb	1 hour	30	13%	15.4	12.6	0.54	82
152 ppb	1 hour	30		7.9	7.1	0.0	90
121 ppb	1 hour	30		6.28	7.6	0.05	121
92 ppb	1 hour	30		4.8	3.22	0.0	67
90 ppb	1 hour	30		4.65	5.59	0.1	120
77 ppb	1 hour	30		3.98	4.64	0.0	116
77 ppb	1 hour	30		4.00	4.84	0.28	121
70 ppb	1 hour	30	30%	3.88	3.42	0.20	88
68 ppb	1 hour	30	60%	3.67	3.46		94
55 ppb	1 hour	30	42%	2.88	2.71	0.0	94

brated by weighing liquid delivered in one hour. Recovery values were calculated from:

$$\% \text{ Recovery} = \frac{\mu g \text{ HNCO found in first scrubber}}{\mu g \text{ HNCO/hour (syringe-delivery rate)} \times \text{collection time (hours)}} \times 100$$

Data shown in Table 3 indicate that breakthrough of HNCO into the second scrubber is negligible.

Recovery values for gas phase HNCO over a range from 55 ppb to 24 ppm are shown in Table 3. No loss of HNCO was observed when humidified air was used. The overall recovery including all the data shown is 96%. Recovery values are based on the contents of the first scrubber. Only two values were observed at or below 70%.

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