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Note

Analysis of isocyanic acid in air by gas chromatography and thermionic nitrogen detection

FIKRY F. ANDRAWES

Stamford Research Laboratory, American Cyanamid Company, Chemical Research Division, Stamford, CT 06904 (U.S.A.)

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Isocyanic acid is a monomer recently synthesized for industrial use by oxidation of hydrogen cyanide¹. It can be used to synthesize a family of isocyanate compounds for a variety of applications. This compound is present as two isomers, cyanic acid $N\equiv C-OH$ and isocyanic acid $HN=C=O$, both of which are very unstable compounds in pure forms. The former is stable at 0°C only for a few hours in a dilute solution. Isocyanic acid on the other hand is relatively stable at room temperature in dilute solution for several weeks². In the vapor phase at room temperature, only isocyanic acid is present².

Analysis of isocyanic acid in air by gas chromatography (GC) has not been previously reported. The object of this report is to describe a method for the analysis of traces of isocyanic acid in air.

The standardization procedure is based on two dynamic steps. The first step utilizes a pump motor driven syringe to generate a constant, yet high concentration of isocyanic acid in an air stream. The second step utilizes an exponential dilution flask which further dilutes the initial concentration generated by the first step down to the detection limit of the system. Samples are separated on a Porapak Q column and detected with a thermionic selective detector. The detection limit is below 1 ppm. This method is evaluated and experimental data are presented.

EXPERIMENTAL

A diagram of the system is shown in Fig. 1. The system consists of a Sage syringe pump (Orion Research, MA, U.S.A.), an exponential dilution flask, a gas chromatograph and switching valves.

The pump is equipped with a speed control. Depending on the dimension of the syringe used, the pump is capable of accurately delivering as little as a few microliters per hour. We used either a 1- or 2-ml syringe, with the needle permanently attached to an inverted-shaped glass tubing device through a PTFE cap.

The exponential dilution flask (Varian) has an internal volume of 250 ml. The connection to the flask is through a four-way valve (Whitney, Cleveland, OH, U.S.A.), which allows pure air or the mixture from the pump to flow through it. When the mixture flows through the flask, the concentration of the acid is calculated

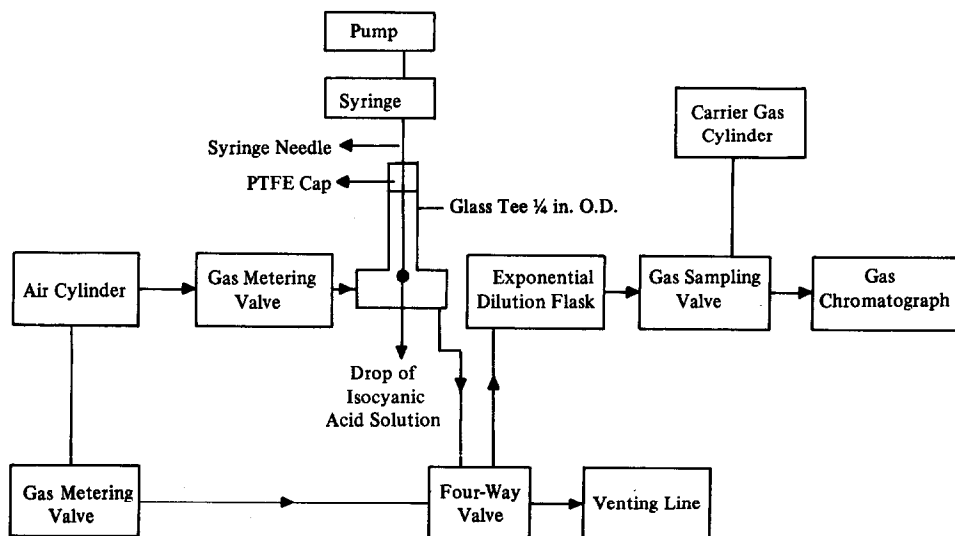


Fig. 1. Schematic diagram of the system.

from (1) the concentration of isocyanic acid in the syringe solution, (2) the pump delivery rate, and (3) the air flow-rate through the system. To calibrate the system for concentrations decreasing from the constant syringe-generated level, the four-way valve is switched to allow pure air to flow through the exponential dilution flask. The concentration of the flask effluent is calculated according to ref. 4.

The Hewlett-Packard Model 5710A gas chromatograph used in this work was equipped with an eight-port gas sampling injection valve (Valco). The 1-ml valve sample loops and all transfer lines were made from cleaned, 3 mm O.D. PTFE tubing. Signals from the thermionic nitrogen detector were recorded on a Hewlett-Packard 7123A strip chart recorder at 1 mV full scale and peak areas were integrated on a Hewlett-Packard 3354 computer. The 2 m \times 3 mm O.D. PTFE column was packed with Porapak Q 80-100 mesh and was conditioned at 150°C with a flow-rate of 28 ml/min of high-purity-grade helium. It was used at a temperature of 110°C.

In order to measure the concentration of cyanic acid from the generator for the purpose of calibration, the effluent was trapped in a N-4-nitrobenzyl-N-n-propylamine solution (nitro reagent). This derivatizing agent converts isocyanic acid into the urea derivative which is subsequently measured by high-performance liquid chromatography (HPLC)⁵. The same derivatizing solution was used to measure the concentration of isocyanic acid solution present in the generator syringe.

A Kratos MS-50 high-resolution mass spectrometer equipped with a Perkin-Elmer Sigma 3 gas chromatograph was used to confirm the identity of the peak eluted from the GC column. The isocyanic acid used in this work was prepared according to ref. 1, diluted with toluene at -20°C, and then stored in a freezer. Prior to use, the solution was assayed with N-4-nitrobenzyl-N-n-propylamine and measured by HPLC as previously mentioned.

RESULTS AND DISCUSSIONS

Several columns and detectors were evaluated for their performance. The column of choice was a Porapak Q, which provided an adequate separation with reasonable analysis time, as shown in Fig. 2. Regarding detectors, isocyanic acid has an

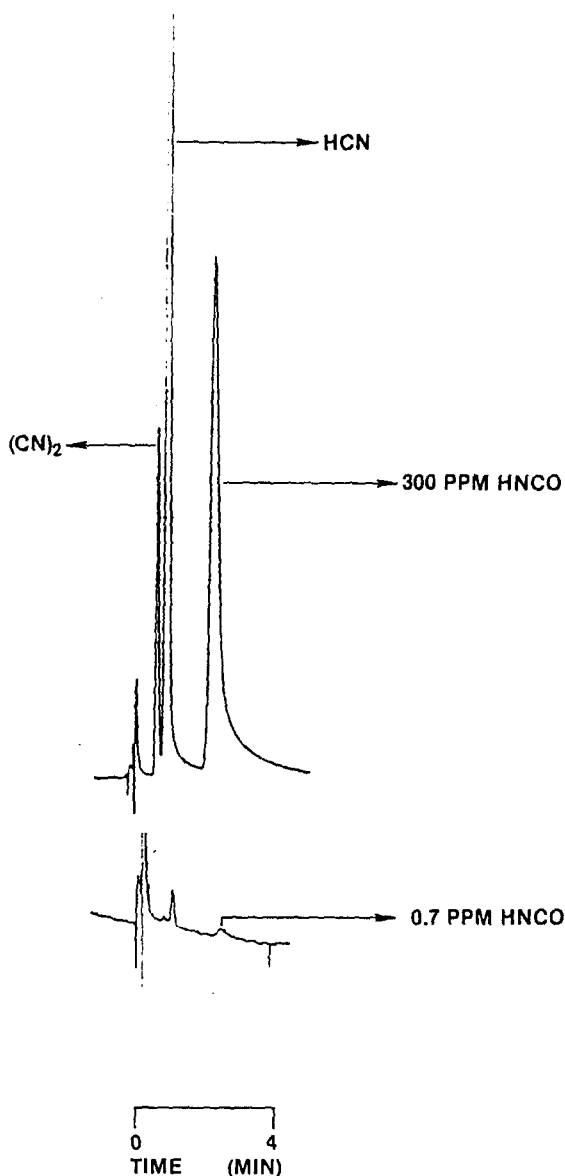


Fig. 2. Detector response to 300 ppm and 0.7 ppm of isocyanic acid in air. Sample size, 1 ml; column, 2 m \times 3 mm I.D. packed with Porapak Q; temperature, 110°C.

ionization potential of 13.2 eV, and cannot be detected with commercially available photoionization detectors. The flame ionization detector lacks sensitivity for this compound. The electron capture detector provides a good response, but also enhances some impurities presents. The thermionic nitrogen detector gives an excellent response with little interference from other compounds present, therefore it was selected for this work. Identification of the GC peak attributed to isocyanic acid was confirmed by GC-mass spectrometry⁶. The generating system shown in Fig. 1 was evaluated for precision and accuracy. Precision was estimated by monitoring the chromatograph signal of the samples analyzed. One filled syringe (2 ml) can deliver solution for as long as 32 h; however, by the end of this period, a 10% reduction in the concentration of isocyanic acid was observed (initial concentration 4%). It is, therefore, not recommended to use the solution in the syringe for more than one working day. The relative standard deviation for 34 samples analyzed during a working day was 4.5% for a gas sample containing 300 ppm of isocyanic acid.

The exponential dilution flask serves as a blender for the gaseous mixture. It is also used to generate a decreasing concentration of isocyanic acid to calibrate and determine the detection limit of the system. A typical detector response is shown in Fig. 2 for 300 ppm and 0.7 ppm of isocyanic acid.

The accuracy of the system was evaluated by trapping the effluent of the generator in nitro reagent followed by HPLC analysis of the urea derivative. More than 95% of the theoretical value was recovered. Minor isocyanic acid losses could occur in the transfer lines, or could trimerize to form cyanuric acid.

Fig. 2 shows the presence of HCN and (CN)₂; both compounds were present in small amounts. The response to HCN and (CN)₂ is *ca.* 1000 times more than the response to isocyanic acid.

During the course of the work, it was observed that solvent peaks as they elute from the column had a sensitizing effect on the detector. Conditioning the column periodically every 2 h for 20 min resolved this problem.

The method reported here was used in an inhalation toxicology study and proved to be quite adequate.

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