NBSIR 76-998

Development of a Solid Sorption Tube and Analytical Procedure for Hydrogen Cyanide in the Workplace Atmosphere

Barry C. Cadoff and John K. Taylor

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Final Report

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National Institute for Occupational Safety and Health
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U.S. DEPARTMENT OF COMMERCE, Elliot L. Richardson, *Secretary*
James A. Baker, III, *Under Secretary*
Dr. Betsy Ancker-Johnson, *Assistant Secretary for Science and Technology*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Acting Director*

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Development of a Solid Sorption Tube and Analytical Procedure for Hydrogen Cyanide in the Workplace Atmosphere

B. C. Cadoff and J. K. Taylor

ABSTRACT

The development of a sampling tube for collecting HCN in the workplace atmosphere is described. The tube contains 4.0 g of flake NaOH and can be readily fabricated in the laboratory. Details are given concerning the construction and use of the tube and data is presented on collection of HCN at levels of five times the TLV, one fifth the TLV, and at the TLV. Analysis of the tube contents using the cyanide ion selective electrode is described. This method is simple, rapid, and relatively free of interferences. Data on the analyses of tubes containing cyanide is described and estimates of the precision and accuracy of the method are given.

KEY WORDS: Air analysis; air sampling; gas analysis; hydrogen cyanide; industrial hygiene; ion selective electrode; sodium hydroxide; work atmosphere.

1. INTRODUCTION

This final report summarizes work on the development of a method for collecting and analyzing HCN present in workplace atmospheres. The approach to the problem has been to devise a solid sorption device which, after the sample has been collected, can be returned to the laboratory where the analysis may be performed simply and rapidly. These solid samplers represent an improvement in convenience and versatility compared with liquid bubblers presently in use since they can be used and handled without fear of spillage. They are also directly applicable to personal sampling.

The sampling device described is a tube filled with NaOH and the analytical procedure employs a cyanide ion selective electrode. Previous work supported by the National Institute for Occupational Safety and Health was reported earlier (1).

2. SCOPE OF THE INVESTIGATION

The major portion of this work deals with the development of a NaOH-filled sampling tube capable of collecting HCN under varying concentrations and sampling rates, and the method of analysis employing a cyanide ion selective electrode. Details such as fabrication of the sampling tube, breakthrough capacities of the tube, reproducibility of measurement and precision and accuracy of the analytical method are given.

Also discussed are two other devices which were investigated. One is an Ascarite-filled tube which proved unsuitable and a cellulose filter pad wetted with NaOH solution and supported in a plastic filter holder which while not fully evaluated, nonetheless, appears promising.

3. EXPERIMENTAL

3.1 Generation of HCN

The HCN in nitrogen used in this work was contained in a size 1A cylinder at a pressure originally of 2000 psig. This material was analyzed by the procedures outlined below and was found to contain 120 ppm HCN. Concentrations of 50, 10 and 2 ppm were obtained with a dilution system (1), consisting of a rotameter and flow controller each for the HCN stream and for the diluent stream ("breathing air" contained in a cylinder), a chamber to mix the two gas streams and finally a port, open to atmosphere, into which the sampling device is placed. (Caution: All work with HCN should be done in a laboratory hood.) Calibration of the rotameters was done using either a 1 liter wet test meter or a bubble flowmeter. The error associated with reproducing the same mixture from day to day is estimated to be ±2 percent.

3.2 Sampling System

The sampling system has been described (1). This system can provide constant flow over a range of flow rates, and for this work flows of 1 liter/min, 200 ml/min and 50 ml/min were used. The sampling rate was calibrated before each series of runs and the flow rate error over a several hour sampling period was no greater than ±2 percent.

3.3 Sampling Tube

The tube is constructed of an approximately 9 cm length of polyethylene tubing, 3/8" I.D., 1/16" wall and 1/2" O.D. A polyethylene tubing connector, 3/8" x 1/4" containing a

cotton wad placed inside the 3/8" diameter portion[1], is inserted into the bottom of the tube. The tube is filled with 4.0 g of flake NaOH (Technical Grade, J. T. Baker Chemical Co.[2]) by putting small portions on a spatula and transferring the contents to the tube. The tube is tapped after each increment to settle the contents. Flakes of various sizes are used. The final increment of flakes is made in the following manner. Several flakes are placed on a small piece of absorbent cotton which is then rolled and placed inside the tube. A second polyethylene tubing connector, 3/8" x 1/4" is inserted into the top of the tube. To increase the breakthrough capacity water is added to the tube in the following way. Water-saturated nitrogen is sampled through the tube at a flow rate of 1 liter/min for about 20 minutes which results in the addition of approximately 0.5 g water. Both ends of the tube are then capped with 1/4" polyethylene caps. A diagram of the tube is shown in Figure 1.

Pressure drops across the tubes are measured by connecting an open U-tube mercury manometer just below the tube and sampling air through the tube at a 1 liter/min. Breakthrough capacity is determined by placing a second tube downstream from the first and determining after a particular sampling period the amount of cyanide collected in the second tube. Breakthrough in this work is defined as occuring when the weight of cyanide in the second tube amounts to 1 percent or more of the total quantity of cyanide collected, as determined using the cyanide ion-selective electrode.

3.4 Solution of Tube Contents

The connectors at both ends of the tube are removed, and a stream of distilled water, from a washbottle, is used to remove the flakes from the tube. The tube and both connectors are throughly washed, and the washings are collected in a polyethylene beaker. The contents are stirred to dissolve the NaOH. The cotton wad (from the top of the tube) is then removed from the solution and rinsed several times with water, and these rinsings are combined with the solution: After cooling to room temperature the solution is transferred to a 50 ml volumetric flask, diluted to mark

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[1]One inch = 2.54 centimeters.

[2]Mention of a product here and elsewhere in the report does not constitute endorsement by the National Bureau of Standards, nor does it imply that the product is necessarily the best available for the purpose.

(yielding a solution that is 2 M NaOH) and then analyzed. If the solution has a higher concentration then 10^{-3} M cyanide an aliquot is diluted with 2 M NaOH to bring the concentration below 10^{-3} M cyanide. This is important since concentrations in excess of 10^{-3} M tend to rapidly destroy the cyanide electrode (2).

3.5 Impinger Procedure

The tube method was compared with a standard sampling procedure employing two midget impingers, in series. Each impinger was filled with 15 ml of 0.1 M NaOH. After sampling, the contents of both impingers were combined, along with the rinsings, and diluted with 0.1 M NaOH to 50 ml.

3.6 Other Sampling Methods

A glass sampling tube of a design described earlier (3) was filled with 4 g. Ascarite, 20-30 mesh (A. H. Thomas Co.). This tube was not suitable for reasons outlined in the Results and Discussion section of this report.

A sampler consisting of a 1.5 inch (3.8 cm) diameter cellulose filter pad, held in a plastic filter holder (Millipore Co.) was used. The cellulose pad was treated with one ml of 3 M NaOH solution.

3.7 Analytical Procedure

A cyanide ion-selective electrode (Orion Model 94-06) and a saturated calomel electrode are clamped in an electrode holder and connected to either a digital pH meter (Orion Model 801) or a dial-type, expanded scale pH meter (Corning Model 12). The electrodes are immersed in a 50 ml polyethylene beaker containing 25 ml of the solution to be analyzed. A small, Teflon-coated, magnetic stirring bar is placed in the beaker and rotated at a constant speed. Reproducibility of stirring speed and placement of electrodes in the solution is necessary for reproducible readings. A millivolt reading is recorded when there is little or no change in millivolt readout, usually within a minute or two.

A calibration curve is drawn by plotting millivolt reading vs. cyanide concentration (10^{-5} to 10^{-3} M) using semilog graph paper. Cyanide standards are made by first preparing 10^{-1} M NaCN in water (or 10^{-1} M KCN in water) and serially diluting this solution with 2 M NaOH for the tube analyses or 0.1 M NaOH for the midget impinger analyses.

4. RESULTS AND DISCUSSION

4.1 Generation of HCN

At the beginning of this investigation it was thought that a humidifier in the generation system would be required to simulate the various humidities that would be encountered in actual field sampling since in some sampling procedures, changes in humidity have an adverse effect on collection efficiency. However, it was found that the most severe condition for NaOH-tube sampling is a dry atmosphere, such as is obtained in the generation system described. In fact, the addition of water to the tube by the sampling of moist atmospheres aids in capturing HCN by increasing the breakthrough capacity (see Section 4.3).

4.2 Sampling of HCN

The sampling system proved to be versatile and precise. In duplicate runs, little or no difference was found in the concentration of the pairs. Thus, the error of the combined HCN generation and sampling systems was less than the error associated with the cyanide electrode analytical procedure.

4.3 Sampling Tube Characteristics

Flake, technical grade NaOH was chosen rather than pellet, reagent grade NaOH because the flakes packed more evenly in the tube and there were fewer voids and channels. No difference in cyanide electrode response was noted using technical grade or reagent grade NaOH as the background solution for the cyanide standards. It was necessary to pretreat the tube with moisture as described in the Experimental Section since adequate capacity could not otherwise be obtained. Thus, breakthrough occurred before 20 liters of 50 ppm HCN had been sampled through a dry tube, while with the moisture - treated tube breakthrough had not occurred even after sampling 120 liters. The moisture treatment, however, did tend to settle the tube contents, resulting in occasional voids, but breakthrough was never observed with these tubes. That the reagent is present in large excess can be shown from the following example. If a tube collects an 8 hour sample at a rate of 200 ml/min a total of 96 liters passes through the tube. If the HCN concentration is 50 ppm and the ambient level for CO_2 is assummed, i.e. 300 ppm, then the number of millimoles of HCN collected is 0.196 while 1.18 millimoles of CO_2 is collected. NaOH reacts in a 1:1 molar ratio with HCN and in a 2:1 molar ratio with CO_2. Thus, 2.56 millimoles or 102 mg of NaOH are required for complete reaction. This means that the tube contains NaOH in a 40 fold excess. In view of this large capacity it was

considered unnecessary to either determine the mesh size of a typical tube or to sieve the NaOH so that a known size range of particles could be used for filling.

A typical tube, before use, has a pressure drop (at 1 liter/min flow) of less than 0.2 inches Hg. After sampling, the pressure drops increase but remain less than 1 inch Hg. However, before the filling procedure outlined in the Experimental Section was adopted, tubes were filled by merely adding 4 g NaOH to the tube and inserting the top cotton wad. Cotton was chosen as the separator rather than glass wool, since it was felt that on storage the glass wool could react with the moisture-treated NaOH. Some of these tubes developed unacceptably high pressure drops due to the crusting of the top layer of NaOH. The new tubes have not crusted over due to the fact that the NaOH flakes in the cotton wad intercept much of the HCN and CO_2 that enter the tube. The cotton fibers act as a separator for the flakes, preventing them from crusting over. Acceptable pressure drops have thus been obtained for 120, 50, 10 and 2 ppm HCN at the following flow rates and sampling times:

1 liter/min for 15 minutes
200 ml/min for 2 hours
200 ml/min for 4 hours

Two tubes have been used to sample room air (55 percent R.H.) at 50 ml/min for 8 hours with resulting pressure drops less than 1 inch Hg.

4.4 Selection of Analytical Method

A major consideration in selecting an analytical method is that it be compatible with the sampling procedure. In table 1 typical sampling rates and times are given along with the amounts of cyanide collected and resulting concentrations, for 2 ppm and 50 ppm HCN. It is seen that the concentrations of the resulting 50 ml solutions are within the optimal operating range (2) of 10^{-5} to 10^{-3} M, with the exception of the 1.96×10^{-3} M solution. This solution, of course, can be readily diluted to put it in the range of the calibration standards.

Another consideration in selecting an analytical method is the accuracy and precision that can be expected. This can be expressed for ion selective electrodes in the following way (4). The potential of an electrode immersed in a solution containing an ion to which it is reversible is given by the Nernst equation,

$$E = E_o - \frac{RT}{nF} \ln fC \qquad (1)$$

Ignoring any variation of the activity coefficient f,

$$dE = \frac{-RT}{nF} \frac{dC}{C} \qquad (2)$$

represents the variation of potential with concentration. For a 1 percent variation in concentration at ordinary temperature,

$$dE = \frac{0.00026V}{n} \qquad (3)$$

For the case of the cyanide electrode, n = 1. Therefore, a 1 mV change in reading is equal to about a 4 percent change in concentration. This aspect is more fully discussed in the Precision and Accuracy Section of this report.

Finally, a suitable analytical method should be reasonably free of interferences. Chloride, iodide and bromide can be tolerated if they are present in ratios with respect to the cyanide concentration of less than 10^6, 0.1 and 5×10^3(2). Sulfide must be completely absent, and an effective method of eliminating this interference has been reported (5). This involves the addition of lead nitrate to precipitate the sulfide.

4.5 Comparison of Impingers and Tubes

In order to compare the results obtained with the NaOH - filled tubes and the more conventional procedures for collecting HCN, a series of runs were made using two midget impingers in series, each containing 15 ml of 0.1 M NaOH. At the same time and under the same conditions a series of runs using tubes were made. Results are given in table 2, which show the nominal concentrations (i.e. the concentrations based on the analyzed cylinder contents and the dilution ratios) and the actual concentrations analyzed. Good agreement is found between the impinger and tube methods except at the 2 ppm level where the impinger procedure gives low results. This discrepancy was not investigated further.

Figures 2 and 3 show typical cyanide calibration curves for 0.1 M NaOH and 2.0 M NaOH, respectively. It is seen that the 0.1 M NaOH curve is linear over the 10^{-5} to 10^{-3} M range. The 2 M NaOH curve is linear from 10^{-3} to about 5×10^{-5} M cyanide at which point a break in the curve occurs. The remaining portion of the calibration curve, from 5×10^{-5} M to 10^{-5} M forms another straight line as shown in figure 3.

4.6 Tube Analytical Results

Table 3 summarizes results obtained at 50, 10, and 2 ppm HCN (5 TLV, TLV and 0.2 TLV) sampled under two conditions of flow rate and sampling time. Generally good agreement is found between the 4 hour runs and the 15 minute runs, and the analyzed concentration agrees well with the nominal or predicted concentration.

4.7 Precision and Accuracy

It should be emphasized that reproducible measurements with the cyanide electrode can only be obtained if details such as electrode placement in the solution and rate of stirring are kept uniform from sample to sample and are consistent with calibration conditions. Also, a sluggish response, especially at low concentrations, may be a problem caused by an etched electrode surface. This can be handled by polishing the crystal surface with a mild abrasive paper.

With a properly operating system of pH meter, reference electrode and cyanide electrode, the reproducibility of three consecutive measurements on a single sample can be expressed as an average value with a range of ±0.3 mV. Over a period of an hour or more the variations in readings can be as large as ±1.0 mV. Furthermore, the calibration line itself has an uncertainty.

The most accurate measurements are made within a short time of each other with calibration standards interspersed among the samples. However, for routine analyses it is estimated readings should not exceed ±7 percent of an average value.

4.8 Ascarite Tube and Filter Pad Methods

The Ascarite tube was found to be an efficient collector for HCN but cyanide was irreversibly adsorbed on the Ascarite particles. Thus, the contents of an Ascarite tube, when added to standard cyanide solutions at 10^{-3} and 10^{-4} M lowered the free cyanide concentrations to about 70 percent of the original level. It was not possible to extract the cyanide from the Ascarite, even after several washings.

Collection of HCN on cellulose filter pads containing 1 ml of 3 M NaOH appears promising based on the fact that no breakthrough occurred during collection of 50 ppm HCN for 4 hours at the 200 ml/min collection rate. In addition, the cellulose pad did not adsorb cyanide when placed in a standard cyanide solution. Further work, however, is necessary to fully appraise the potential of this sampling method.

5. SUMMARY AND CONCLUSIONS

The NaOH sampling tube is a quantitative sorber for HCN and has more than adequate capacity for sampling HCN at levels as high as 50 ppm (5 x TLV). Its design is simple and can be fabricated easily using items commonly found in a laboratory. The analytical procedure, employing a cyanide ion selective electrode is also simple and rapid and lends itself to the routine determination of large numbers of samples.

6. REFERENCES

1. B. Greifer, B. C. Cadoff, J. Wing, and J. K. Taylor, "Development of Solid State Samplers for Work Atmospheres," NBSIR 74-527 (June 1974).

2. Instruction Manual for Cyanide Activity Electrode, Model 94-06, Orion Research Incorporated (1972).

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5. O. P. Bhargava, G. W. Deline and W. G. Hines, "Rapid Determination of Cyanide in Waste Waters," in "Water Quality Parameters," American Society for Testing and Materials, Philadelphia, Pa., 1975.

Table 1. Expected cyanide concentrations in solution under varying sampling conditions

Flow rate	Sampling time	50 ppm		2 ppm	
		µg collected	conc. (50 ml)	µg collected	conc. (50 ml)
1 l/min	15 min	798.2	6.14×10^{-4} M	31.93	2.45×10^{-5} M
200 ml/min	4 h	2554	1.96×10^{-3} M	102.2	7.86×10^{-5} M
50 ml/min	8 h	1277	9.82×10^{-4} M	51.08	3.93×10^{-5} M

Table 2. Comparison of tube and impinger collection methods

Nominal conc. (ppm)	Flow rate (l/min)	Sampling time (min)	Tube or impinger	Analyzed conc. (ppm)
120	1.01	5	Tube	125
120	1.01	5	Tube	126
120	1.01	5	Impinger	129
120	1.01	5	Impinger	131
50	1.01	12	Tube	54
50	1.01	12	Tube	53
50	1.01	12	Impinger	57
50	1.01	12	Impinger	58
10	1.01	12	Tube	10.2
10	1.01	12	Tube	10.2
10	1.01	12	Impinger	9.7
10	1.01	12	Impinger	9.7
2	1.01	30.5	Tube	1.91
2	1.01	30.5	Tube	1.95
2	1.01	30.5	Impinger	0.78
2	1.01	30.5	Impinger	0.89

Table 3. NaOH tube analytical results

Nominal conc. (ppm)	Flow rate (l/min)	Sampling time	Analyzed conc.
50	1.03	15 min	54
50	1.03	15 min	52
50	0.204	4 h	51
50	0.204	4 h	48
10	1.01	15 min	10.3
10	1.01	15 min	10.2
10	0.198	4 h	9.8
10	0.198	4 h	9.6
2	1.01	15 min	1.89
2	1.01	15 min	1.92
2	0.200	4 h	1.95
2	0.200	4 h	2.01

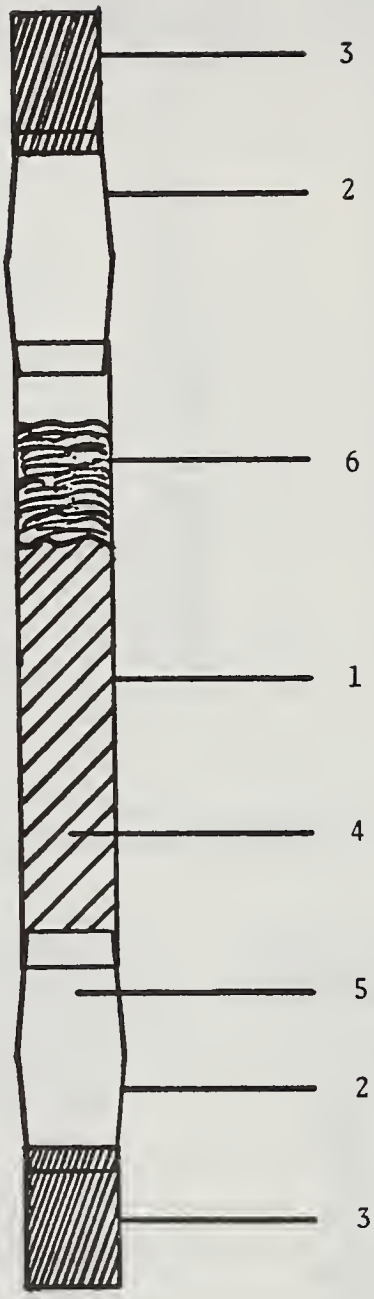

Figure 1. Diagram of NaOH-filled tube

1 - polyethylene tube
2 - polyethylene connectors
3 - polyethylene caps
4 - NaOH flakes
5 - cotton wad
6 - cotton wad

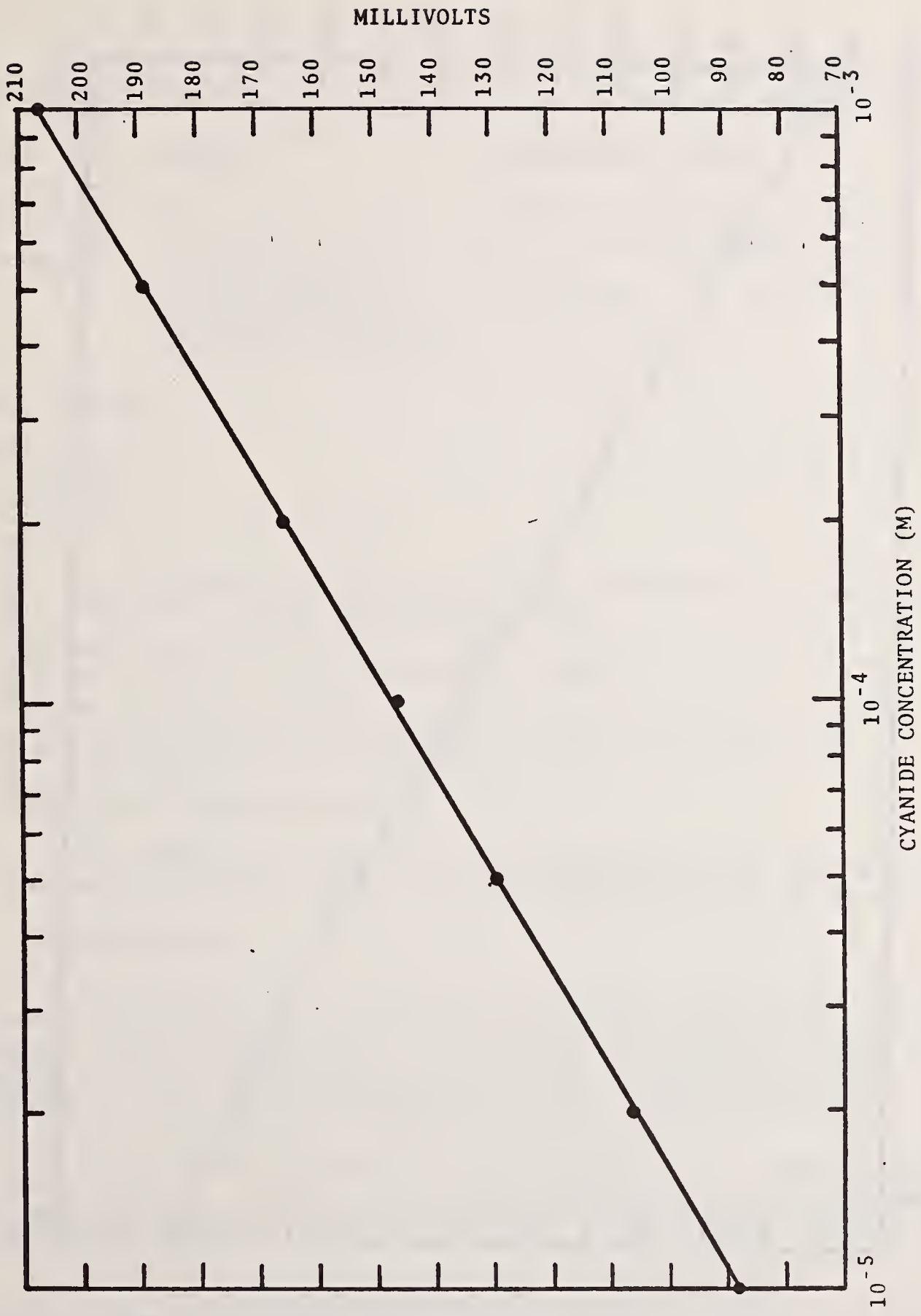

Figure 2. Typical calibration curve for cyanide in 0.1 M NaOH

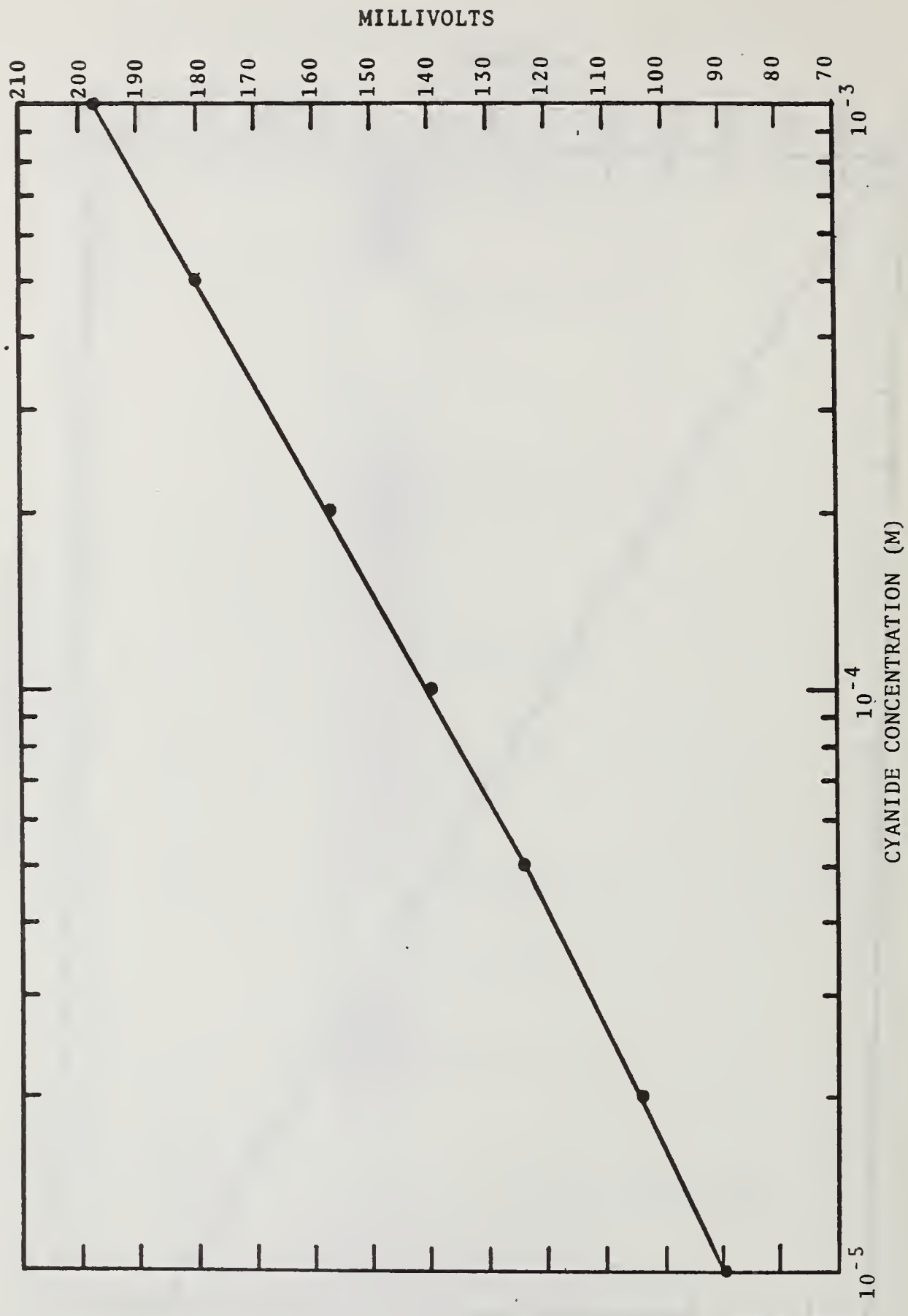

Figure 3. Typical calibration curve for cyanide in 2 M NaOH

APPENDIX

Analytical Procedure: Hydrogen Cyanide in the Atmosphere

Analyte: Cyanide

Matrix: Air

Procedure: Collection via solid sorption tube/ion selective electrode analysis

Method No. P&CAM

Range: 2-50 ppm or 13 µg per sample

Precision: ±7 percent

Classification:

Date issued:

Date revised:

1. Principle of the Method

1.1 Hydrogen cyanide in air is collected by a sorption tube containing sodium hydroxide flakes.

1.2 Samples are dissolved in water.

1.3 The resulting solution is analyzed using the cyanide ion selective electrode.

2. Range and Sensitivity

The recommended range for the method is 2-50 ppm HCN. Recommended smallest sample size is approximately 13 µg.

3. Interferences:

3.1 Sulfide ion irreversibly poisons the cyanide ion selective electrode and must be removed if found in the sample. Check for presence of sulfide by touching a drop of sample to a piece of lead acetate paper. The presence of sulfide is indicated by darkening of the paper.

3.2 Sulfide is removed by the additon of a small amount of lead nitrate. Check with lead acetate paper to determine the completeness of sulfide removal. Avoid a large excess of lead nitrate (2).

3.3 After precipitation of all sulfide, filter solution through filter paper and proceed with the analysis.

4. Precision and Accuracy

The estimated precision and accuracy of the method is ±7 percent.

5. Advantages and Disadvantages of the Method

5.1 Advantages: The hydrogen cyanide is efficiently collected and the analytical procedure is highly selective for cyanide ions. The procedure involves few steps, is simple to perform and the technique can be readily acquired. Commonly available equipment and reagents are used.

5.2 Disadvantages: Close attention to operating details such as uniform rate of stirring and placement of electrodes in solution must be observed. An occasional slow or erratic response of the electrode occurs, which can be corrected by polishing the crystal surface with a mild abrasive paper.

6. Apparatus

6.1 Sampling Apparatus

6.1.1 Sorption tube for hydrogen cyanide.

6.1.2 Personal sampling pump or other source of vacuum.

6.1.3 A wet test meter or other suitable device for measuring flow rates.

6.1.4 Thermometer.

6.1.5 Stopwatch.

6.1.6 Manometer.

6.2 Analytical Apparatus

6.2.1 Orion 94-06 Cyanide electrode or equivalent

6.2.2 Saturated colomel electrode or other suitable reference electrode.

6.2.3 Expanded scale pH/millivolt meter.

6.2.4 Magnetic stirrer and stirring bars.

6.2.5 Polyethylene bottles.

6.2.6 Polyethylene beakers, 50 ml.

6.2.7 Stainless steel forceps.

6.2.8 Volumetric flasks, 50 ml, for dilution of sorption tube contents. Other sizes required for preparation of standard solutions.

6.3 Sorption Tube Components.

6.3.1 Polyethylene tubing, 3/8" I.D., 1/2" O.D. approximately 9 cm long.

6.3.2 Surgical cotton.

6.3.3 Polyethylene tubing connectors, 3/8" x 1/4".

6.3.4 Polyethylene caps, 1/4" I.D.

7. Reagents

7.1 Distilled water.

7.2 NaOH, flake, technical grade.

7.3 NaOH, 2 M. Dissolve 80 g NaOH, flake, technical grade, in distilled water and dilute to 1 liter.

7.4 Sodium cyanide, reagent grade.

7.5 Lead acetate test paper.

7.6 Lead nitrate.

7.7 Sodium cyanide standards.

7.7.1 Prepare stock solution of 10^{-1}M[CN^-] by dissolving 4.90 g NaCN in 1 liter of distilled water.

7.7.2 Dilute 1 ml of 10^{-1}M [CN^-] to 100 ml with 2 M NaOH for 10^{-3}M [CN^-] (26 µg/ml).

7.7.3 Dilute 25 ml of 10^{-3}M [CN^-] to 50 ml with 2 M NaOH for 5 x 10^{-4}M [CN^-] (13 µg/ml).

7.7.4 Dilute 10 ml of 10^{-3}M [CN^-] to 100 ml with 2M NaOH for 10^{-4}M [CN^-] (2.6 µg/ml).

7.7.5 Dilute 25 ml of 10^{-4}M [CN^-] to 50 ml with 2M NaOH for 5 x 10^{-5}M [CN^-] (1.3 µg/ml).

7.7.6 Dilute 10 ml of 10^{-4}M [CN^-] to 100 ml with 2M NaOH for 10^{-5}M [CN^-] (0.26 µg/ml).

8. Procedure

8.1 Cleaning of Equipment. All glassware is washed in detergent solution, rinsed in tap water and then rinsed with distilled water.

8.2 Preparation of Sorption Tube.

A polyethylene tubing connector, containing a cotton wad in the 3/8" diameter portion, is inserted into the bottom of the polyethylene tube. The tube is filled with 4.0 g of flake NaOH by placing small portions on a spatula and transferring the contents to the tube. The tube is tapped after each increment to settle the contents. Flakes of various sizes are used. The final increment of flakes is added in the following manner: several flakes are placed on a small piece of absorbent cotton which is then rolled and placed inside the tube. A second polyethylene connector is inserted at the top of the tube. Water-saturated nitrogen is sampled through the tube at a flow rate of 1 liter/min for about 20 minutes which results in the addition of about 0.5 g water. Both ends of the tube are capped with polyethylene caps.

8.3 Collection of Samples.

8.3.1 The polyethylene caps are removed from the sampling tube and the tube is attached with flexible tubing to the sampling pump.

8.3.2 The pump is turned on to begin sample collection. Flow rate or volume measurements should be made accurately. Flow rates ranging from 50 ml/min to 1 liter/min can be selected.

8.3.3 After sampling, the tube is disconnected from the pump and is capped with the polyethylene caps.

8.4 Analysis of Samples.

8.4.1 The caps are removed from the tube and the top polyethylene connector is removed. Forceps are used to remove the cotton wad. The contents of the tube, along with the cotton wad are transferred to a beaker. The bottom connector is removed. The tube and

connectors are then washed with a stream of water from a washed bottle into the beaker. The contents are stirred until all the NaOH dissolves. The cotton wad is removed from the solution with forceps and thoroughly rinsed with water with the washings being added to the beaker. The contents of the beaker are then quantitatively transferred to a 50 ml volumetric flask and diluted to mark with water. The solution is then stored in a polyethylene bottle.

8.4.2 Twenty-five ml of sample are transferred to a 50 ml polyethylene beaker containing a magnetic stirring bar. The cyanide electrode and reference electrode are placed in the solution and the millivolt reading is recorded after the meter has stabilized. Stirring rates are kept constant during analysis of both samples and standards.

9. Calibration and Standards.

9.1 Obtain the millivolt readings from each cyanide standard.

9.2 Plot the millivolt readings vs the cyanide ion concentrations of the standards on semi-log paper. The cyanide ion concentration in µg/ml is plotted on the log axis.

10. Calculations.

10.1 The millivolt readings from the analysis of the sample are converted to µgCN/ml of solution using the calibration curve.

10.2 The µg content of the sample is multipled by the sample volume to obtain the total µgCN in the sample.

10.3 Convert the volume of air sampled to standard conditions of 25°C and 760 mm Hg:

$$V_s = V \times \frac{P}{760} \times \frac{298}{T+273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg

V = volume of air in liters as measured

P = Barometric Pressure in mm Hg

T = Temperature of air in degree centrigrade.

10.4 The concentration of CN in the air sampled can be expressed in µg CN per liter or mg CN per cubic meter.

$$mg/m^3 = \mu g/liter$$

$$mg/m^3 = \frac{\text{total } \mu g \text{ CN}}{V_s}$$

10.5 The concentration of CN can also be expressed in ppm, defined as µl of component per liter of air.

$$ppm = \mu lCN/V_s = R/MW\ \mu gCN/V_s$$

$$= 0.94 \times \mu gCN/V_s$$

where:

R = 24.45 at 25°C, 760 mm Hg.

MW = 26.02

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NBS-114A (REV. 7-73)

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET	1. PUBLICATION OR REPORT NO. NBSIR 76-998	2. Gov't Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE

Development of a Solid Sorption Tube and Analytical Procedure for Hydrogen Cyanide in the Workplace Atmosphere

5. Publication Date January 1976

6. Performing Organization Code

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8. Performing Organ. Report No.

9. PERFORMING ORGANIZATION NAME AND ADDRESS

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

10. Project/Task/Work Unit No.

11. Contract/Grant No.

12. Sponsoring Organization Name and Complete Address (Street, City, State, ZIP)

National Institute for Occupational Safety and Health
Division of Laboratories and Criteria Development
Cincinnati, Ohio 45202

13. Type of Report & Period Covered Final Report

14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

The development of a sampling tube for collecting HCN in the workplace atmosphere is described. The tube contains 4.0 g of flake NaOH and can be readily fabricated in the laboratory. Details are given concerning the construction and use of the tube and data is presented on collection of HCN at levels of five times the TLV, one fifth the TLV, and at the TLV. Analysis of the tube contents using the cyanide ion selective electrode is described. This method is simple, rapid, and relatively free of interferences. Data on the analyses of tubes containing cyanide is described and estimates of the precision and accuracy of the method are given.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Air analysis; air sampling; gas analysis; hydrogen cyanide; industrial hygiene; ion selective electrode; sodium hydroxide; work atmosphere.

18. AVAILABILITY

[X] Unlimited

[ ] For Official Distribution. Do Not Release to NTIS

[ ] Order From Sup. of Doc., U.S. Government Printing Office Washington, D.C. 20402, SD Cat. No. C13

[X] Order From National Technical Information Service (NTIS) Springfield, Virginia 22151

19. SECURITY CLASS (THIS REPORT)	21. NO. OF PAGES
UNCLASSIFIED	25
20. SECURITY CLASS (THIS PAGE)	**22. Price**
UNCLASSIFIED	$3.50

USCOMM-DC 29042-P74