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A System for Producing Test Atmospheres Containing Hydrogen Cyanide

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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary
NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

A System for Producing Test Atmospheres Containing Hydrogen Cyanide

ABSTRACT

A system capable of producing well-defined test atmospheres of HCN in air (or any other desired diluent) and an analytical system for the analysis of these gas mixtures is described. This system provides a means of calibration of the various analytical systems for HCN now in use. The analytical unit of the system can also be used for the determination of hydrogen cyanide in industrial atmospheres. By collecting the HCN in a sodium hydroxide solution, and measuring the cyanide content by the use of a cyanide-ion selective electrode, concentrations of HCN in air between 5 and 500 ppm were measured. This method is rapid and convenient and can easily be performed by a technician or adapted to automation.

1. INTRODUCTION

This report describes a system capable of producing well defined test atmospheres containing concentrations of hydrogen cyanide for the calibration of analytical instruments and evaluation of analytical methodology. The system developed and described was designed to produce concentrations in the industrial hygiene range of 5 to 500 ppm but other concentrations could be achieved by suitable adjustment of the operational parameters.

2. EXPERIMENTAL

2.1 Apparatus

This system produces mixtures of hydrogen cyanide in air over a wide concentration range. It consists of two units; a gas mixing unit and an analytical unit. The gas mixing unit produces low concentrations of HCN by combining a relatively high concentration of HCN in nitrogen (the bulk mixture) with a stream of clean, dry air (the diluent). The analytical unit consists of a system which directs the bulk mixture through an impinger where the HCN is trapped and subsequently determined by use of a cyanide ion selective electrode. Reanalysis of the bulk mixture prior to use serves to confirm that it has not deteriorated between analyses or serves to assess the extent of deterioration.

The gas mixing unit and the analytical unit are combined in one system. Figure 1 shows a diagram of the gas flow of this system. The bulk mixture and the diluent air are mixed in known proportions and are directed to the sampling manifold from which a sample, or samples, may be withdrawn.

2.1.1 Gas Mixing Unit

The flow of diluent air is controlled by (V-1) and the flow of the bulk mixture of HCN in nitrogen is controlled by (V-2). The flow rates are measured by means of (FM-1) and (FM-2), respectively. The differential flow controllers, (DFC-1) and (DFC-2), maintain a constant flow in each leg of the system after the initial setting of the flow control valves and will maintain this constant flow until these valves are readjusted. Valves 4 and 5 are shut-off valves and isolate the unit when it is not in use.

The "dryer" shown in Figure 1, contains both activated charcoal and silica gel and is intended only as a final dryer for the diluent air. The streams of diluent and bulk mixtures combine in the mixing chamber and pass to the sampling manifold. The concentration of HCN in the air in the manifold is calculated from the observed flow rates and from the measured concentration of HCN in the bulk mixture. The concentration of HCN in the bulk mixture or dilutions is determined using the analytical unit.

2.1.2 Analytical Unit

A 3-way valve, (V-9), is located downstream from FM-2 in the bulk-mixture stream. In the "mixing" position the valve directs the flow to the mixing chamber. In the "analysis" position, the sample is directed to a 3-way solenoid valve (V-7). In the normal position (V-7) vents the sample to the exhaust. When the solenoid is energized, the sample is directed to the glass socket joint marked (A). A midget impinger containing a measured volume of base is connected to this socket. A timer is connected in parallel with the circuit which energizes (V-7). When the switch which controls (V-7) is in the "on" position, the bulk gas mixture flows through the impinger at the flow rate indicated by (FM-2) and the timer operates. When the collection is complete, the solenoid is de-energized by opening the switch so that both the flow of bulk mixture through the impinger and the timer are stopped. The time and the observed flow rate allow a calculation of the total volume of gas which passed through the impinger. This total volume is required for calculation of the amount of HCN in the measured volume of bulk mixture.

Samples may also be drawn at a controlled flow rate from the sampling manifold. In this case, the midget impinger is connected at (B) and (C) of Figure 1 and the vacuum system draws the sample from the manifold as indicated. The flow rate is controlled with (V-3) and measured with (FM-3). With solenoid valve, (V-8), in the normally open position, the flow rate through this portion of the system is adjusted by drawing air through the vent. When the solenoid is energized, the flow is directed from the manifold at the preset rate, through the impinger and then through the control system to the vacuum line.

In both of the above cases, the cyanide concentration is measured using a cyanide-ion selective electrode and a digital research pH meter.

2.1.3 Gases, Gas Mixtures

A pressurized cylinder containing a bulk mixture of HCN (99.5 percent) in nitrogen was prepared with a nominal HCN concentration of 500 ppm. The cylinder was pressurized to a total pressure of 1200 psi corresponding to approximately 3600 liters of the 500 ppm mixture at ambient conditions. The source of diluent air can be either a pressurized cylinder of "breathing" air or "house" air from the bench. In either case the air is passed through a silica gel-charcoal dryer to remove major contaminants.

2.1.4 Calibration

The solution contained in the impinger consists of 25.0 ml (0.025_6 l) of 0.1 M NaOH. The KCN standards in the range of 10^{-2} to 10^{-6} M were made using reagent grade KCN and stored in polyethylene bottles. A 0.1 M NaOH solution was used as the diluent instead of distilled water to simulate the impinger solution.

2.1.5 Procedure

Using the system described in Figure 1, the sample of HCN in air is bubbled through a solution of 0.1 M NaOH in the midget impinger where the HCN quantitatively is trapped. The cyanide ion concentration of the solution is determined by use of a cyanide ion selective electrode and comparison of the electrode potential with a calibration curve. The concentration of HCN in the sample is calculated by use of the following equation.

$$C_{HCN} = \frac{2.45 \times 10^{7} \cdot M \cdot \nu}{V}$$

where,

C_{HCN} = HCN concentration (ppm).

M = CN^- concentration in the impinger solution.

v = volume of liquid in the impinger (liters).

V = volume of gas sample (liters).

The concentration of HCN, C_x, in the dilute mixtures produced when the bulk mixture is blended with air is calculated using the following equation.

$$C_x = \frac{F_{HCN} \cdot C_{BULK}}{F_{HCN} + F_{AIR}}$$

where,

C_x = dilute HCN concentration (ppm).

F_{HCN} = bulk HCN flow (cm^3/min).

C_{BULK} = bulk HCN concentration (ppm).

F_{AIR} = air flow (cm^3/min).

The dilute mixtures of HCN can also be analyzed directly using the same procedure as outlined above for the bulk mixture.

3. PERFORMANCE EVALUATION

3.1 Electrode Performance

The cyanide electrode exhibits a 58 mv change in potential for each tenfold change in cyanide ion activity over the concentration range of $5x10^{-6}$ to $1x10^{-3}$M. Accordingly, a sufficient volume of gas should be collected to produce cyanide concentrations in this range.

3.2 Effect of pH

Hydrogen ion complexes cyanide ion to form the weak acid HCN. The greater the hydrogen ion activity, the greater the amount of cyanide ion which is complexed. Figure 2 shows the

fraction of free cyanide ion as a function of pH. At pH 8, less than 10 percent of the cyanide is free; 50 percent is free at pH 9.2; and at pH 12 virtually all the cyanide is in the form CN^-. For this reason, the collection medium in the impinger is 0.1 M NaOH.

3.3 Collection Efficiency

In order to determine the collection efficiency of the system, two impingers containing identical solutions were connected in series and samples were collected. These solutions were analyzed and it was found that more than 99 percent of the HCN in the sample was absorbed in the first impinger at flow rates up to 1 liter per minute.

3.4 Flow Rate

In order to determine the effect of flow rate upon collection efficiency, samples of HCN in air of the same concentration and same sample size were collected at various flow rates. Measurements showed that all of the HCN was absorbed at flow rates up to 1 liter per minute which is the practical limit for the midget impingers used.

3.5 Dilutions

Dilutions of the HCN bulk mixture were made by mixing it with clean, dry air as outlined earlier in the report. Figure 3 shows a plot of the observed concentration of HCN (as determined by analysis of the dilute mixture) versus the calculated concentration of HCN (calculated from the bulk concentration and the respective flow rates of the bulk stream and the diluent air stream). A linear relation with a slope of 1.00 is expected. The observed values were always lower than the calculated values indicating a loss of HCN in the dilution system. Since HCN is a reactive gas, this loss could be due to reaction or adsorption of the HCN within the dilution system. However, the mechanism was not investigated. Since it is not possible to reliably predict the concentration, it is necessary to analyze the gas in the manifold each time a mixture is prepared with the dilution system.

3.6 Stability

Figure 4 shows the results of a series of analyses performed on samples from the bulk mixture cylinder. After an initial rapid decrease in concentration, the HCN mixture in the cylinder appears to be fairly stable. For this reason, the mixture should not be used until it is 1 week old.

4. CONCLUSIONS

The system described in this report is capable of producing well-defined test atmospheres of HCN in air in the concentration range of industrial hygiene interest. The system described for verifying the composition of these mixtures is also useful for direct analysis of industrial atmospheres.

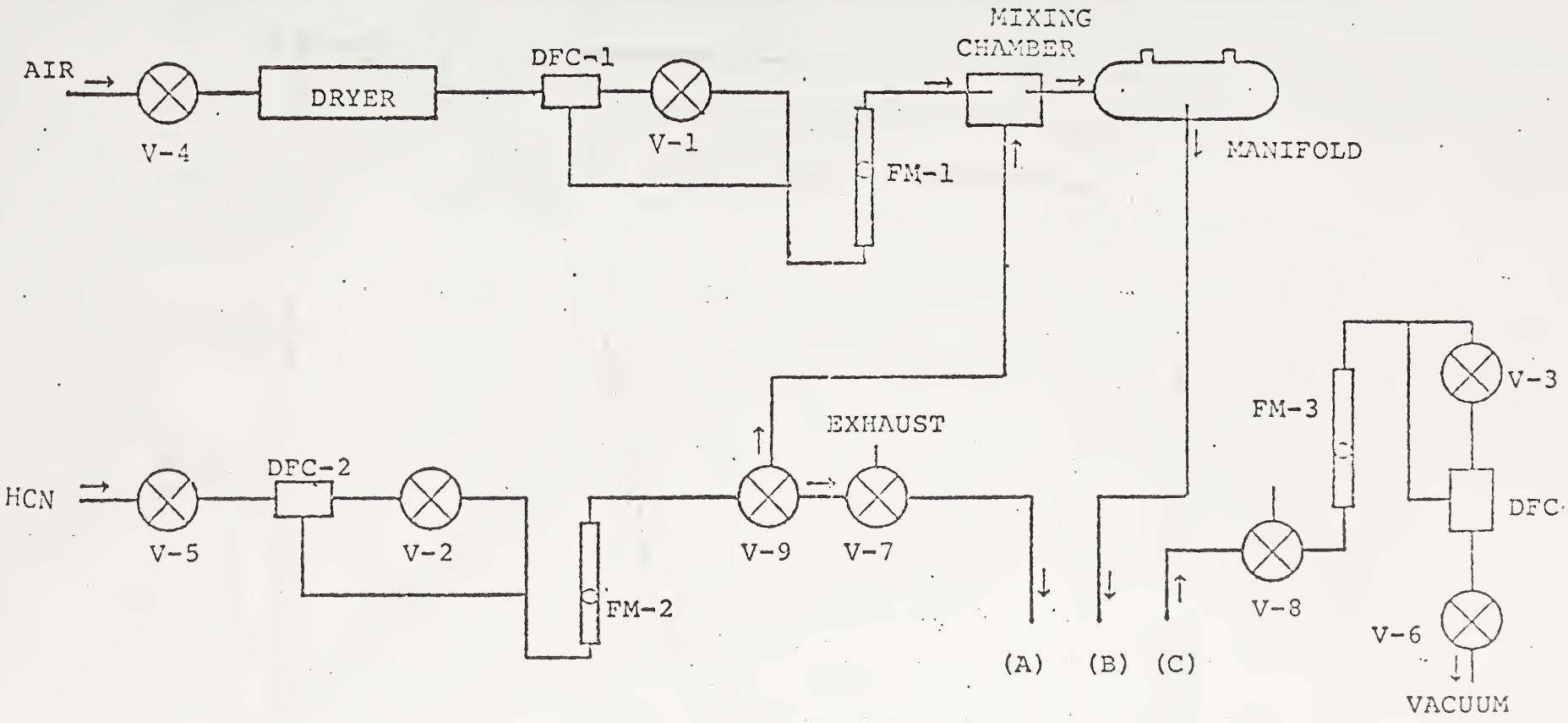

Figure 1. Generating and analysis system for hydrogen cyanide.

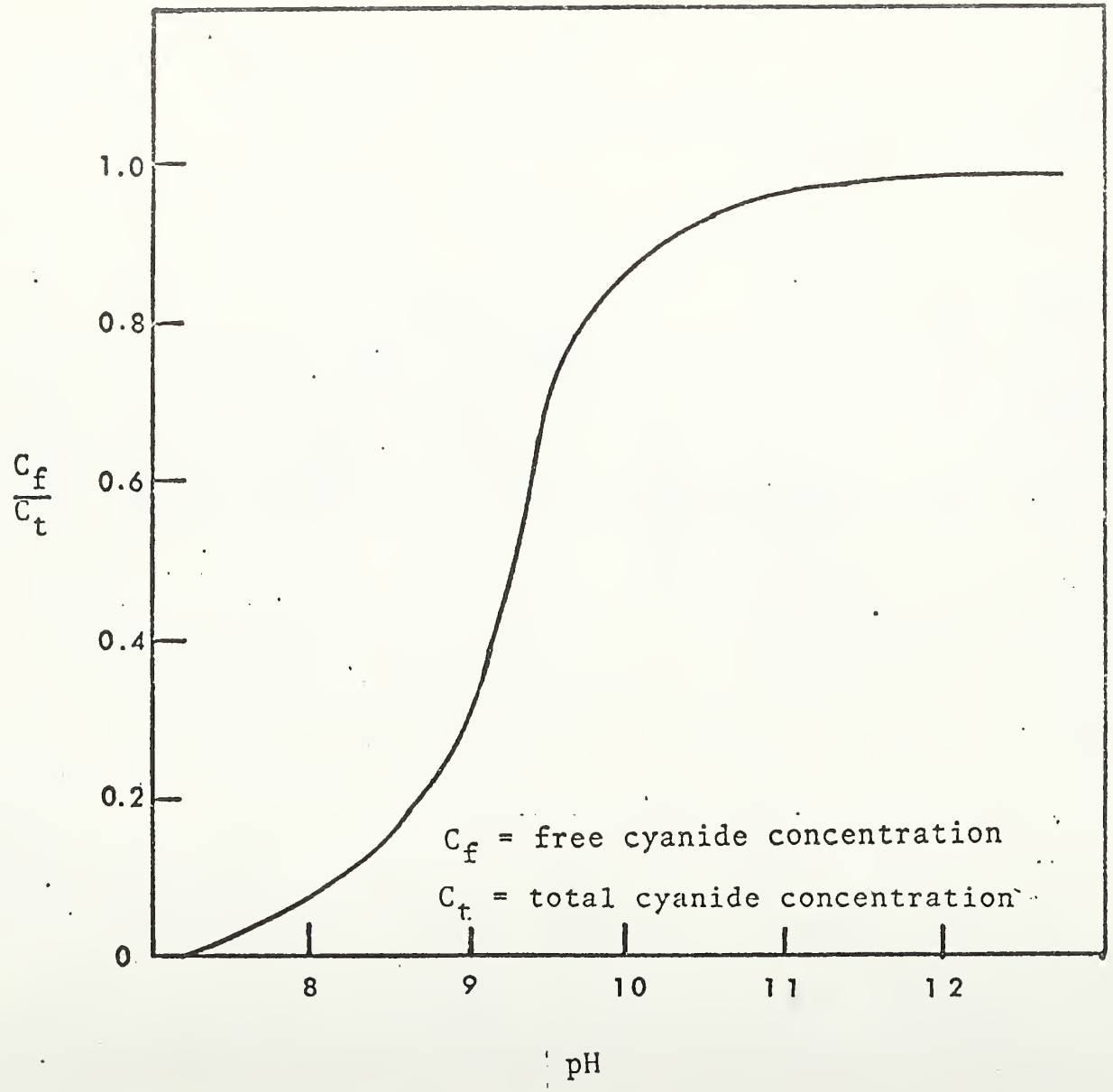

Figure 2. Effect of pH on free cyanide concentration.

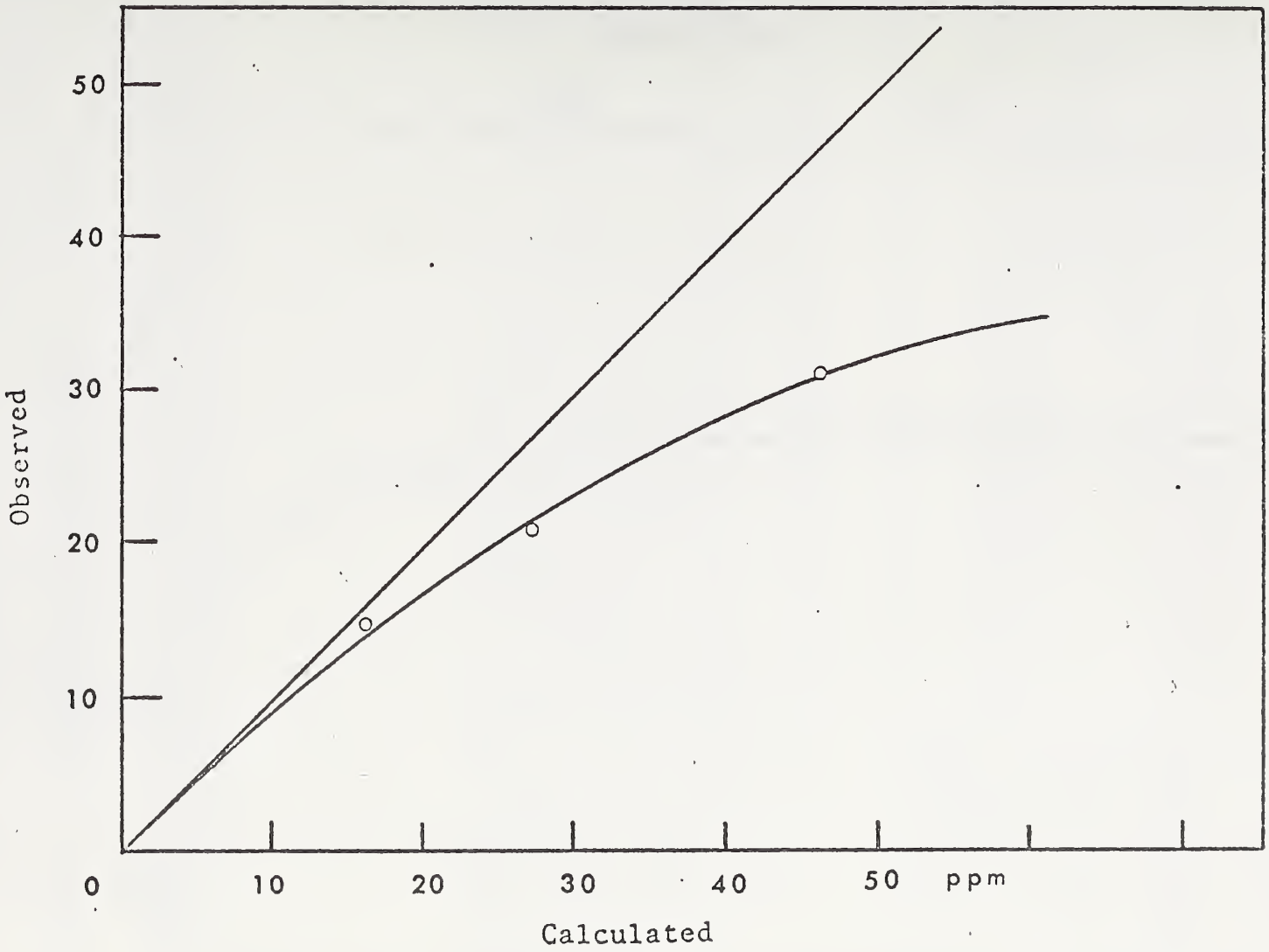

Figure 3. Observed concentration obtained on dilution of mixtures of hydrogen cyanide.

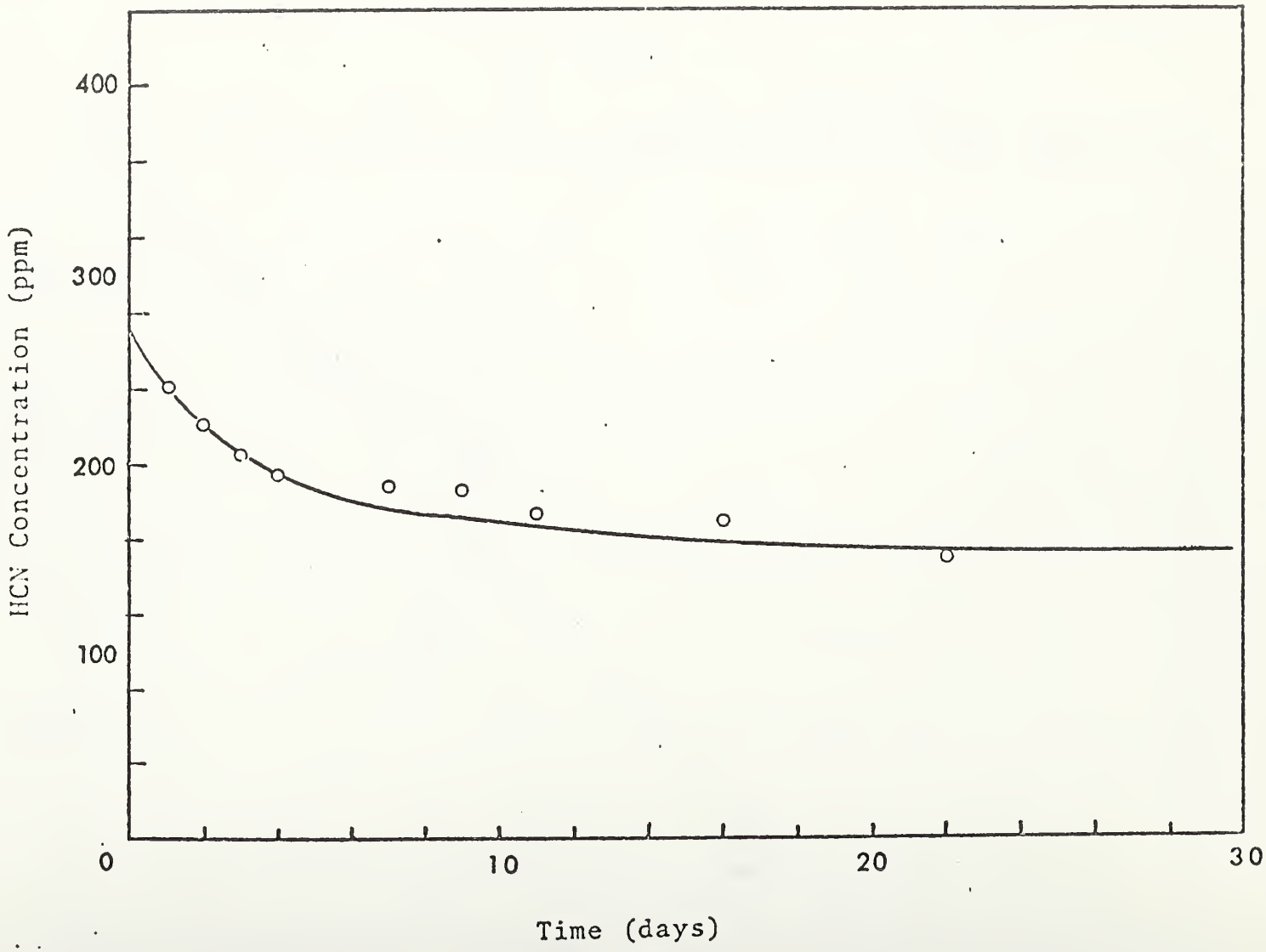

Figure 4. Stability of hydrogen cyanide mixtures in gas cylinders.

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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.)

A system capable of producing well-defined test atmospheres of HCN in air (or any other desired diluent) and an analytical system for the analysis of these gas mixtures is described. This system provides a means of calibration of the various analytical systems for HCN now in use. The analytical unit of the system can also be used for the determination of hydrogen cyanide in industrial atmospheres. By collecting the HCN in a sodium hydroxide solution, and measuring the cyanide content by the use of a cyanide-ion selective electrode, concentrations of HCN in air between 5 and 500 ppm were measured. This method is rapid and convenient and can easily be performed by a technician or adapted to automation.

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)
Gas blending system; hydrogen cyanide; ion selective electrode; occupational safety.

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