

Development and Evaluation of a Source Sampling and Analysis Method for Hydrogen Cyanide

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ABSTRACT

Laboratory studies were carried out to develop a method for the sampling and analysis of hydrogen cyanide from stationary source air emissions using a dilute NaOH solution as the collection medium. The method evaluated extracts stack gas from the emission sources and stabilizes the reactive gas for subsequent analysis in dilute sodium hydroxide solution. A modified Method 0050 sampling train was evaluated by dynamically spiking hydrogen cyanide into the heated probe while sampling simulated or actual source gas.

INTRODUCTION

Hydrogen cyanide (HCN) is listed as one of the 189 hazardous air pollutants in Title I of the Clean Air Act. In a study¹ of the 66 hazardous organic compounds tested, HCN was found to be the second most difficult compound to incinerate, surpassed only by cyanogen [(CN)₂]. The emissions of HCN are associated with industrial processes such as refining metallic ores, electroplating, production of acetonitrile and coke, manufacturing automotive catalytic converters, and chemical manufacturing.

The purpose of this work was to continue developing an HCN source emissions test method. Sample collection and analysis experiments were conducted. The IC analytical techniques were run using a direct, cyanide-specific IC detector, resulting in a more time efficient and precise analysis. Also, extensive collection efficiency trials were conducted in the presence of gases which were suspected to be analytical interferences. Finally a field test program was conducted in order to validate the method according to EPA Method 301² protocols.

ANALYTICAL METHOD

HCN collected in an alkaline aqueous medium dissociates into cyanide ion (CN⁻). The concentrations of CN⁻ in solution were determined using either a wet-chemical or instrumental analysis technique. For this work, concentrations of CN⁻ were determined after separation with electrochemical detection. Electrochemical detection is preferred over the conductivity detection because it measures CN⁻ concentration directly. Also, conductivity detectors are only sensitive to cyanate (CNO⁻) and not to CN⁻. IC conductivity analyses require extensive sample preparation procedures to oxidize all dissolved CN⁻ to CNO⁻. The oxidation step requires additional sample handling which increases the potential for analytical inaccuracy. Therefore, electrochemical detection is preferred over conductivity detection.

The electrochemical technique followed the IC manufacturer's recommendations for equipment operation (Dionex Applications Update 107). Qualitative identification of CN⁻ and other analyses of interest were based on the retention time of the analyte. Quantification of CN⁻ was performed using a

calibration curve with four standards that bracketed the expected sample levels. The calibration levels used were 0.5, 1.0, 1.5, and 2.0 ppm CN^- . Any sample with a concentration greater than the highest standard was diluted into the calibration range and reanalyzed. The analytical system was calibrated on a regular basis by periodically analyzing a single calibration standard. The standard prepared daily at 1 or 1.5 ppm was analyzed before the first sample analysis of that day, after every 10 samples, and after the last sample analyzed that day. The accuracy of the analytical system was checked daily by analyzing at least one sample spiked with CN^- (matrix spike). At least one sample was analyzed in duplicate per day. Usually, the sample used for the matrix spike was also the sample analyzed in duplicate. Sample results were not corrected for method blanks. Blank values were very low in comparison to the sample results.

HCN Spiking Standards and Equipment

HCN gas was injected (spiked) into the sample trains both in the field and in the laboratory using gas standards (35 ppm in nitrogen). The configuration of the spiking system is shown in Figure 1. Spiking rates ranged from 0.2 L/min to 0.5 L/min. Gas was spiked into a full-sized sample train approximately 2 feet upstream of the sample filter, through the sample probe.

Sample Collection Trains

A variety of sampling trains were tested for HCN collection efficiency with and without the presence of interfering gases. The simplest train (Figure 2, the "NaOH train") was a modified EPA Method 0050³ train which used only 0.1N NaOH absorbing solution. The sample stream was first pulled through a heated, glass probe, and then through a heated glass fiber filter. into a series of four Greenburg-Smith (GS) plate type impingers: two impingers containing 0.1N NaOH, followed by an empty, knockout impinger then a silica gel impinger. After the impinger train, the gas stream passed through the pump, gas meter, and orifice meter. All equipment used was standardized Method 5⁴ stack sampling equipment.

The second impinger train was exactly the same as the NaOH train except that an impinger was added upstream of the four described above: First a GS impinger containing 10% lead acetate acidified to a pH of 4.5 or below, and the knockout impinger was moved to prevent transfer of the lead acetate solution into NaOH solution ("Pb Acetate/NaOH" train, Figure 3).

The third train tested was a standard EPA Method 0050 train containing two GS impingers with 0.1N H_2SO_4 followed by two with 0.1N NaOH followed by the silica gel impinger (Figure 4).

Analytical Optimization, Detection Limit, and Interference Study

Initial studies were undertaken to optimize the IC electrochemical detector. The range of calibration was 500 to 2000 ppb CN^- in solution. Most of the sampling train spiking trials targeted a 1.5 ppm-solution as a good mid-point along the IC calibration curve. Additional ions were added to analytical standards to determine if they interfered with the analyses. Sulfate (SO_4^-), cyanate (CNO^-), and chloride (Cl^-) ions did not interfere with the analysis. Sulfide (S^-) did interfere at concentrations greater than 50 ppm. Of the four ions tested, the electrochemical detector only responded to S^- . Large quantities of S^- interfere because the S^- peak tails into the CN^- peak. At S^- concentrations of 50 ppm and below, the S^- was well resolved from the CN^- . However, in the presence of S^- at any concentration, CN^- is degraded over a period of time.

An instrument detection limit was determined by the Federal Register method for determining detection limits.⁵ A 0.1 ppm CN^- standard was prepared and injected into the analytical system seven times. The instrument detection limit was found to be 30 ppb. Quality control procedures for the IC analysis for this project followed the quality control procedures recommended for HCl in the Quality Assurance/Quality Control Handbook.⁶

Laboratory Train Evaluations

Prior to laboratory evaluations of a full size train, cylinder gas standard concentrations were verified from 101 to 106%; all recoveries met the $\pm 10\%$ criterion.

Sampling train evaluations to determine collection efficiency were conducted by spiking HCN into the three sampling trains (NaOH, Pb acetate/NaOH, Method 0050 train). Collection efficiency was considered acceptable based on CN^- recoveries of $100\% \pm 10\%$. Table 1 presents CN^- recoveries for train evaluations conducted without spiking any additional interfering gases (i.e., H_2S). HCN was spiked from a 36.7 ppm cylinder at rates ranging from 0.2 to 0.5 L/min into a sample stream following at 0.5 cubic feet per minute (cfm) through the impingers to produce HCN gas concentrations ranging from 0.5 to 1 ppmv. The sample stream consisted of either ambient air with moisture at 2%, dry ambient air with moisture at 0%, or ambient air with elevated moisture ranging from 9 to 28%. Test runs varied from 20 to 60 minutes.

Recoveries were acceptable for all train configurations and moisture levels except for Runs 4-6 which used the Method 0050 train. For these test runs some of the HCN was collected in H_2SO_4 , thereby lowering the recovery in the NaOH. These recoveries are only slightly low and may not be significant. Both the NaOH and Pb acetate/NaOH trains collected HCN at acceptable levels.

The results from laboratory spiking trials conducted with approximately 10 ppm of H_2S present in the sample stream are shown in Table 2. The first 12 runs were conducted in August, 1995. These tests fall into four experimental cases: Runs 10-13 employed the Pb acetate/NaOH train spiked with HCN, H_2S and no moisture. The second case (Runs 13-16) was the same with the exception that moisture was added. The third case (Runs 17-19) was the same as the second except that a NaOH train was used. The fourth case (Runs 20 and 21) was the same as the third except that 10 ppm of SO_2 was added in addition to the HCN and H_2S . Variation in the results may indicate poor experimental execution. Therefore, these trials were repeated in September on Runs 31 through 34. These results show slightly higher recoveries. Recoveries were also slightly high for the Pb acetate train without H_2S interferences added (Runs 20 and 21, Table 1). The reasons for this variation are not known.

Other Laboratory Experiments

To evaluate the effects of sample hold time, samples analyzed immediately after laboratory spiking trials were re-analyzed several months later. When S^- is not present, CN^- is stable in basic solution for approximately 4 months. When S^- is present, the CN^- is stable for less than one month. The S^- apparently reacts with the CN^- over time to form $\text{S}^- \text{CN}^-$ as indicated by the disappearance of both the S^- and CN^- peaks.

Good HCN collection efficiency is dependent on maintaining a high pH in the NaOH absorbing solution. Because of this sensitivity, the use of colorimetric pH indicators added to NaOH was examined. Indicators that changed pH between 9 and 11 and that were soluble in water were preferred. Alizarin-Yellow R, red at pH greater than 10.2 and yellow at pH below 10.2, was prepared as a 0.1% solution in water. Thymolphthalein changes from blue to colorless when the pH decreases below 9.4 and was prepared as a 0.1% solution in ethanol. Typically, 10 drops of indicator are added to 100 mL of absorbing solution.

Indicators in HCN absorbing solutions were evaluated to determine if they cause any analytical matrix effects. Indicators were added to CN^- standards at pH 9 and 13 and then the solutions were analyzed. Generally, CN^- recoveries were not effected by either of these indicators at pH 9 or 13. Because neither indicator interfered with the analysis, Alzarin-Yellow R was used as the indicator in the impinger solution because it changed color at a higher pH than Thymolphthalein.

FIELD METHOD VALIDATION TEST RESULTS

Exhaust gases from a liquid waste burner burning liquid hazardous wastes and pumpable sludges were tested. Waste streams included petroleum refinery solvents, halogenated solvents, chemical plant residues, pesticides, herbicides, pharmaceutical and laboratory wastes, and low melting solids. Following

the incinerator, the exhaust gas train consisted of a heat recovery boiler, fabric filter, quench, and an acid gas scrubber. The scrubber used once-through water (without recycle) or feed water pH adjustment to remove acid gases. Approximate stack gas emissions parameters were: temperature, 150 - 160°F; velocity, 45 - 50 fps; moisture, saturated.

A Method 301² "quad" system was used with each sampling train employing four impingers: Two containing 100 mL of 0.1 NaOH, an empty impinger, and a silica gel impinger. Ten 1-hour tests were conducted the week of July 24th. HCN recoveries from spiked train samples revealed no CN⁻ detected in any of the test runs except those conducted on Day 3 (Runs 6 [79%], 7 [89%], and 8 [67%]). For the majority of these runs, both the spiked trains as well as the unspiked trains collected more CN⁻ in impinger 2 than impinger 1, strong evidence that CN⁻ breakthrough occurred. Therefore, something occurred on Day 3 which did not happen on the other days which allowed CN⁻ to be collected.

A decrease in pH of the impinger solution to allow the spiked HCN to pass through the NaOH solutions is the most likely reason that no spiked CN⁻ was detected. There were indications that the stack gas was extremely acidic: The stack gas is extremely corrosive and the scrubber exit water had a pH of 1. The measured pH of the final samples (after NaOH recovery rinses) was approximately 12. Based on calculations, the pH of the impinger solutions may have dropped to below 7 during the testing, allowing HCN to pass through uncollected. A possible train configuration to prevent loss of HCN would add two modified lead acetate containing impingers upstream of the NaOH impingers and possibly to add stronger caustic either by more impingers or increase the strength of the NaOH solution to remove acidifying gases from the NaOH collection solution. Further research is needed.

CONCLUSIONS AND RECOMMENDATIONS

This work produced additional data to be used in refining the HCN source emission testing method. Advances were made both in analysis and sample collection. Electrochemical detection is a good measurement technique, but the guard column must be periodically replaced in order to prevent poisoning of the separation column and/or electrode. The highly variable CN⁻ recoveries from the field test program reveal that the train is susceptible to low HCN collection efficiency when acidic gases lower the pH of the impinger solution pH causing the HCN to pass through the collection media. H₂S interferes both with the sample stability as well as IC analyses, because of this Pb acetate solution should be used upstream of the NaOH to remove acid gases and/or other interferences.

The following experiments are recommended:

- Spike HCN into the NaOH/indicator train. This will determine if the pH indicator has any effect on HCN collection efficiency.
- Examine the use of acidified Pb acetate/NaOH sampling trains for HCN collection in the presence of interfering gases such as H₂S, SO₂, HCl, CO₂, CO, and others. Initial work in this area has been completed with promising results (See Runs 31-34).
- If 0.1N NaOH does not appear to collect HCN adequately in acidifying or oxidizing stack gas matrices first a stronger NaOH solution or a stronger high pH buffered solution such as 0.05 M Na₃PO₄ (pH:12.04) or saturated CA(OH)₂ (pH:12.45) may be more appropriate. A zinc acetate solution precipitates zinc cyanide upon collection. The Zn (CN)₂ is then distilled into NaOH and analyzed by a variety of techniques.

Following additional laboratory tests, the refined sample train should be tested under field conditions to demonstrate that the train is not subject to any stack gas matrix effects which could bias HCN collection recoveries. EPA Method 301 field method validation test runs could then be performed.

REFERENCES

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2. Protocol for the Field Validation of Emissions Concentrations from Stationary Sources, 40 CFR, Part 63.
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5. Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit Revision 1.11, Federal Register. Vol. 49, No. 209. Friday, October 26, 1984.

DISCLAIMER

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Table 1. Laboratory HCN spiking results, without interferences.

Run	Date	Train Conf. ^a	Sample Gas Concentrations		Recovery (%)	Comments
			HCN (ppm) ^b	H ₂ O (%)		
1	May	F, NaOH	1.2	0	95	
2	May	F, NaOH	1.2	0	101.6	
3	May	F, NaOH	1.2	0	94.5	
				Average	97.0	
4	May	F, H ₂ SO ₄ , NaOH	1.2	13	72.2	~10% HCN recovered in H ₂ SO ₄
5	May	F, H ₂ SO ₄ , NaOH	1.2	29	66.9	
6	May	F, H ₂ SO ₄ , NaOH	1.2	9	78.9	
				Average	72.7	
7	May	F, PbAc, NaOH	1.2	23	94.7	
8	May	F, PbAc, NaOH	1.2	25	92.5	
9	May	F, PbAc, NaOH	1.2	28	93.4	
				Average	93.5	
22	Sept	F, NaOH	1.2	2	101	HCN = 0.2 L/min for 60 min, ambient air
23	Sept	F, NaOH	1.2	2	117	
				Average	109	
24	Sept	F, NaOH	1.2	2	98	HCN = 0.5 L/min for 60 min, ambient air
25	Sept	F, NaOH	1.2	2	103	
				Average	100	
26	Sept	F, NaOH	1.2	0	103.1	HCN = 0.5 L/min for 20 min, dry air
				Average	103.1	
27	Sept	F, NaOH	1.2	23	102	HCN = 0.5 L/min for 20 min, with moisture
28	Sept	F, NaOH	1.2	23	102	
				Average	102	
29	Sept	F, PbAc, NaOH	1.2	22	121	HCN = 0.5 L/min for 20 min, with moisture
30	Sept	F, PbAc, NaOH	1.2	24	117	
				Average	119	

^aF = Filter, NaOH = 0.1N NaOH, H₂SO₄ = 0.1N H₂SO₄, PbAc = 10% Acidified lead acetate (all CN⁻ was collected in the NaOH).

^bHCN cylinder gas concentration of 36.7 ppm was injected into the sample gas resulting in the HCN concentrations shown.

Table 2. Laboratory HCN spiking results, with interferences.

Run	Date	Train Conf.*	Sample Gas Concentrations				Recovery (%)	Comments
			HCN (ppm) ^b	H ₂ O (%)	H ₂ S (ppm)	Other		
10	Aug	F, PbAc, NaOH	0.5	0	10		30	
11	Aug	F, PbAc, NaOH	0.5	0	10		67	
12	Aug	F, PbAc, NaOH	0.5	0	10		72	
						Average	56.3	
13	Aug	F, PbAc, NaOH	0.5	13	10		76	
14	Aug	F, PbAc, NaOH	0.3	29	10		33	pH of 1st impinger dropped from 12 to 9
15	Aug	F, PbAc, NaOH	0.5	9	10		80	
16	Aug	F, PbAc, NaOH	0.5	23	10		57	
						Average	67.0	
17	Aug	F, NaOH	0.5	25	10		56	
18	Aug	F, NaOH	0.5	28	10		62	
19	Aug	F, NaOH	0.5	28	10		90	
						Average	69.3	
20	Aug	F, PbAc, NaOH	0.5	26	10	10 ppm SO ₂	78	
21	Aug	F, PbAc, NaOH	0.5	27	10	10 ppm SO ₂	ND	
						Average	39	
31	Sept	F, PbAc, NaOH	1.0	0	10	0	111	HCN = 0.5 LPM for 20 min, no moisture
32	Sept	F, PbAc, NaOH	1.0	0	10	0	122.5	
						Average	116.8	
33	Sept	F, H ₂ SO ₄ , NaOH	1.0	0	10	0	113	HCN = 0.5 LPM for 20 min, no moisture
34	Sept	F, H ₂ SO ₄ , NaOH	1.0	0	10	0	98	
						Average	106	

*F = Filter, NaOH = 0.1N NaOH, H₂SO₄ = 0.1N H₂SO₄, PbAc = 10% Acidified lead acetate (all CN⁻ was collected in the NaOH).

^bHCN cylinder gas concentration of 36.7 ppm was injected into the sample gas resulting in the HCN concentrations shown.

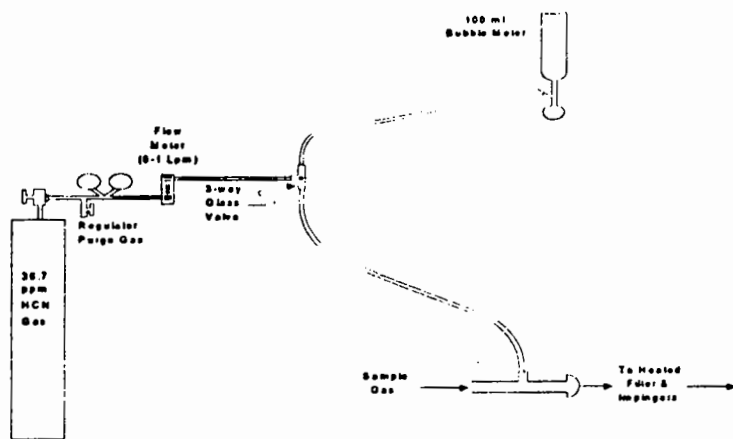


Figure 1. HCN gas spiking equipment configuration.

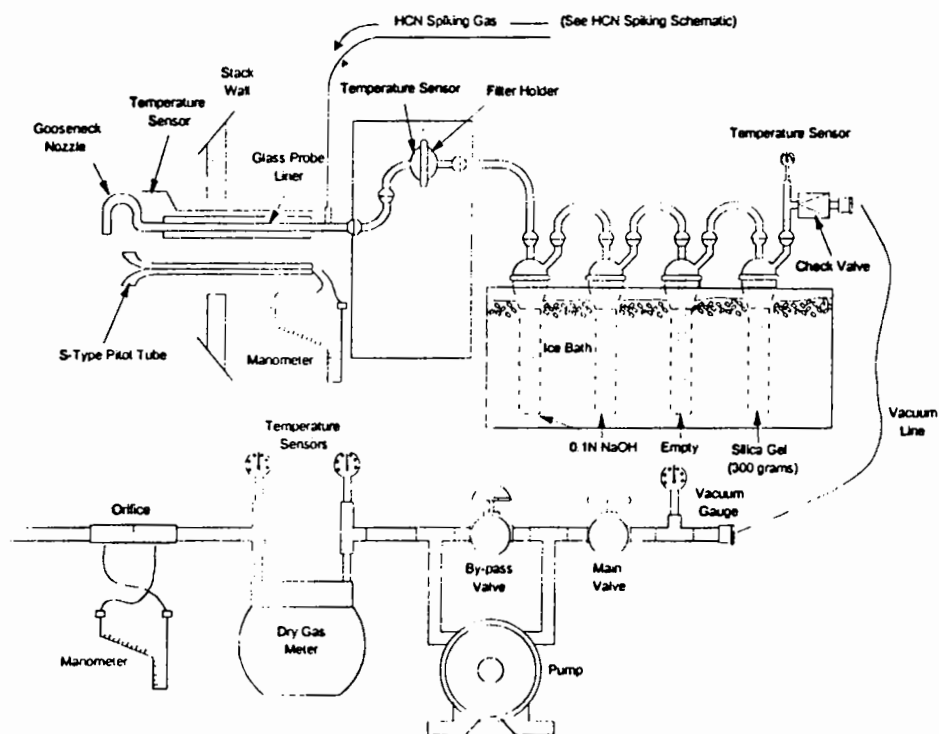


Figure 2. HCN sampling train, NaOH configuration.

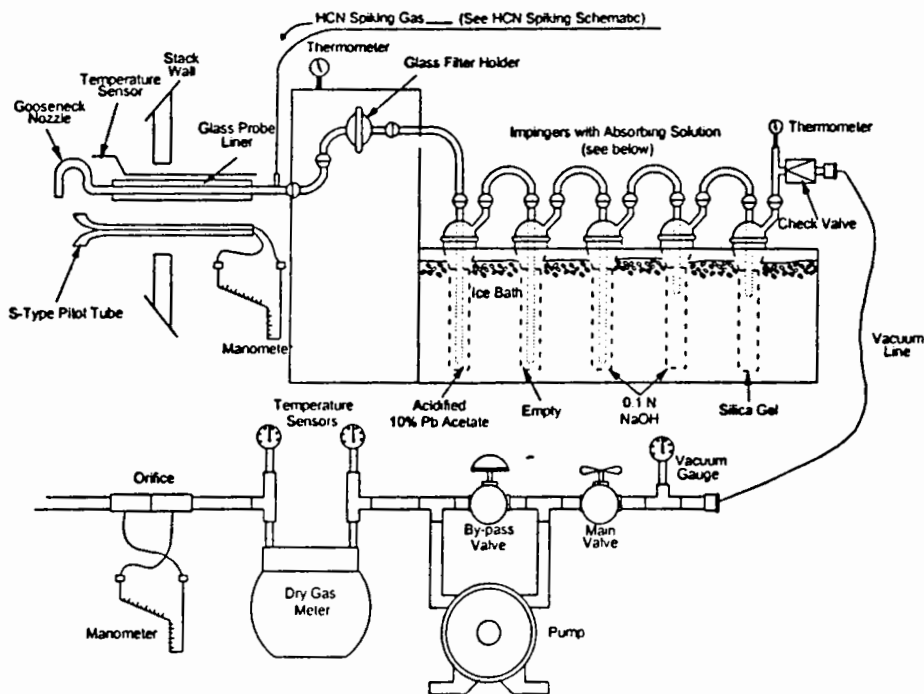


Figure 3. HCN sampling train, lead acetate/NaOH configuration.

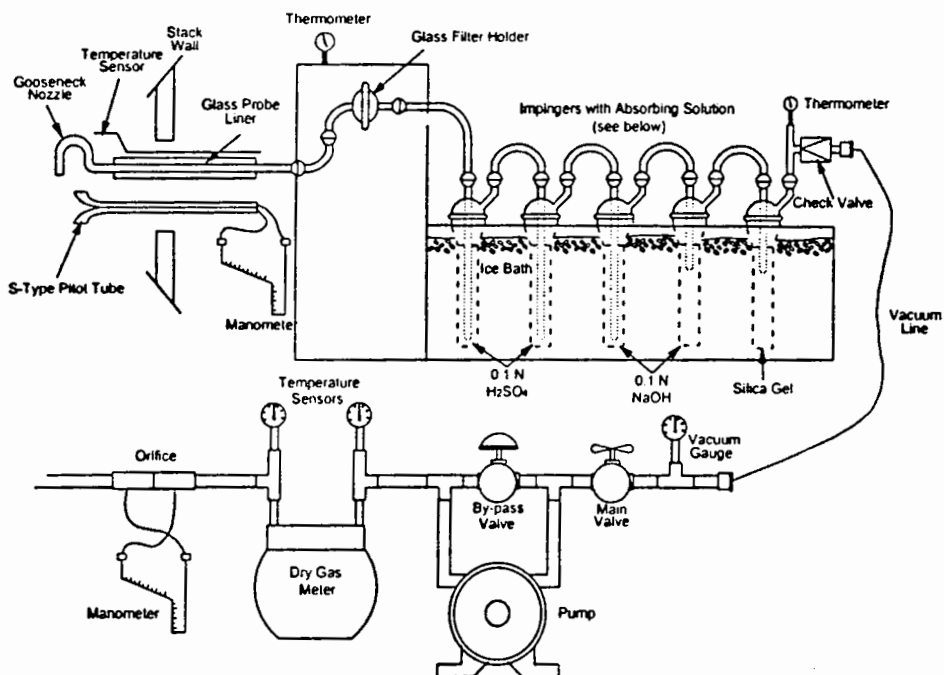


Figure 4. HCN sampling train, Method 0050 configuration ($H_2SO_4/NaOH$).

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