Progress Toward Developing a Monitoring Method for Hydrogen Cyanide in Air

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The development of an analytical procedure for measuring free cyanide, the various solid and liquid sorbents tested, and the instability problems encountered during research to establish a monitoring method for hydrogen-cyanide (74908) (HCN) in air are described. The original goals of the project were the development of improved sampling and analytical methods for hydrogen-fluoride (7664393), HCN, and particulate cyanides by replacing liquid impinger samplers with solid sorbent samplers and using an ion chromatographic analytical technique. The approach taken was: to analyze for cyanide ion by ion chromatography with electrochemical detection; to test the permeation by HCN of filters for the collection of particulate cyanides; to screen solid sorbents for the collection of HCN; and, if a suitable solid sorbent for HCN was not found, to investigate liquid sorbents with the intention of their eventual use in passive monitors. While the study did not yield the hoped for results, the author suggests that attempts be made to collect HCN in an iron or cobalt salt solution to form a stable complex with cyanide ion. Such a solution could be used in a passive monitor or coated onto silica gel. Alternate nonaqueous solvents should be investigated for desorption of HCN from charcoal. Various oxidizing agents should be studied to convert cyanide to the more stable cyanate and a subsequent analytical method for the determination of cyanate be undertaken.

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INTRODUCTION

The study on hydrogen cyanide and particulate cyanides was undertaken as a segment of the Ion Chromatography/Solid Sorbent Methods Development project. The original goals of this project were the development of improved sampling and analytical methods for hydrogen fluoride (HF), hydrogen cyanide (HCN), and particulate cyanides by replacing liquid impinger samplers with solid sorbent samplers and by utilizing an ion chromatographic (IC) analytical technique.

The project was started in fiscal year 1983 (10/82) with research pursuant to the development of a sampling and analytical method for HF. The silica gel sorbent tube developed for sampling inorganic acids was successfully evaluated for the collection of HF. Fluoride ion (F^-) can be measured by the same ion chromatographic procedure as the other common inorganic anions (1). The outputs of the HF phase of the research were: (a) incorporation of HF into the revised Inorganic Acids Method No. 7903 (2); (b) a presentation at AIHC in Las Vegas, May 23, 1985 (3); and a publication describing the HF work, "Laboratory Evaluation of Silica Gel Sorbent Tubes for Sampling Hydrogen Fluoride" (4).

Current analytical methods for the determination of HCN in air, e.g., P&CAM 116 (5), S288 (6), and Method 7904 (2), collect HCN in impingers or bubblers containing alkaline solutions, and subsequently determine cyanide ion (CN^-) by ion specific electrode (ISE). The ISE for CN^- responds to numerous interferences (S, Cl, I, Br, Cd, Ag, Zn, Cu, Ni, and Hg). The proposed IC method with electrochemical (amperometric) detection is free from these interferences including S^{2-}. A battery-operated personal monitor is commercially available; however, it expensive and is also prone to interference from S^{2-} and to a lesser extent by halogen gases. Direct-reading instruments are cumbersome for field use, expensive, and prone to the same interferences as the other monitoring systems. This study sought to improve cyanide monitoring through the development of a solid sorbent sampler and the utilization of an interference free analytical technique.

Laboratory work for the cyanide phase of the project began in the fourth quarter of fiscal year 1984 (7/84). Because HCN is rapidly fatal at high concentrations, a stringent safety protocol was formulated and implemented. The approach taken for the cyanide study was: (a) to analyze for CN^- by IC with electrochemical detection (7), (b) to test the permeation by HCN of filters for the collection of particulate cyanides, (c) to screen solid sorbents for the collection of HCN, and (d) if a suitable solid sorbent for HCN was not found, to investigate liquid sorbents with the intention of their eventual use in passive monitors. An analytical procedure was developed for the determination of CN^- based on reference 7; mixed cellulose ester membrane filters were found suitable for the collection of particulate cyanides; however, a suitable solid sorbent for HCN was not found. Liquid sorbents were then investigated in which compounds more stable than free CN^- were formed, because the instability of the collected cyanide was found to be a substantial problem.

The project was terminated on October 15, 1985, for lack of significant progress toward the development of a suitable sampler for HCN. This report describes the analytical procedure developed for measuring free cyanide, discusses the various solid and liquid sorbents tested, the instability problems encountered, and suggests approaches for future research.

EXPERIMENTAL SECTION

Generation System

In the interest of safety during the sorbent screening process, the quantity of HCN produced was kept to a minimum through the use of a single sample generation system in which the source of HCN was a Dynacal^R permeation device (VICI Metronics, Santa Clara, CA), 10 cm in length, with an output of 340 ng/min/cm at 30°C. The generator consisted of a VICI Metronics Dynacalibrator Model 340 permeation oven set at 30°C, attached to the sampler inlet with Teflon^R PFE fittings and 1/4" Teflon tubing which was wrapped from the oven exit to approximately half its length (40 cm) with heating tape maintained at 60°C. The sampler outlet was connected via Teflon tubing and fittings directly to a Kin-Tek CN80 HCN Analyzer (Texas City, TX) with a sample pump rate of 0.299 L/min. With dried house air as the carrier gas, the output from the permeation oven measured 10 ppm HCN. The described system arrangement allowed for calibration of the HCN output and provided an indication of breakthrough when a sampler was placed in line.

Analytical Instrumentation

Analyses were performed on a Dionex System 2020i ion chromatograph (Dionex Corp., Sunnyvale, CA) with a Dionex Potentiostat electrochemical detector, the assembly of which is shown in Figure 1. The IC was interfaced with a WISP 710B autosampler (Waters Associates, Milford, MA) and a Hewlett-Packard 3357 Laboratory Data System (Hewlett-Packard, Avondale, PA). The instrumental parameters for determining CN^- were as follows:

Eluent:	1 mM Na_2CO_3/10 mM NaH_2BO_3/15 mM ethylenediamine
Flow Rate:	2.0 mL/min
Columns:	HPIC-AS4 separator, HPIC-AG4 Guard (Dionex)
Injection Volume:	50 uL
Detector:	Amperometric
Electrodes:	Working - Ag
	Counter - Pt
	Reference - Ag/AgCl
E_{app}:	0.0 V
Output Range:	1 uA/V

Reagents

All chemicals were ACS reagent grade or better. The eluent, a buffer solution at approximately pH 11, consisted of an aqueous solution containing the following reagents at the specified concentrations: 1 mM Na_2CO_3 (Aldrich Chemical Co., Inc., Milwaukee, WI), 15 mM ethylenediamine (Aldrich), and 10 mM NaH_2BO_3 which was prepared from H_3BO_3(Fisher Scientific, Fair Lawn, NJ) and NaOH (Alfa Products, Danvers, MA). Working cyanide standards were dilutions of a 1000 ug CN^-/mL stock solution which was prepared from KCN (Aldrich) in eluent buffer. The cadmium complexing solution was cadmium nitrate [$Cd(NO_3)_2$ (Aldrich)] at a concentration of 0.01 M in deionized water.

Samplers

The samplers used in this study were, for the most part, commercially available sorbent tubes (see Table I). The coated Carbopack B and Ambersorbs XE-340, XE-347 and XE-348 were hand packed into either 6-mm or 8-mm OD glass tubes to a bed length of 30 mm. A glass wool plug was placed at the inlet and a urethane plug at outlet. Alkali-impregnated charcoal from three small tubes (SKC 226-67) was packed into an 8-mm OD glass tube. Liquid sorbents were placed in fritted-glass bubblers or, in one case, a Liquid Media Sampler (LMS).

RESULTS AND DISCUSSION

Analysis

The ion chromatographic technique successfully separates CN^- from potentially interfering anions including sulfide (S^{2-})(8), essentially eliminating the need for an interference removal step which is necessary with traditional wet methods (9). However, the HCN eluting from the IC column exhibits low conductivity because of its low dissociation. Rocklin and Johnson (7) reported a method for determining CN^- by IC with electrochemical detection. The method is based on the ability of a silver working electrode in a amperometric electrochemical flow-through cell (Fig. 1) to produce a current which is directly proportional to the CN^- concentration. The reaction follows the equation

$$Ag^0 + 2\ CN^- \longrightarrow Ag(CN)_2^- + e^- \qquad (1)$$

Although the Ag working electrode is oxidized rather than the species in solution being oxidized, the sensitivity of the electrode is maintained over a relatively long period of time. Mechanical polishing of the electrode is necessary only weekly to maintain sensitivity.

The response of the cell (uA), and consequently the size of the peak produced, are dependent on the potential applied to the cell. The optimum applied potential (E_{app}) for CN^- was determined to be 0 volts (7). A precision of 0.027 was found for the mid-point of the calibration curve, as determined by the relative standard deviation (s_r) of replicate injections (n=9) of a 0.5 ug/mL standard. The limit of detection (LOD) was determined at 8 ng/mL, somewhat greater than the literature values of 1 ng/mL (10) and 2 ng/mL (7). The limit of quantitation within a s_r of 10% was 20 ng/mL.

The calibration graph (Fig. 2) shows that the response for CN^- is linear up to 1 ug/mL when using the parameters stated in the Experimental Section. This is in keeping with values found in the literature (7, 10). The use of a less sensitive output range (e.g. 3 uA/V or 10 uA/V) does not extend the linear range. At concentrations greater than 1 ug/mL the response becomes nonlinear. The smaller increases in current at higher concentrations are caused by uncompensated resistance in the cell (7). The upper limit may be extended by increasing the applied potential or by decreasing the volume of the injection loop or, more realistically, by dilution of the sample.

Sorbent Screening

Three groups of sorbents were screened for collection of HCN: commercially prepared solid sorbent tubes, laboratory prepared solid sorbent tubes, and liquid sorbents in bubblers. The goal of this project was to find a solid sorbent suitable for the collection of HCN in air. If a suitable solid sorbent was not found, liquid sorbents were to be investigated with the intention of their eventual use in passive monitors.

The ability of each sorbent to collect HCN was determined from the time required for 10 ppm HCN at a flow rate of approximately 0.3 L/min to breakthrough the sorbent and be detected by the HCN continuous monitor. The criterion for breakthrough was an effluent HCN concentration of 0.5 ppm, 5% of the influent concentration. The backup sections of the commercial sorbent tubes were removed before testing, so that breakthrough was measured for only the primary sorbent bed. The silver filter, used as a sorbent for HCN, was contained in a Swinnex 25-mm filter holder. The breakthrough data are listed in Table I.

With the exception of the charcoals, Ambersorb active carbons, and coated silica gel, all solid sorbents experienced breakthrough within 2 minutes or less ($\leq$ 0.6 L) at 10 ppm HCN (1XPEL). The alkali-treated charcoal (SKC 226-67) exhibited an unusual breakthrough pattern in which the effluent concentration remained constant for periods of approximately six minutes at levels of approximately 4 ppm, then 5 ppm, etc. This stepwise pattern indicated that a reaction was taking place but at a rate slower than the residence time of HCN. To increase the capacity and bed length of the sampler, charcoal from three of the commercial tubes was packed into an 8-mm OD x 10 cm glass tube. When 10 ppm HCN was passed through this tube, the alkali-treated charcoal trapped all the influent HCN for 17 minutes, after this time the effluent concentration increased gradually (ca. 4 ppm/h).

The material from which the charcoal was prepared made a significant difference in its ability to trap HCN. The petroleum-based Qazi-Ketcham tube (ORBO-33) experienced breakthrough in 3.5 minutes, while the breakthrough time for coconut-based charcoal (ORBO-32) was 42 minutes although the latter tube contained approximately half the amount of charcoal of the former. When sampling at a rate of 0.09 L/min, breakthrough occurred in 4 hours 35 minutes. The effluent concentration increased very gradually; after 7 hours the CN80 continuous monitor read 1.8 ppm (ca. 0.45 ppm/h). The ORBO-32 coconut charcoal tube showed the most promise with its ability to sample for over four hours at a rate of 0.09 L/min; unfortunately, the HCN could not be desorbed from the charcoal.

Since charcoals prepared from naturally occurring materials contain chemisorbed oxygen, it was theorized that the collected cyanide was oxidized to cyanate (OCN^-) and, therefore, not detected with the amperometric conditions stated. Based on the fact that charcoal was the best sorbent for HCN and on the assumption that entrapped oxygen reacted with the HCN, synthetic charcoals were tested: Ambersorbs XE-340, XE-347, XE-348 and Carbopack B coated with 4% carbowax and 0.8% KOH. These sorbents were hand-packed into 8-mm or 6-mm OD glass tubes to a bed length of 30 mm.

Breakthrough data (Table I) show that Ambersorb XE-340 and the coated Carbopack B were poor collectors of HCN. Ambersorb XE-348 showed good collection properties at a sampling rate of 0.171 L/min; however, recovery data (Table I) showed that, as with coconut charcoal, recovery was very poor. Recovery was based on the theoretically calculated mass of HCN sampled by the sorbent.

Silica gel was coated with a solution of one part 0.01 M $Cd(NO_3)_2$ and one part eluent buffer. Twenty microliters of the solution were spiked onto a silica gel tube (ORBO-53) and allowed to dry overnight. Breakthrough for this sampler occurred in 82 minutes at a flow rate of 0.036 L/min. Although the recovery of HCN was good at 89.1%, the presence of residual moisture on the silica gel from the spiking operation may have been a salient factor in the collection of HCN. Further testing would be required to determine the amount of absorbed water necessary to yield reproducible HCN recoveries. Investigation of the cadmium nitrate/eluent coating was not pursued at this point because of a growing awareness of the instability of cyanide whether in the form of working standards, aqueous solutions, particulate salts, or some of the cyanide complexes.

Stability of Cyanide

One of the most significant problems in cyanide monitoring is the instability of the collected cyanide. Although deterioration of working standards had been observed, the enormity of the instability problem impacted fully only when field samples from health hazard evaluations were collected. In much of the literature the stability of cyanides is not addressed (7,8,10), although Standard Methods for Water and Wastewater provides an excellent discussion (9).

In aqueous solution HCN is a very weak acid (at 25°C, $pK_a = 9.21$) (11)

$$HCN \overset{H_2O}{\rightleftharpoons} H^+ + CN^- \qquad pK_a = 9.21$$

At a low pH the predominant species is molecular HCN, which can readily escape from the solution. At pH 11 or greater cyanide is in the ionic form and relatively stable (12). Air samples are usually collected in NaOH solution contained in impingers; however, the CO_2 in the air will also react with the solution thereby lowering the pH and releasing HCN gas. Cyanide compounds also undergo photodecomposition with UV light. Standard Methods for Water and Wastewater states that: 1) oxidizing agents may destroy most of the cyanide during storage and manipulation; 2) because most cyanides are very reactive and unstable, samples should be analyzed immediately; and 3) adding NaOH pellets to raise the pH to 12-12.5 and storing in a closed, dark bottle in a cool place is recommended (9).

Particulate cyanides are known to decompose in moist air with the liberation of HCN. Six mixed cellulose ester filters were spiked with KCN in 0.1 N NaOH at concentrations of 10 and 30 ug CN^- per filter (3 at each level); mean recoveries were 9% and 36% respectively. The decomposition of cyanide in the form of particulates is dependent on relative humidity, particle size, and total surface area exposed (13). Since sample instability appears to be the overriding concern in cyanide sampling, a means of stabilizing the samples was necessary. One means of stabilizing the cyanide is to complex it with a heavy metal.

Metal Cyanide Complexes

Cyanide complexes of the transition metals and those immediately following the transition series are characterized by their remarkable stabilities, often unaffected by acid (14). Hence, the formation of metal cyanide complexes was investigated. The complexes of cadmium and zinc with cyanide [$Cd(CN)_4^{2-}$ and $Zn(CN)_4^{2-}$] completely dissociate under the chromatographic conditions used in the analysis, allowing the cyanide to be measured as free CN^- (7). Complexes of gold, iron, and cobalt [$Au(CN)_2^-$, $Fe(CN)_6^{3-}$, $Co(CN)_6^{3-}$] are undissociated. Thus they cannot be measured as free CN^-, although they may be measured as the complex under different chromatographic conditions (15).

Cadmium was chosen as the metal to complex with HCN because the complex will dissociate allowing measurement as free cyanide and because cadmium is less likely than zinc to be found in conjunction with cyanide in the workplace. HCN was sampled at 0.089 L/min in a bubbler containing 15 mL of 0.01 M $Cd(NO_3)_2$ and a Liquid Media Sampler (LMS) containing 20 mL of the solution (Table II). The LMS showed a gradual breakthrough of approximately 0.25 ppm/minute; when sampling was stopped after 30 minutes the bubbler showed no breakthrough, because of the greater surface contact between gas and liquid in the bubbler. Recovery of CN^- from these samplers was poor at 64% and 69%, respectively, for the LMS and bubbler.

It was assumed from the breakthrough and poor recovery that either the rate of complex formation was too slow or perhaps a higher pH was necessary. Mixtures of an aqueous solution of 0.01 M $Cd(NO_3)_2$ and eluent buffer solution (see Experimental Section) were tested in ratios of 2:1 (6.7 mM $Cd(NO_3)_2$/0.3 mM Na_2CO_3/3.3 mM NaH_2BO_3/5 mM ethylenediamine) and 1:1 (5 mM $Cd(NO_3)_2$ /0.5 mM Na_2CO_3/5 mM NaH_2BO_3/7.5 mM ethylenediamine). Bubblers containing the 1:1 $Cd(NO_3)_2$/eluent absorbent collected HCN at three sampling rates. Flow rates of 0.036 and 0.171 L/min exhibited good collection and recoveries; however, at 0.299 L/min recovery was only 62%. Breakthrough was not the cause of the low recovery because the HCN continuous monitor detected no HCN in the bubbler effluent. The low recovery may have been caused by: 1) the relatively large volume of air sampled (9.6 L) contributing to the instability of the sample, or 2) incomplete formation of the complex since the sample was analyzed on the day of generation (day 0). Table II shows that other $Cd(NO_3)_2$ solutions exhibiting low recoveries were also analyzed on day 0 and also sampled a larger volume of air (4.5 L) than the next lowest at 2.6 L. A sample of HCN collected in a bubbler containing a carbonate/borate buffer (the eluent without ethylenediamine) had a recovery of 80%, poorer than the cadmium complexing solutions.

The complexing of HCN with Cd did not significantly improve the stability of the HCN samples. A formal storage study was not conducted; however, aliquots of bubbler samples stored under refrigeration (ca. 5°C) were diluted and analyzed periodically (Table III). The only provisions made to prevent evaporation from the bubblers was covering the openings with plastic caps of the type used with sorbent tubes.

The recovery data in Table III indicate that the $Cd(CN)_4^{2-}$ complex may not be completely formed on the day of generation. After 1 week of refrigerated (5^oC) storage 99.5% was recovered; however, when stored at ambient temperature (25^oC) only 28% of the CN^- was recovered after 1 week. The high recovery at 5 weeks storage may have been the result of evaporation of the sample matrix. The only stability statement that can be made is that no loss was indicated. Another sample stored for 6 weeks showed a CN^- loss of 56%. Samples stored at ambient temperature whether in eluent buffer solution or complexed with cadmium showed CN^- losses of 70 to 80%.

When $Cd(CN)_4^{2-}$ complex samples are refrigerated and protected from light, they may be stable for up to 5 weeks. When stored at ambient temperatures without any specific protection from light, the samples decompose as much as 10% per day, as was noted with working standards. Complexing of HCN with cadmium was not the answer to the instability problem.

SUMMARY & RECOMMENDATIONS

Although this study has been terminated without a successful sampler for HCN being developed, progress has been made toward the improvement of cyanide monitoring.

- An analytical procedure has been developed for determining free cyanide by ion chromatography with electrochemical (amperometric) detection.
- Sample stability has been identified as the prime area to be addressed in the selection of a sampler for HCN.
- Coconut charcoal collected HCN efficiently, but it could not be recovered.
- The more labile metal-cyanide complexes, e.g. $Cd(CN)_4^{2-}$, are not sufficiently stable to improve the sample monitoring method integrity.

Recommendations for future research are:

1. The investigation of collecting HCN in an iron or cobalt salt solution to form a stable complex with CN^-. Such a solution could be used in a passive monitor and/or coated onto silica gel.
2. The investigation of alternate non-aqueous solvents for desorption of HCN from charcoal. HCN is soluble in all proportions with ethyl alcohol, which in turn is compatible with the ethylenediamine in the eluent. Ethylenediamine may also be tested for desorbing HCN.
3. The investigation of oxidizing agents to convert cyanide to the more stable cyanate and the development of an analytical method for cyanate.

These recommendations are listed according to their likelihood of success. The formation of an iron or cobalt complex should form a stable cyanide system, free of interference from any cyanate compounds which may be present in the work environment. Since it has been demonstrated that coconut charcoal will collect HCN, a solvent may be found to recover the cyanide. However, the stability of HCN on the charcoal would then need to be investigated, and the

stabilty of particulate cyanides would need to be addressed. The conversion of cyanide to cyanate would result in a more stable compound; however, the free cyanide collected would be indistinguishable from any cyanates found in conjunction with it. Any means of stabilizing free cyanide will require derivitization and, consequently, the development of an appropriate analytical procedure.

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TABLE I

BREAKTHROUGH OF 10 ppm HCN ON SOLID SORBENTS

SOREENT	SOURCE	SORBENT WT. (mg) Front/Backup	TUBE SIZE OD (mm)	TUBE SIZE Bed Length (mm)	FLOW RATE (L/min)	5% BREAKTHROUCH TIME	5% BREAKTHROUCH VOL. (L)	RECOVERY* (%)
TEA/Molecular Sieve	SKC 226-40-02	400/200	7	22	0.3	Immediate	0.3	--
Molecular Sieve	SKC 226-12-03	145/72	7	15	0.3	Immediate	0.3	--
XAD-2	SKC 226-30-06	400/20	8	42	0.3	Immediate	0.3	--
Supelpak 20u	Supelco ORBO-43	100/50	8	10	0.3	Immediate	0.3	--
Chromosorb 102	SKC 226-49-22-102	200/100	8	22	0.3	Immediate	0.3	--
Na_2CO_3/Chromosorb P	Army	500/0	8	40	0.3	Immediate	0.3	--
Ag filter	Millipore	--	25-mm dia.		0.3	Immediate	0.3	--
Tenax	SKC 226-35-08	100/50	6	25	0.3	Immediate	0.3	--
Moleculer Sieve 5A	SKC 226-12-05	145/72	7	15	0.3	2 min.	0.6	--
Silica Gel (Acids)	Supelco ORBO-53	400/200	7	27	0.3	2 min.	0.6	--
Petroleum Charcoal	Supelco ORBO-33	700/390	8	55	0.3	3.5 min.	1.0	--
KOH/Charcoal	SKC 226-67	100/50	6	15	0.3	1 min.	0.3	ND
KOH/Charcoal	Charcoal from 3 tubes	450	8	30	0.3	17 min.	5.1	ND
Coconut Charcoal	Supelco ORBO-32	400/200	8	30	0.3	42 min.	12.6	ND
Coconut Charcoal	Supelco ORBO-32	400/200	8	30	0.089	275 min.	24.5	ND
Carbopack B/4% Carbowax/0.8% KOH	Hand packed	--	6	30	0.171	Immediate	0.3	7.5
Ambersorb XE-340	Hand packed	--	8	30	0.171	5 min.	0.8	ND
XE-347	Hand packed	--	8	30	0.171	50 min.	8.5	--
XE-348	Hand packed	583	8	30	0.171	105 min.	18.0	32.2
XE-348	Hand packed	244	6	30	0.171	70 min.	12.0	9.0
$Cd(NO_3)_2$/Eluent coated Silica Gel	20uL Soln on ORBO-53 Tube	400	7	30	0.036	82 min.	3.0	89.1

* Recovery based on theoretical mass of HCN sampled.
ND = less than 0.1% recovered

TABLE II

HCN RECOVERY FROM LIQUID SORBENTS

Sorbent	Vol./Sampler (mL)	Flow Rate (L/min)	Air Vol. (L)	Day Anal.	Recovery[a] (%)
0.01 M $Cd(NO_3)_2$	15/Bubbler	0.089	4.5	0	69
0.01 M $Cd(NO_3)_2$	20/LMS[b]	0.089	4.5	0	64
$Cd(NO_3)_2$/Eluent (2:1)[c]	15/Bubbler	0.036	0.4	1	94
$Cd(NO_3)_2$/Eluent (1:1)[d]	20/Bubbler	0.036	0.4	1	113
$Cd(NO_3)_2$/Eluent (1:1)	15/Bubbler	0.171	2.6	1	91
$Cd(NO_3)_2$/Eluent (1:1)	15/Bubbler	0.299	9.6	0	62
Na_2CO_3/NaH_2BO_3 [e]	15/Bubbler	0.171	2.6	1	80

[a] Based on theoretical mass of HCN sampled
[b] Liquid Media Sampler
[c] 6.7 mM $Cd(NO_3)_2$/0.3 mM Na_2CO_3/3.3 mM NaH_2BO_3/5 mM ethylenediamine
[d] 5 mM $Cd(NO_3)_2$ /0.5 mM Na_2CO_3/5 mM NaH_2BO_3/7.5 mM ethylenediamine
[e] Aqueous solution containing 1 mM Na_2CO_3 and 10 mM NaH_2BO_3

TABLE III

STABILITY OF HCN SAMPLES

Matrix	Day Gen.	Storage Time(wks)	Recovery(%)[a] Ambient	Refrigerated
$Cd(NO_3)_2$/Eluent(1:1)[b]	8/21	0	62%	--
	8/21	1	28%	99.5%
	8/21	5	--	121%
$Cd(NO_3)_2$/Eluent(1:1)[b]	8/13	6	--	44%
Eluent[c]	8/13	1	22%	

[a] Based on theoretical mass of HCN sampled
[b] 5 m$\underline{M}$ $Cd(NO_3)_2$/0.5 m$\underline{M}$ Na_2CO_3/5 m$\underline{M}$ NaH_2BO_3/7.5 m$\underline{M}$ ethylenediamine
[c] 1 m$\underline{M}$ Na_2CO_3/10 m$\underline{M}$ NaH_2BO_3/15 m$\underline{M}$ ethylenediamine

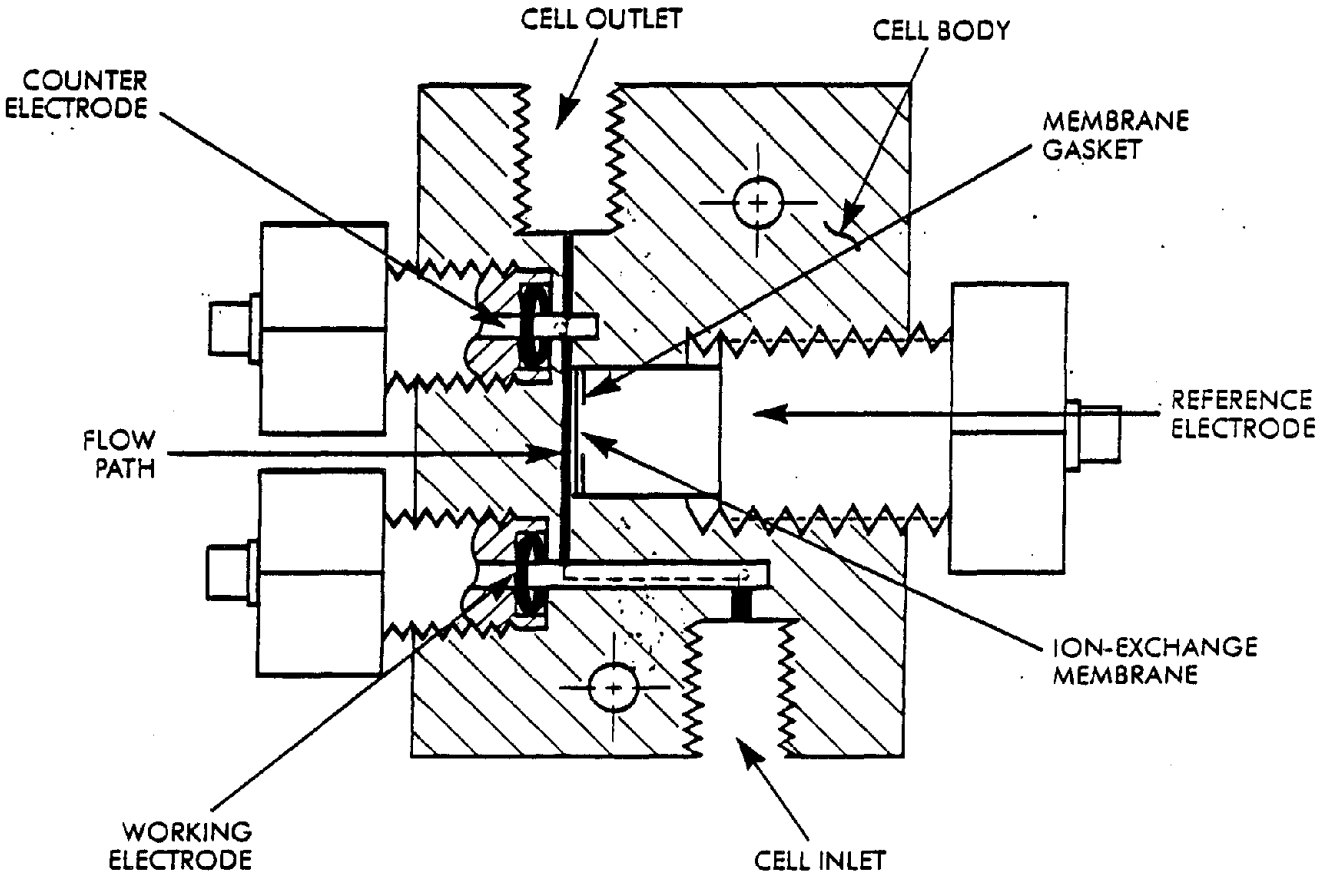

Figure / Assembly of the Electrochemical Cell

FIGURE 1

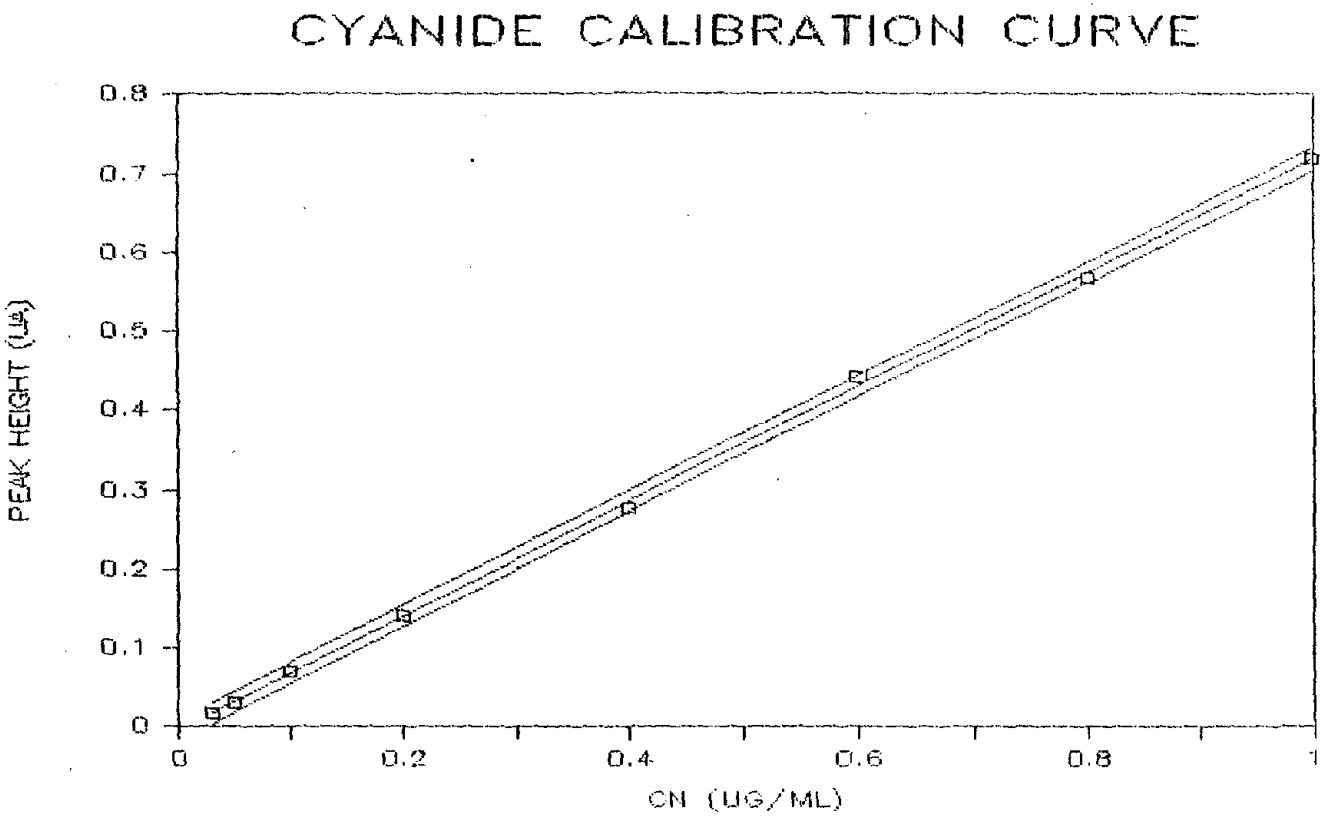
CYANIDE CALIBRATION CURVE
PEAK HEIGHT (UA)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
CN (UG/ML)

FIGURE 2