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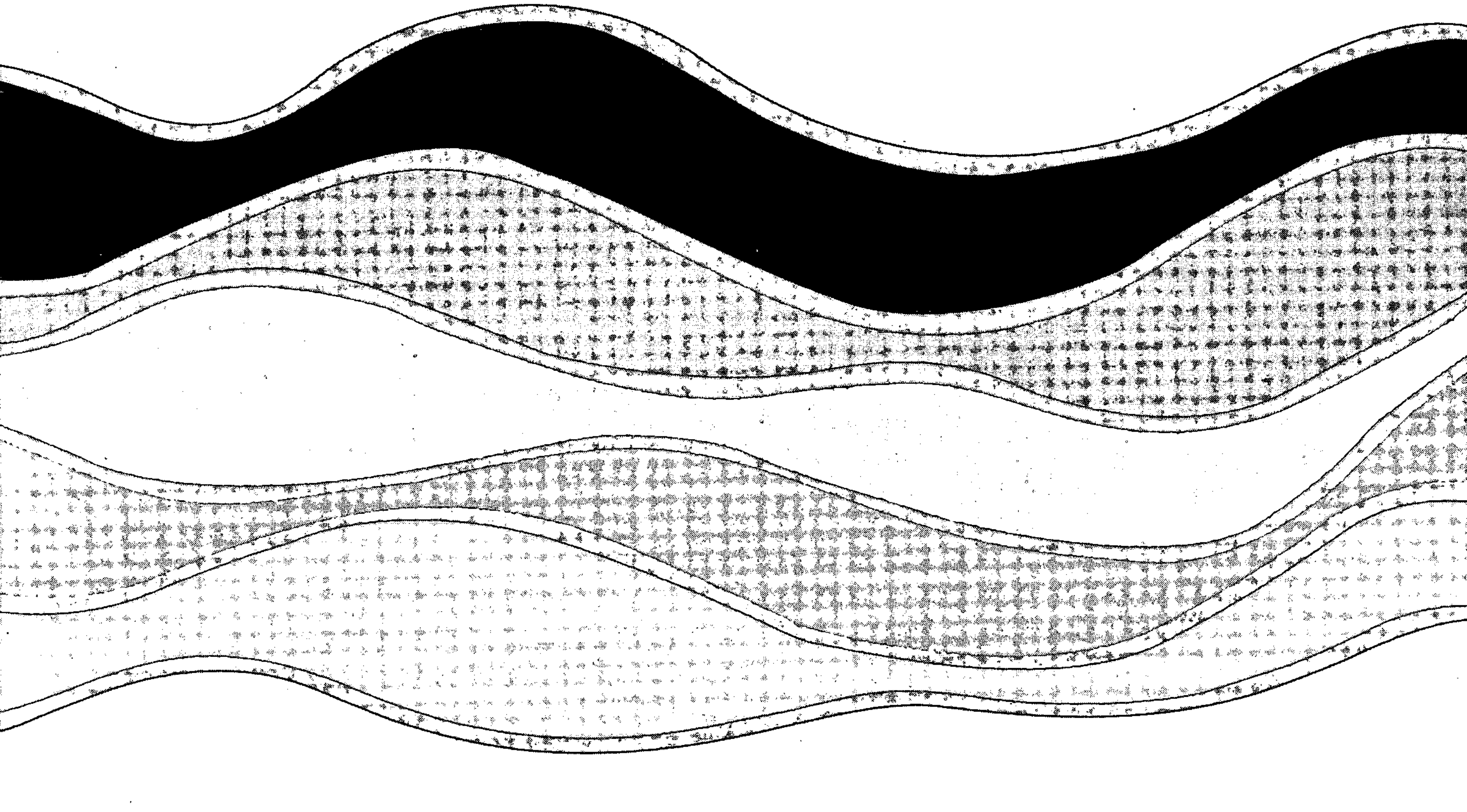

DETERMINATION OF CYANIDE BY CONTINUOUS FLOW ISO-THERMAL DISTILLATION WITH AMPEROMETRIC DETECTION

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NWRI CONTRIBUTION 91-108

MANAGEMENT PERSPECTIVE

Various forms of cyanide compounds are common constituents in a variety of industrial wastes such as quench water from coke plants and blast furnaces, and the rinse water from heat treating and metal finishing operations. In addition, other industries, particularly chemical, pharmaceutical and mining utilize and discharge cyanide compounds. Because of the extreme toxicity of the cyanide ion to aquatic life and to humans, rigorous treatment of wastewater in respect to the content of cyanide is required. This in turn requires the availability of sensitive, selective and efficient analytical methodology for the determination of cyanides in a variety of aquatic environmental samples.

Existing methods for the determination of cyanides have been a subject of debate and dissatisfaction among analytical and environmental scientists for long time.

The developed method based on iso-thermal distillation in a continuous flow system is rapid, selective and interference free. It is suitable for the automated determination of various forms of cyanide. The method is capable of analyzing large number of samples on routine basis. The variable sensitivity of the method ranges from mg/L down to ng/L concentration levels.

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PERSPECTIVE-GESTION

Différentes formes de composés cyanurés sont des constituants courants de divers déchets industriels comme l'eau de trempe provenant des cokeries et des hauts fourneaux, et l'eau de rinçage provenant du traitement thermique et de l'apprêtage. De plus, d'autres industries, en particulier les industries chimiques, pharmaceutiques et minières utilisent et déversent des composés cyanurés. En raison de la forte toxicité de l'ion cyanure pour les organismes aquatiques et l'homme, il est nécessaire de faire subir un traitement rigoureux aux eaux résiduaires pour en éliminer le cyanure. Ce traitement exige par la suite le recours à des méthodes d'analyse sensibles, sélectives et efficaces pour doser les cyanures dans divers échantillons prélevés dans le milieu aquatique.

Les méthodes existantes de dosage des cyanures ont été longtemps l'objet de débats et de mécontentement de la part de scientifiques spécialistes des mesures analytiques et de l'environnement.

La méthode fondée sur la distillation isothermique dans un système à débit continu est rapide, sélective et exempte d'interférences. Elle convient bien au dosage automatique de différentes formes de cyanure. La méthode permet d'analyser un grand nombre d'échantillons de façon systématique. La sensibilité de la méthode permet de déceler des teneurs comprises entre 1 mg/l et 1 ng/l.

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ABSTRACT

In this report a rapid, sensitive, selective and automated method for the determination of cyanide is described. The principle of the method is a continous flow, carrier-sample alternating system. It utilizes the iso-thermal distillation of HCN gas as the separation and preconcentration step. The quantitation of various forms of cyanide is derived from the amperometric response of the silver electrode. The distinction between "free", "weak" and "total cyanides" is made by the determination of the signals at pH 6 followed by the measurement at pH 1 and finally the response of the detector is recorded after the in-line irradiation of the sample with ultraviolet light. The sensitivity of the method is regulated by varying the flow rate of the sample and by adjusting the duration of the accumulation step. Analysis at the ug/L concentration levels requires 10 to 60 s of accumulation time, whereas the determinations at ng/L range is accomplished by using 100 to 600 s of collection time. Relative standard deviation of 2 to 10 % and recoveries of 95 to 100 % were obtained. The method is practically free of interference. Only high concentration of thiocyanate in the sample increases the response by a factor 1:10 in the case of the determination of "total cyanide". A large number of actual samples were successfully analyzed. The technique has been in operation in our laboratory for over two years.

RÉSUMÉ

L'auteur du présent rapport décrit une méthode rapide, sensible, sélective et automatisée de dosage du cyanure. Le principe de la méthode est un système à débit continu d'alternance du véhicule et de l'échantillon. Elle utilise la distillation thermique du HCN comme étape de séparation et de préconcentration. La quantité des différentes formes de cyanure est dérivée de la réaction ampérométrique à l'électrode d'argent. La distinction entre "libre", "à lien faible" et "cyanure total" est établie par la détermination des signaux à pH 6, suivie par la mesure à pH 1, et finalement, la réponse du détecteur est enregistrée après l'irradiation, en cours de traitement, de l'échantillon à la lumière ultraviolette. La sensibilité de la méthode est réglée en faisant varier le débit de l'échantillon et en ajustant la durée d'accumulation. L'analyse pour des teneurs exprimées en μg/L nécessite un temps d'accumulation de 10 à 60 s, tandis que pour le dosage dans la plage des ng/L, il faut de 100 à 600 s. Un écart-type relatif de 2 à 10 % et des récupérations de 95 à 100 % ont été obtenus. La méthode est pratiquement exempte d'interférences. Seule une concentration élevée de thiocyanate dans l'échantillon augmente la réponse d'un facteur de 1:10 dans le cas de la détermination du "cyanure total". Un grand nombre d'échantillons réels ont été analysés avec succès. La technique est utilisée dans notre laboratoire depuis plus de deux ans.

INTRODUCTION

Numerous chemical and physico-chemical methods for the determination of cyanides in various matrices and at various concentration ranges can be found in the literature. The methods have been a subject of debate and dissatisfaction among analytical and environmental scientists for many years. The complexing properties of the cyanide ion, useful in other applications, make the quantitative measurement and species definition difficult. Well recognized and accepted extreme toxicity of cyanide compounds leads to the requirement of sensitive, selective, accurate, precise and reliable methodology for the determination of cyanides in environmental samples. The details of spectro-photometric and electrochemical methods are given elsewhere (1,2).

With the variety of methods available and the lack of concensus among analysts regarding the most reliable and efficient method, we felt it was worthwhile to examine the application of the iso-thermal distillation technique (3) as the separation and preconcentration step. Its incorporation into a continous flow system containing the interference removing treatment and combined with an amperometric quantitation (4,5) resulted in the development of the method described in this report.

The various cyanide species are grouped within commonly accepted classification (1). The first group contains the species that exist under given environmental conditions as the molecular undissociated acid (HCN) or as the cyanide ion (CN-). The second group consists of relatively "weak" metal-cyanide complexes (Cd, Zn). The "strong" metal cyanide complexes (Fe, Cu, Ni, Ag, Hg, Co) are included in the third category. In the final class - "total cyanide" - is the sum of all various forms. Due to the dependence of the stability and dissociation constants on the pH of the sample, there do not exist definite boundaries among these categories. From the practical point of view, the "free" or "simple" cyanides are those existing at pH 6 and higher. The cyanides released from the complexes at pH 1 are in the "weak" category. The cyanides accessible for the determination in acidified solution after the decomposition of the "strong" complexes by ultraviolet light irradiation are classified as "total" cyanides.

The objective of this study was to develop an interference free, sensitive and automated analytical system for the determination of "free", "weak complex" and "total" cyanides in water samples. The reliability, efficiency and economy of the method were other goals of the study.

EXPERIMENTAL

All chemicals used were of reagent grade quality. Concentrated cyanide and sulfide stock solutions were prepared using deoxygenated, distilled-deionized water and were stored in dark bottles under nitrogen atmosphere. The stock solutions were standardized by the argentometric titrations with potentiometric control. Working solutions were prepared by dilution under anaerobic conditions. Stock solutions of ferri-, ferro-, cobalti-, cobalto-, silver-, zinc-, cadmium-, copper-, mercury- and nickel-cyanides were prepared from their potassium salts and held at pH 12 by the addition of potassium hydroxide. All were stored under light and heat protected conditions.

The acidification solution was 1.0 M sulfuric acid with 1% of hypo-phosphoric acid acting as an oxygen scavenger preventing the oxidation of cyanide during UV irradiation (6). For the determination of "free" cyanides, the pH of the sample was adjusted to the value of 6.0 with an orthophosphate buffer containing 1% of EDTA. To eliminate the interfering effect of sulfide all cyanide releasing solutions were made 0.001 M with respect to Bi (7).

Actual samples were preserved by making them 0.05 M in potassium hydroxide and were stored in dark.

Instrumentation

Figure 1 outlines the block scheme of the instrumental assembly. The Dionex test tube autosampler, Watson-Marlow multichannel peristaltic pump, two Valco four port switching pneumatically operated valves were the basic components of the continous-flow system. The use of properly designed switching valves and their integration into the analytical system is very important. Chemical and physical inertness toward the components of the sample, reagents and chemical processes are the prerequisites for all materials used in the system. Valves with zero volumes fittings, excellent outport and crossport leak tightness and with uniform flowpath are also necessary.

The modules of the sample treatment part of the assembly were an Alpkem UV irradiator, a Haake constant temperature bath and a home made iso-thermal distillation cell (Fig. 2). The cell was furbished with W.L. Gore Inc. teflon membrane of 0.2 um porosity.

The measurement section of the apparatus comprised a BAS LC4B amperometric detector with a home-made three electrode flow-through cell. The spiral silver wire was the working electrode. The Ag/AgCl and platinum wire were the reference and auxiliary electrodes respectively. The cell is illustrated in Figure 3. The signal of the detector (uA) was registered at the constant potential of -0.3 V. For recording the signals a Philips PM825A strip chart recorder and Spectra Physics Minigrator were used.

All connections of the flow system were made with teflon tubing and connectors. For the section after the point of sample acidification, the PharMed tubing which has a very low gas permeability was used. The scheme of the continuous flow arrangement is given in Figure 4. The operation of all components of the assembly was controlled by the programmable Xanadu timer-sequencer.

Industrial waste water samples of various origins were obtained by the courtesy of the National Water Quality Laboratory. The results using a "Standard Method" were generated by NWQL also.

Procedure

For establishing the detector's baseline, the first three tubes of the autosampler are filled with distilled water. The next four tubes contain a set of standard cyanide solutions. The detector response of these standards is used to constitute the calibration curve. Samples with strategically located blanks and standards are placed in the sampler. During the operation of the system the samples, blanks and standards are mixed with the cyanide releasing buffer or acid solutions. In the case of the total cyanide determination, the flow-through UV irradiator is turned on. The stream then flows through the coil inserted in the constant temperature bath into the gas diffusion cell and then to the waste. During the passage through the cell, the hydrogen cyanide gas penetrates the hydrophobic membrane and by the reaction with the stagnant accumulating solution, is converted into the CN- ionic form. After the preselected period of time, the segment of the collecting solution containing the accumulated cyanide ions is introduced to the amperometric detector cell and then flows to the waste. The changes of the detector signal are recorded in the form of uA vs. time peaks and are converted to the concentration of the cyanide in the sample on the basis of calibration curves. During this measurement cycle, the system is automatically rinsed with distilled water and a new sample is introduced. This principle of operation is different from segmented flow or flow-injection techniques. It can be described as a continous, carrier-sample alternating flow system. The process of optimizing the performance of the method by tuning the sample flow rate with the timing of the accumulating and measuring cycles will be described later.

RESULTS AND DISCUSSION

Iso-thermal distillation

Iso-thermal distillation (gas diffusion) of an analyte in the gaseous form from a sample solution (donor) into a reagent solution (acceptor) where the gas dissolves and reacts with suitable reagent for subsequent determination is a well established technique. The driving force of the iso-thermal distillation process is the concentration gradient (from the chemical point of view) or the difference in partial pressures (from the physical point of view) on two sides of the membrane. Because the concentration of HCN gas is kept at zero level on the alkaline side of the membrane due to its conversion to the ionic form, the process of diffusion can not reach the equilibrium. This process has been used as static or segmented flow reflux distillation (7) as well as in the continuous flow technique for the determination of ammonia, amines, carbon dioxide, sulphur dioxide, cyanide and chlorine (8). In the case of the continous flow system the donor and acceptor streams, flowing in parallel, are separated by a hydrophobic porous membrane (9,10). This system is well-suited for samples containing mg/L and higher concentrations of the analyte. For this study, the requested limit of detection was 0.1 ug/L. To achieve this sensitivity a stop and go system has been adapted. In this system the stream of the acceptor solution is kept stagnant for a preselected period of time. During this time the sample (donor) solution is passing through the cell. By proper timing of the stop and go action, the concentration of the accumulated species of interest in the stagnant segment of the accepting solution can be regulated. This allows tuning of the system according to the sensitivity of the detector and required detection limit. During the accumulation cycle, the acceptor stream bypasses the diffusion cell maintaining a constant flow through the detector cell. This arrangement is necessary in order to produce a steady baseline and to improve the signal to noise ratio.

Application of in-line accumulation (preconcentration) allows the detection limit to become a variable and manageable parameter. A longer accumulation time produces higher peaks and increases the sensitivity of the method, whereas a shorter accumulation time is suitable for samples with higher content of cyanide. In a similar manner, the flow-rate of the sample solution influences the concentration of cyanide in the stagnant segment of the accumulating solution. A higher flow-rate increases the sensitivity whereas a slower flow rate decreases the sensitivity of the system. By proper manipulation of timing and flow-rate, the operator has the choice of balancing the needs of sensitivity and time efficiency with to respect to the number of samples and expected levels of cyanide. The theoretical aspects of the iso-thermal distillation are described in Appendix 1.

Amperometric detection

After preliminary tests of the suitability of various detection systems, the amperometric detector using a silver metal working electrode has been selected. It compares favorably with the spectrophotometric and potentio-metric methods of detection and quantitation. It is sensitive down to 10 M, simple and inexpensive. No reagents are involved and the time response is very fast. The reproducibility is less than 5% of RSD and it is easy to automate.

The tests of the three electrode system in 0.1M NaOH supporting electrolyte at a potential of -0.3 V vs. a silver-silver chloride reference electrode and using a platinum auxiliary electrode indicated very good performance with well developed anodic current signals. The current concentration function was linear over four orders of magnitude from 1.0 ug/L to 10 mg/L. To optimize the performance of the detector, several designs of different geometry were tested. The most well-suited results, in terms of signal magnitude, peak contour, time response, baseline stability, signal to noise ratio and reproducibility, were obtained with the three electrode flow through cell depicted in Figure 3.

The reaction mechanism of the system can be described by three basic reactions:

1. Conversion of cyanide species into the gaseous form:

$CN^- + H^+ = HCN\ (g)$ at $pH < 7.2$ [1]

2. Accumulation and conversion into the ionic form:

$HCN (g) = CN^- + H^+$ at pH > 11.2 [2]

3. Amperometrically controlled reaction:

$2 CN^- + Ag = Ag(CN)_2^- + e^-$ at - 0.3 V [3]

Performance optimization

In order to establish the effect of the sample flow rate on the accumulation of cyanide in the collecting solution, the signals (peak hights in cm) generated by six different cyanide concentration during seven different sample flow rates were registered. The constant collection time of 60 s was used. The results summarized in Figure 5, indicate that the 10 mL/min flow rate is optimal for the measurements in the concentration range of 1.0 to 100.0 ug/L. The determination at low concentration level (0.01 ug/L) can be accomplished with 50 mL/min flow rate. For the analysis at 0.1 to 10 mg/L the flow rate of 2 mL/min is optimal. The data in Fig. 6 illustrate the signals obtained with constant sample flow rate of 10 mL/min using eight different collection times. Seven concentrations of cyanide ranging from 0.01 ug/L to 10 mg/L were tested. Collection times of 500 and 600 s are suitable for determination down to the 0.01 ug/L level. High concentrations (> 0.1 mg/L) can be measured using 20 to 60 s collection times.

The selection of flow rate and timing depends on the particular situation. The determining factors are the expected concentration of cyanides, available size of the sample and number of samples to be analyzed. Other factors influencing the performance characteristics of the system are the geometry and dimensions of the diffusion and amperometric cells and the porosity of the teflon membrane.

Performance parameters

Using the apparatus and procedure as described, the reproducibility and recovery of "free", "weak", "strong" and "total" cyanides were studied. A number of standard solutions and natural waters "spiked" with cyanide were analyzed using this iso-thermal distillation process. Typical results are shown in Table 1. They show that essentially 100% recoveries down to levels as low as 0.1 ug/L can be obtained. They also indicate that the differentiation can be made between various forms of cyanides.

Four samples containing 0.1, 1.0, 10.0 and 100.0 ug/L cyanide respectively on 12 replicate determinations gave the relative standard deviation of 2.5%.

The detection limit (the concentration which gives a signal twice that of the background noise) using 60 s collection time and 30 mL/min sample flow rate is 0.01 ug/L.

Efficiency of UV irradiation

Cyanide co-ordinate to many metals. Some of these co-ordinate bonds are so strong that they do not break even during acid reflux distillation procedures. Photodecomposition by ultraviolet light offers several advantages over traditional strong acid distillation methods. It is more efficient, safe and simple, reduces analysis time, improves accuracy and precision and is easily adaptable for automation. The inconsistencies reported in the literature concerning the effectiveness of various photodecomposition systems are likely a result of the differing experimental parameters and conditions used for these studies (11). In general, the effectiveness of the UV irradiation depends on the wavelength, power and duration of the irradiation, geometry of the irradiator and the chemical composition of the irradiated solution.

Using given experimental arrangement and conditions, the effectiveness of UV irradiation to decompose complex cyanides of iron, cobalt, mercury, nickel, copper, and silver was tested. From the results of these tests summarized in Figure 7, it can be concluded that the decomposition of most of the complex cyanides is essentially completed during 60 s of residential time in the irradiation coil. The exceptions are the cyanides of cobalt and mercury. Their decomposition is very slow and only reaches values of 60-85 % even after 120 s of the irradiation.

Interferences

From the ions conceivably existing in natural waters and industrial effluents only sulfide and thiocyanate interfere with this method. A positive interference of sulfide ion is eliminated by the addition of bismuth to the cyanide releasing solutions. Thiocyanate ion interferes only with the deter-mination of "strong" cyanide because it is apparently broken down in the UV irradiation step to yield cyanide and sulfide ions (7). Because the break-down process is slow and because the sulfide ion is removed by the reaction with bismuth, the effect of the thiocyanate interference was found to be approximately 10 SCN- : 1 CN- on the molar equivalent basis.

Actual samples analysis

A number of actual samples of various origin were analyzed using the above method and by the method recommended by EPA (1). Some of these samples were also analyzed after "spiking" with known amount of cyanide. The results are shown in Table 2. They show that the developed method will measure a wide range of cyanide concentration in all types of waters. It is capable of measuring cyanides at levels not detectable by the standard method.

CONCLUSIONS

The method reported makes it possible to determine various forms of cyanides in environmentally significant water samples. The use of the in-line isothermal distillation as the preconcentration and separation step in combination with the amperometric detection results in a very versatile method. This automated method is virtually interference free, selective and sensitive. It is capable of measuring cyanide in concentrations ranging from 0.01 ug/L to mg/L levels. It cannot determine completely the cyanide from the cobalt and mercury complexes (cca 60 % recovery). High concentration of thiocyanate interferes in the ratio of 10:1 with the determination of cyanides from strong complexes.

This report was presented at the II. Int. Conf., Kinetics in Analytical Chemistry, Dubrovnik, Yugoslavia, 1989.

The authors wish to thank National Water Quality Laboratory for supplying the samples and gratefully acknowledge the assistance during the course of the work.

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TABLE 1

% Recovery of Cyanide

Sample	ug/L CN added			ug/L CN found			
	Free	Weak	Strong	Free	Weak	Strong	%
Dist. Water	0.01			0.007			70
	0.1			0.11			110
	1.0			1.1			110
	10.0			9.9			99
	100.0			103.0			103
		0.01			0.012		120
		0.10			0.11		110
		1.0			1.0		100
		10.0			9.8		98
		100.0			97.5		98
			0.01			0.004	40
			0.10			0.08	80
			1.0			0.95	95
			10.0			9.8	98
			100.0			97.0	97
	0.1	0.1	0.1	0.09	0.12	0.08	97
	1.0	1.0	1.0	1.1	1.0	0.9	100
	10.0	10.0	10.0	10.2	10.1	9.9	101
	100.0	100.0	100.0	100.0	99.0	96.0	98
Tap Water	0.1	0.1	0.1	0.08	0.10	0.07	83
	1.0	1.0	1.0	1.0	1.1	1.2	110
	10.0	10.0	10.0	9.7	9.9	9.7	98
	100.0	100.0	100.0	99.0	102.0	101.0	101
Lake Ontario Water	0.1	0.1	0.1	0.13	0.12	0.11	120
	1.0	1.0	1.0	1.1	1.2	1.3	120
	10.0	10.0	10.0	10.3	10.0	10.4	102
	100.0	100.0	100.0	100.2	100.7	102.0	101
Niagara River Water	0.1	0.1	0.1	0.11	0.09	0.08	93
	1.0	1.0	1.0	1.1	1.3	0.8	107
	10.0	10.0	10.0	10.2	10.2	9.8	101
	100.0	100.0	100.0	103.0	98.9	97.5	100

Free CN ---- Potassium
Weak CN ---- Zinc and Cadmium
Strong CN ---- Iron [II], Iron [III], Copper [II], Silver [I]
Nickel [II]

TABLE 2

Analysis of Actual Samples
Cyanide in ug/L

Water		This Method			Standard Method	
Sample	Free	Weak	Strong	Total	Free	Total
Industrial						
1	10.2	2.1	3.5	15.8	5.3	10.1
2	127.0	52.0	34.9	213.9	170.0	196.3
3	78.9	27.3	88.0	194.2	101.1	167.8
4	467.7	123.4	142.5	733.6	549.0	729.7
5	342.2	76.2	78.8	497.2	427.0	488.8
Effluent						
1	121.4	58.9	42.2	222.5	165.3	205.5
2	87.6	24.7	34.1	146.4	108.7	135.9
3	247.0	69.2	44.7	360.9	311.3	345.7
4	35.2	44.5	37.8	117.5	64.7	91.5
Polluted						
1	21.3	8.7	4.2	34.2	19.0	27.9
2	5.5	2.3	2.0	9.8	3.2	5.1
3	1.6	0.9	2.1	4.6	n.d.	2.5
4	0.6	1.0	0.5	2.1	n.d.	n.d.
5	0.2	0.2	0.4	0.8	n.d.	n.d.
6	n.d.	0.1	0.2	0.3	n.d.	n.d.
Treated Waste						
1	1.2	1.4	0.8	3.4	n.d.	n.d.
2	4.4	3.9	1.5	9.8	n.d.	5.0
3	7.8	11.5	4.1	23.4	n.d.	11.0
4	0.3	0.8	0.9	2.0	n.d.	n.d.
5	n.d.	0.1	0.2	0.3	n.d.	n.d.
6	0.1	n.d.	0.1	0.2	n.d.	n.d.

Figure 1
INSTRUMENTATION SCHEME

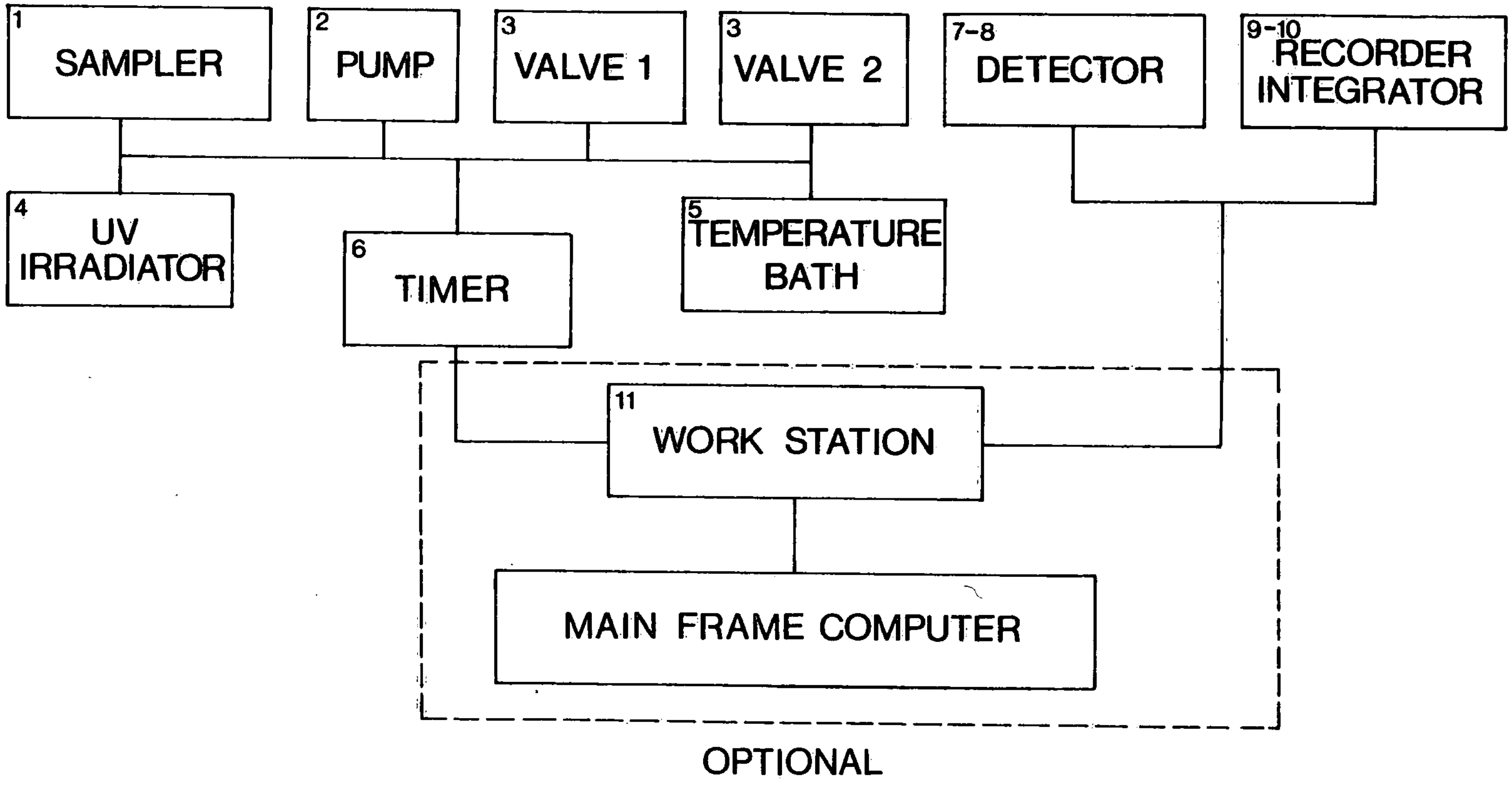


Figure 2
ISO-THERMAL DISTILLATION CELL

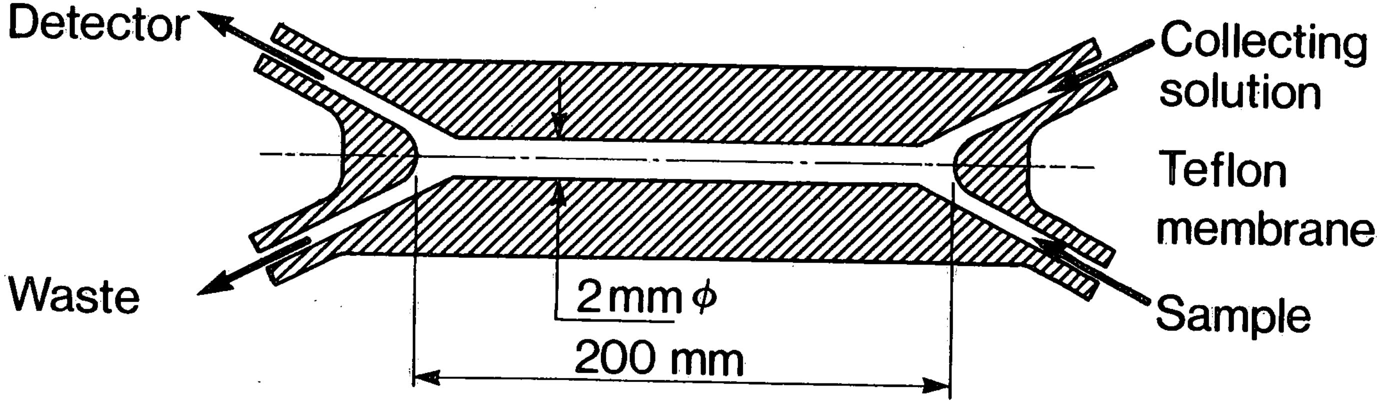


Figure 3
AMPEROMETRIC CELL

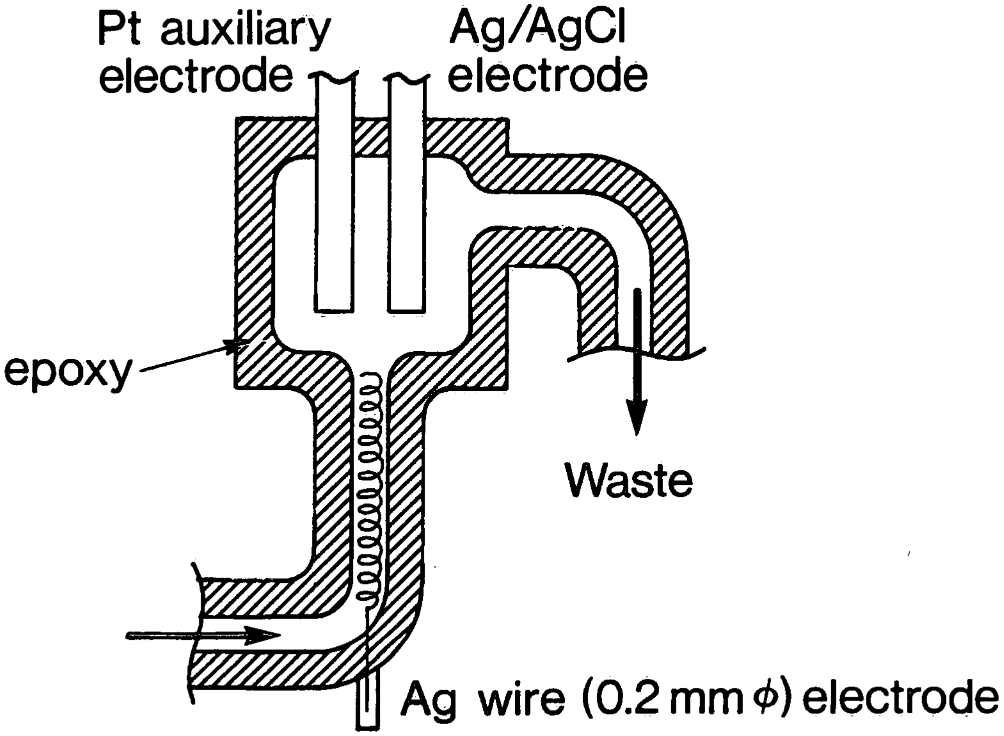


Figure 4
CONTINUOUS-FLOW SCHEME

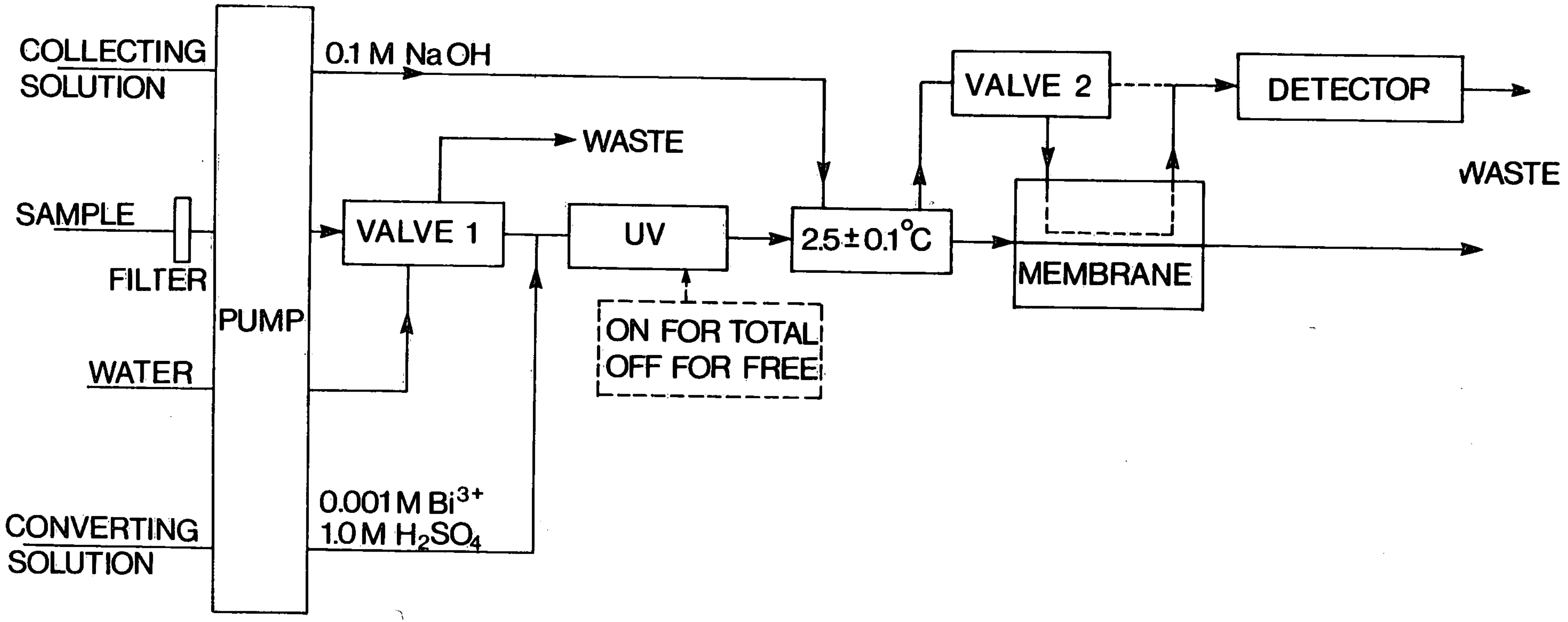
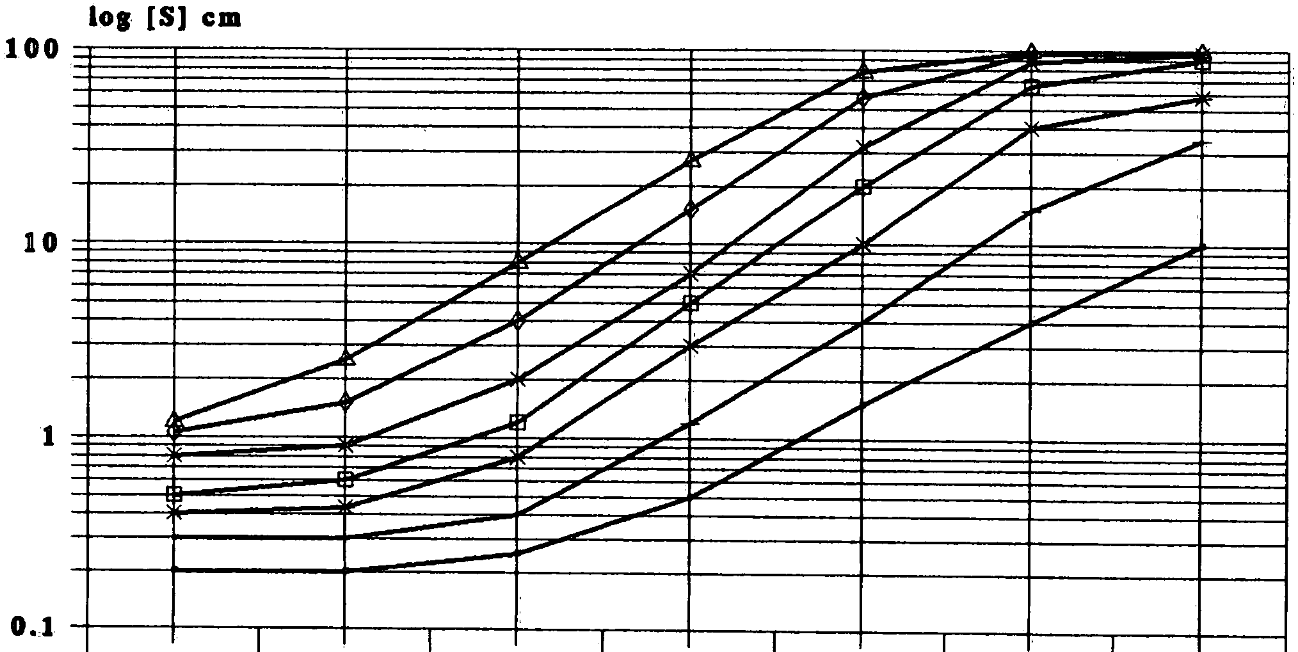


Figure 5

Signal vs Conc. vs Flow-Rate



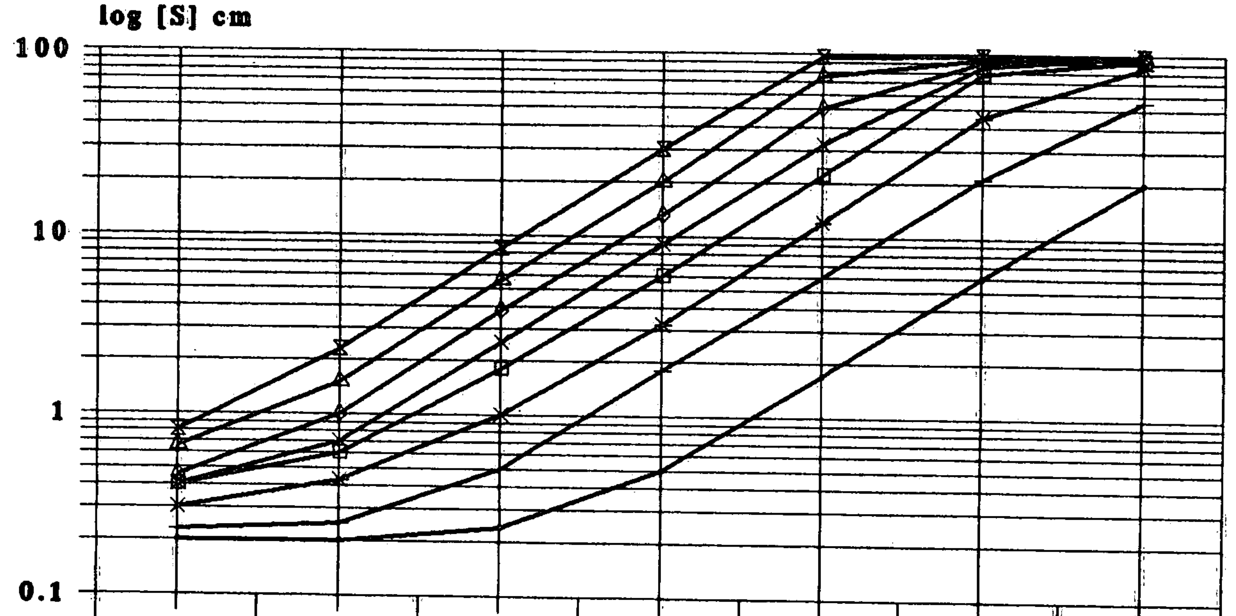
	0.01	0.1	1	10	100	1000	10000
50 mL/min △	1.2	2.5	8	27	78	99	99
40 mL/min ◇	1.05	1.5	4	15	57	96	98
30 mL/min ×	0.8	0.9	2	7	32	87	97
20 mL/min □	0.5	0.6	1.2	5	20	66	90
10 mL/min ✳	0.4	0.43	0.8	3	10	40	58
5 mL/min +	0.3	0.3	0.4	1.2	4	15	35
2 mL/min —	0.2	0.2	0.25	0.5	1.5	4	10

log [C] µg/L

Collection Time 60 s

Figure 6

Signal vs. Conc. vs. Collection Time



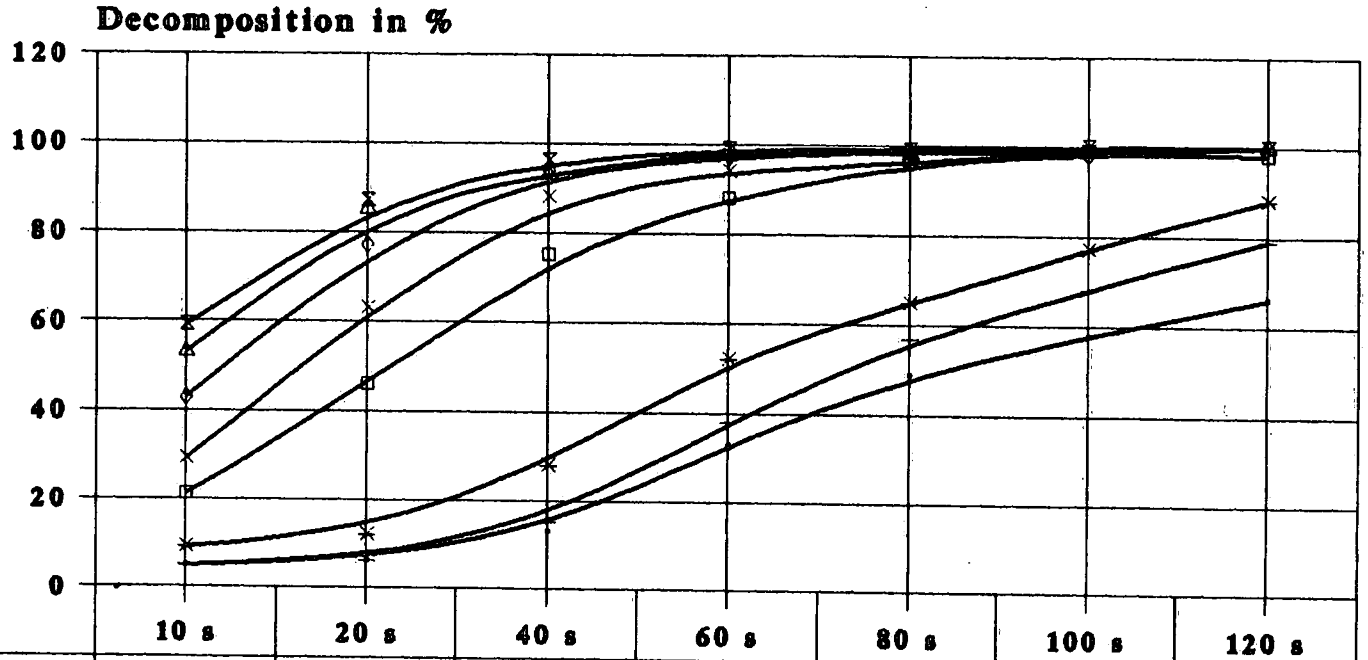
		0.01	0.1	1	10	100	1000	10000
600 s	⧖	0.8	2.3	8.4	30	97	98	99
500 s	△	0.65	1.5	5.6	20	75	94	98
400 s	◇	0.45	1	3.8	13	50	90	97
300 s	×	0.4	0.7	2.5	9	32	85	99
200 s	□	0.4	0.6	1.8	6	22	78	94
100 s	✳	0.3	0.43	1	3.2	12	45	85
50 s	+	0.23	0.25	0.5	1.8	6	21	55
20 s	—	0.2	0.2	0.24	0.5	1.7	6	20

log [C] µg/L

Flow rate 10 mL/min.

Figure 7

Decomposition of Complex Cyanide by UV



	10 s	20 s	40 s	60 s	80 s	100 s	120 s
Hg[II]	5	6	13	33	49	58	66
Co[III]	5	6	15	38	57	68	79
Co[II]	9	12	28	52	65	77	88
Fe[III]	21	46	75	88	96	99	98
Fe[II]	29	63	88	94	96	99	100
Cu[II]	43	77	94	97	99	98	100
Ni[II]	53	85	93	99	98	99	100
Ag[I]	59	87	96	99	99	100	100

Time in s

APPENDIX 1

Gas Transfer During the Iso-Thermal Distillation

To develop a model of a mathematical expression for gas compartments of the gas-diffusion cell, the diffusive flux (J) of the component of interest is the basic factor. It can be derived from Fick's law leading to the equation where A is the contact area

$$J = k\,D\,(A / L)\,dc \qquad [1]$$

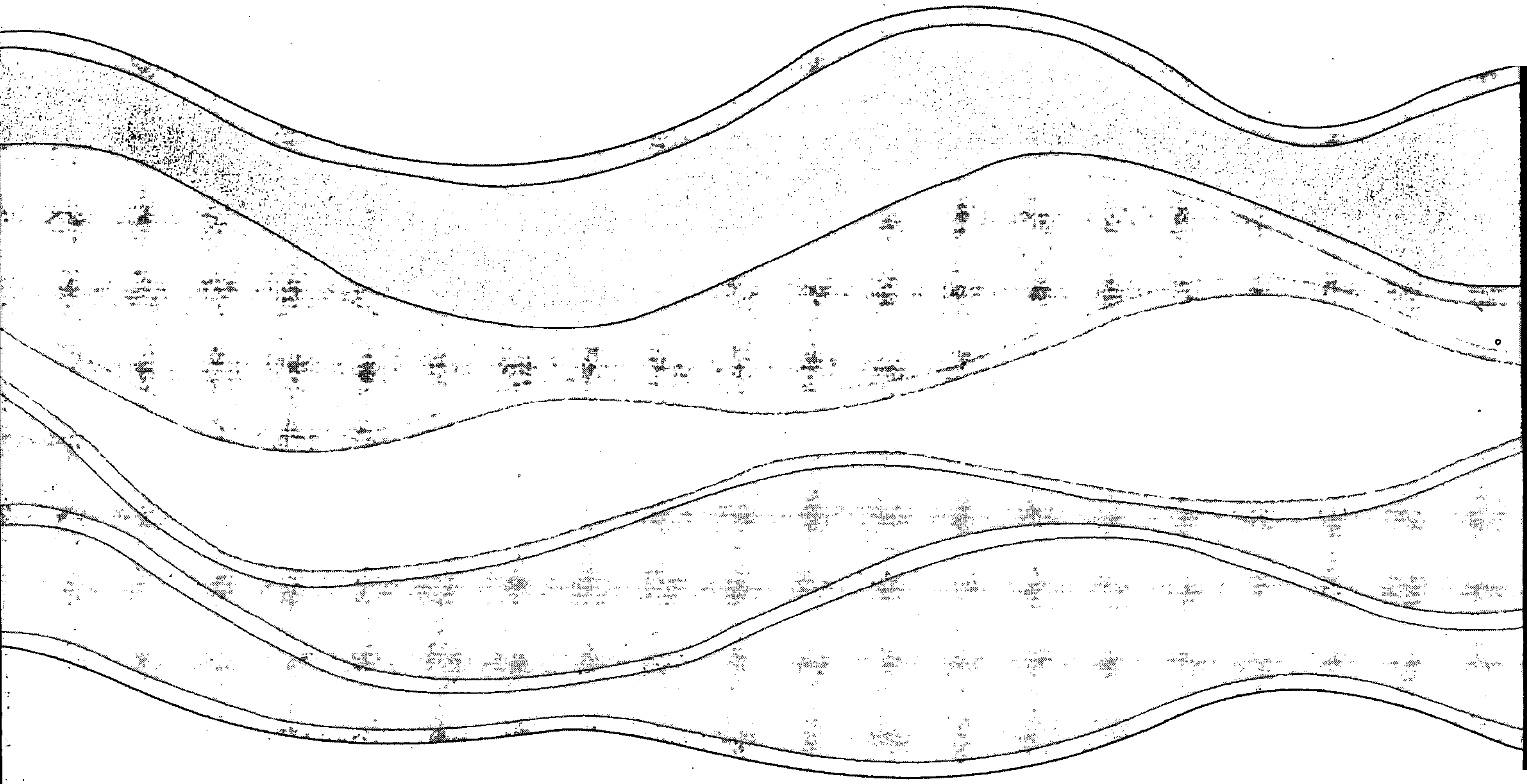
between donor and acceptor solutions, L the membrane thickness, D the diffusion coefficient of HCN in air, dc the concentration gradient and k a lump constant including gas transport in the aqueous phase.

A closer examination of the real meaning of k shows that the experimental parameters as well as physicochemical properties of the gas and the membrane influence its magnitude. The diffusion coefficient in the aqueous phase, for instance, is temperature dependent and the porosity of the membrane is not consistent. The volatility of the gas depends on its solubility and partial pressure which in turn are influenced by temperature, pressure and ionic strength. Small k values indicate that the transfer rate will be limited by the rate of the transport of the analyte to the liquid/gas boundary and the gas volatility. Accordingly, for high k values, the gas transfer may become rate-limited. In most practical cases, the gas diffusing through the membrane is taken up as the ionic species, e. g. CN- from HCN diffusion, so that the concentration of gaseous compound in the accepting solution can be regarded as zero. Hence, the diffusive flux for any experimental set-up (i.e. cell design and experimental conditions) depends solely on the concentration of gaseous compound in the donor solution. Because of the gas diffusion process, however, this concentration decreases during sample transport through the cell. The main parameter governing the degree of decrease is the mean residence time of analyte molecules in the donor channel of the gas diffusion unit. The mass transfer (m) across the membrane is given by the equation $m = J\,t$ where t is the sample residence time in the donor channel. Qualitatively two extremes can be considered, depending on the intended application.

At high donor flow rates, which are equivalent to a short molecular residence time, the overall diffusive flux is high but the HCN transfer efficiency (i.e. the decrease of HCN in the donor line) is low. This situation is favorable if sample volumes are not limited as in continous flow measurements. Here, the mass transfer increases linearly with the sample aspiration time. In situations where sample volumes are commonly small (Flow-Injection systems), sufficiently low flow rates of the donor stream are appropriate and should guarantee high transfer efficiency. This is particularly true of low level determinations, because in this case the absolute masses are correspondingly small. Low donor flow rates, however, cause reduced sampling rates. Considering equation [1], for any desired transfer efficiency, higher flow rates are possible if larger contact areas are used. With regard to mass transfer, a compromise has to be found between donor flow rate, sample volume and sampling frequency.

So far, only the parameters affecting gas transfer have been discussed; detection, however, takes place in the acceptor line. Obviously, the concentration of the trapped compound depends on the mass transfer and the recipient volume, i.e. the part of the acceptor solution passing the cell or residing in the cell during diffusive gas transport across the membrane. Again continous flow and flow injection conditions will be distinguished. If the sample is continuously supplied, a similarly continous and constant diffusive flux leads to a constant concentration of analyte in the acceptor solution. This concentration in the recipient (cR) is given by cR = J / vA, where vA is the acceptor flow rate. Because J increases with increasing donor flow rate for a given diffusion unit, maximum analyte concentration can be obtained at high vD / vA ratio. In other words, the stagnant donor solution (zero flow rate) assures highest analyte concentration in the segment of the collecting solution.

Under flow injection conditions, the situation becomes more complicated. First, the above mentioned consideration about the influence of the donor flow rate on the diffusive flux and mass transport have to be obtained in practice. Secondly, it has to be born in mind that the sample injected undergoes dispersion before entering the diffusion cell. Hence, the diffusive flux can not be assumed constant for any period of time. A peak shaped concentration profile occurs in the recipient stream, the area and height of which depend on the mass transfer and acceptor flow rate, respectively. Because peak height is commonly used in FIA, low acceptor flow rates are appropriate. The limitation in choosing slow flow rates is the sampling rate required.



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