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Enhanced conductometric detection of cyanide in suppressed ion chromatography

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Abstract

Weak-acid anions such as borate and cyanide, present problems in chemically suppressed ion chromatography, since the acids are weakly ionised, giving low conductivity and therefore decreased sensitivity. For borate this problem was overcome by converting the weak acid to its sodium salt, by the use of a second anion micromembrane suppressor (AMMS) as an ion exchange reactor (IER), flushed by EDTA reagent, to supply sodium ions for the conversion. This paper will discuss the use of this IER system to determine cyanide, which is also a very weak acid, with a similar pK_a to borate. The detection limit for cyanide of 50 μM compare favourably with indirect conductivity detection. © 2000 Published by Elsevier Science B.V.

Keywords: Conductivity detection; Detection, LC; Cyanide; Inorganic anions

1. Introduction

The most common method for determining anion concentrations in solution, is via ion chromatography (IC), usually with suppressed conductivity [1]. Chemical suppression works well for strong acid anions whose conjugate acids give a high conductivity and thus high detector response. Those of weak acids however, are only weakly ionised, and so give a low detector response. The ion exchange reactor (IER) system used in this work [2,3], is a novel approach which uses a second commercially available micromembrane suppressor (AMMS), in series after the first suppressor (used for chemical suppression in the usual way), to supply cations to the weak acids. For borate the optimum reagent used to flush the IER was found to be 20 m*M* EDTA at pH 9 [4] which supplies sodium ions, thus converting the weak acids to their sodium salt, increasing their conductivity and hence their sensitivity. For a solution of 5.0 m*M* boric acid, the sodium salt produced 250- and 1400- fold increases in peak height and area, respectively [2,3], when compared to normal suppressed IC.

Cyanide is also a very weak acid ($pK_a = 9.22$) [5], with a pK_a similar to borate ($pK_a = 9.24$) [5], and so might be expected to show similar increases in conductometric detection to those observed with borate. Cyanide is often indirectly determined as cyanate, after the oxidation of cyanide with sodium hypochlorite [6,7]. Direct conductometric analysis of cyanide is not possible under chemically suppressed IC conditions, since the corresponding acid, HCN, is not ionised at neutral pH [8].

The IER system used in this work makes it possible to analyse cyanide via conductivity in

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solution directly, with a simple NaOH eluent, without oxidation to cyanate. This paper will discuss the optimisation and problems associated in the conductometric determination of cyanide using the IER system.

2. Experimental

2.1. Ion chromatography analysis

2.1.1. Chemicals

Reagent-grade water was obtained from a Milli-Q system (Millipore Corp.). All chemicals were BDH analytical-reagent grade, unless otherwise specified and all glassware was A grade.

2.1.2. Equipment

A Dionex 4500i ion chromatograph, a Dionex GP40 programmable gradient pump, a Dionex IonPac AG11, 4 mm (P/N 4478) guard column in series with a Dionex IonPac AS11, 4 mm (P/N 44076), followed by two Dionex Anion MicroMembrane Suppressors (AMMS-II, P/N 043074) placed in series just before the conductivity detector. The detector was operated with a default factor of 1.7 for the auto temperature compensation mode. Delta chromatography computer software (Version 5.0) was used to acquire peak heights and peak areas. Regenerant solution and IER reagent were forced through the micromembrane suppressors, under 5 p.s.i. pressure (1.2 ml/min; 1 p.s.i.=6894.76 Pa). A Metrohm 650 pH meter (calibrated over the pH range of 4–7, using Activon capsule buffers), a Pt 100 temperature probe, and a combined glass/silver, silver chloride electrode were utilised to measure the pH of solutions.

2.1.3. Solution preparation

All standard solutions, eluents, regenerants and reagents were prepared with Milli-Q water, degassed under vacuum and filtered through 0.2 μm membrane filters (PTFE), prior to use. Eluent was sodium hydroxide (5 m*M*). The first suppressor was regenerated by sulphuric acid (50 m*M*). The second suppressor was flushed with EDTA solution, 20 m*M*, adjusted to pH 9 by the addition of sodium hydroxide solution. An eluent flow-rate of 1.0 ml/min was used, unless otherwise stated. The second suppressor was flushed with Milli-Q water after the use of the EDTA reagent to avoid crystallisation and damage to the suppressor membrane.

2.1.4. Standard preparation

Stock solutions of sodium cyanide were 1 to 10 m*M*. Solutions of sodium cyanide (10–1000 μ*M*) were prepared by dilution of the stocks with Milli-Q water or 5 m*M* NaOH. Solutions were injected into the IC via a 20 μl injection loop. Three replicate injections of each sample were made and the results averaged.

2.2. Colorimetric analysis

The cyanide was determined by the pyridine–barbituric acid standard method, 4500-CN E [9]. The eluent and regenerant samples were adjusted to a final matrix alkalinity equal to 0.04 *M* NaOH prior to the colorimetric analysis.

3. Results and discussion

3.1. Cyanide lost across the AMMS membrane

Initially experiments involved the analysis of cyanide standards (10 to 1000 μ*M*) using the IER system, with 20 m*M* EDTA flushing the second suppressor. Preliminary results obtained were not consistent with the increases in sensitivity that were observed with borate. Several parameters were tested such as degassing of the Milli-Q diluent and flushing of the injector system, with nitric acid, in the autosampler to pacify the metal surface, to prevent oxidation of the cyanide, but no difference was seen in the responses from cyanide. The unexpected results obtained with cyanide led us to postulate that the cyanide was being lost somewhere in the IC system, either by loss of cyanide as gaseous HCN or oxidation of the cyanide in the IC tubing or connections. These hypotheses are consistent with findings made by Okada and Dasgupta [10,11], who utilised a helical, filament-filled perfluorosulfonate membrane suppressor, and found that transmembrane loss can be significant for highly volatile acids such

as HCN. However there was no quantitative data shown indicating the extents of cyanide loss, hence studies to determine the amount of cyanide lost in this system were required.

Studies were undertaken to determine the amount of cyanide lost across the AMMS membrane. The IC was set-up with the pump delivering 5 m*M* NaOH, containing either 0, 0.25, 0.50, 0.75 and 1.0 m*M* NaCN at two flow-rates; 0.2 and 1.0 ml/min, respectively. Initially the NaCN–NaOH eluent flowed directly into one AMMS, being regenerated by 50 m*M* sulphuric acid. The output from the eluent and regenerant streams were collected, in basic solution, and along with the original NaCN–NaOH eluent were analysed via a spectrophotometric method involving the reaction of cyanide with chloramine-T to form CNCl [9]. After this initial reaction is complete the addition of a pyridine–barbituric acid reagent, forms a red–blue dye, and the absorbance is read at 578 nm [9]. Cyanide standards prepared in either the eluent matrix or in the regenerant matrix, were also analysed in the same way.

The results shown in Table 1, are expressed as a percentage of the concentration of cyanide in the original NaCN–NaOH eluent. The percentage of cyanide not recoverd in either stream is also shown. The results at 1.0 ml/min, show an increase in the proportion of cyanide leaking into the regenerant stream (from the eluent stream), as the concentration of cyanide was increased from 0.25 to 1.0 m*M* corresponding to 5.4 to 9.0% CN found in the regenerant stream. The opposite trend was seen with the proportion of cyanide lost, which decreased from 16.0 to 1.3% CN. For the eluent results the percentage in the eluent stream increased from 78.6% at 0.25 m*M* to 89.7% at 0.50 m*M* and then tapered off at this level. In comparison, the results at 0.2 ml/min, show a similar trend for the percentage of cyanide found in the regenerant stream. Also the amount found in the regenerant streams at both flow-rates was approximately equal (Table 1), indicating that the flow-rate of the eluent does not greatly influence the amount of cyanide leaking across the membrane into the regenerant stream. Furthermore an interesting observation was made when the percentage and amounts lost in the IC system, were compared. It was observed that the percentage of lost cyanide decreased as concentration increased, for both flow-rates, but the amounts at 0.2 ml/min increased from 0.081 to 0.256 m*M*, while at 1.0 ml/min the amount lost decreased, from 0.041 to 0.013 m*M* cyanide. Hence at 0.2 ml/min there was a significant increase in the loss of cyanide from the eluent stream, for example the 0.75 m*M* NaCN eluent, approximately 34.4% (0.501 m*M*) compared to 11.6% (0.675 m*M*) at 1.0 ml/min. This indicates that a higher percentage of cyanide is being lost in

Table 1
Comparisons of the amounts and percentages of recovered and lost cyanide calculated, in the eluent and regenerant streams, across one suppressor (being regenerated by sulphuric acid) from eluents containing various concentrations of NaCN in 5 m*M* NaOH, at 1.0 and 0.2 ml/min flow-rates, respectively

[NaCN] (m*M*)	Eluent (m*M*)	SD[a]	Eluent stream (m*M*)	SD[a]	Regenerant stream (m*M*)	SD[a]	Cyanide lost (m*M*)	Eluent stream (%)	Regenerant stream (%)	Cyanide lost (%)
	1.0 ml/min									
0.25	0.257	1.6	0.202	34	0.014	1.3	0.041	78.6	5.4	16.0
0.50	0.493	7.9	0.442	11	0.023	2.3	0.028	89.7	4.7	5.6
0.75	0.764	7.8	0.675	11	0.069	1.8	0.020	88.4	9.0	2.6
1.00	0.999	15	0.896	0.8	0.090	0.5	0.013	89.7	9.0	1.3
	0.2 ml/min									
0.25	0.257	1.6	0.158	10	0.018	0.2	0.081	61.5	7.0	31.5
0.50	0.493	7.9	0.317	4.4	0.039	3.3	0.137	64.3	7.9	27.8
0.75	0.764	7.8	0.501	1.6	0.062	4.6	0.201	65.6	8.1	26.3
1.00	0.999	15	0.664	0.6	0.079	1.2	0.256	66.5	7.9	25.6

[a] SD values expressed in the form $\times 10^{-3}$.

the system, as either gaseous HCN (since there is longer time for the HCN to diffuse through the membrane, and/or the cyanide has longer contact time with the suppressor at the lower flow-rate, thus a higher conversion to HCN), or absorption of the cyanide with the connections or tubing in the IC system. To test the latter, the tubing was cut to approximately half its length (i.e. 15 cm), to minimise both the path length of the streams and the contact of the cyanide with the tubing. A 1.0 m*M* NaCN–NaOH eluent was run again at both flow-rates, with the shorter tubing. The results obtained were similar to the percentages calculated previously with the longer tubing, hence the length of tubing used appears not to affect retention or loss of cyanide in this system.

Even though the previous set of results show a considerable amount of cyanide being lost through the IC system, it does not mimic exactly what occurs in a real analysis. In the previous set of experiments the cyanide was run as an eluent, on a continuous basis and the output analysed. Studies on injections of cyanide into the IC system were then undertaken. Both 1 m*M* and 10 m*M* solutions of NaCN, prepared in 5 m*M* NaOH, were injected (via a nominal 20 μl injection loop) under the following IC conditions and the output collected and analysed spectrophotometrically, as before:

Set 1, 5 m*M* NaOH eluent and no column or suppressors;

Set 2, 5 m*M* NaOH eluent, anion column and no suppressors;

Set 3, 5 m*M* NaOH eluent, anion column and suppressor 1 (regenerated by sulphuric acid);

Set 4, 5 m*M* NaOH eluent, anion column, suppressor 1 (regenerated by sulphuric acid) and suppressor 2 (flushed by EDTA reagent).

The data in Table 2, are expressed as a percentage of the concentration of cyanide calculated from Set 1, i.e. an injection of cyanide going straight through the system, with no column or suppressors. There seems to be some loss (3.2–4.5%), of cyanide when it passes through the analytical column (Set 2), most likely through adsorption onto the column and/or oxidation to cyanate. Another interesting observation was the fact that the percentages of lost cyanide from the 1 m*M* cyanide injections (4.5–25%) were almost double those lost from the 10 m*M* injections (3.2–6.4%), but the actual amounts lost were similar at both concentrations, in fact the amount lost in the IC system from the 10 m*M* cyanide injections were slightly higher. Also at both concentrations the amount (Table 2) of cyanide crossing the first membrane (being regenerated by sulphuric acid) is almost twice the amount crossing the second membrane (being flushed by EDTA). Overall approximately 3–5% was lost in the column, 5–10% lost through suppressor 1 and 2–6% through suppressor 2. The observed losses of cyanide through the suppressors are indicative only. The losses will

Table 2
Recoveries of 20 μl injections of 1 m*M* and 10 m*M* NaCN under the four IC conditions described in Section 3.1 paragraph 4

Set	[NaCN] (m*M*)									Cyanide (%)			
	NaCN Injection	SD[a]	Column Stream	SD[a]	Reagent 1 Stream	SD[a]	Reagent 2 Stream	SD[a]	Cyanide Lost	Column Stream	Reagent 1 Stream	Reagent 2 Stream	Cyanide Lost
1 m*M* NaCN													
1	0.0044	0.3											
2			0.0042	0.6					0.0002	95.5			4.5
3			0.0037	0.1	0.0002	0.6			0.0005	84.1	4.5		11.4
4			0.0030	1.0	0.0002	0.1	0.0001	0.2	0.0011	68.2	4.5	2.3	25.0
10 m*M* NaCN													
1	0.0218	0.6											
2			0.0211	1.3					0.0007	96.8			3.2
3			0.0186	0.7	0.0021	0.7			0.0011	85.3	9.6		5.1
4			0.0172	0.1	0.0020	0.3	0.0012	0.1	0.0014	78.9	9.2	5.5	6.4

[a] SD values expressed in the form $\times 10^{-3}$.

depend upon physical factors such as the membrane thickness, area and porosity, which can vary between suppressors and with time. Losses are also dependant on residence time of analyte in the suppressor, as we have observed by changing eluent flow-rate. These results show a significant loss of cyanide in the IC system, but not so much that the cyanide cannot be determined.

3.2. IER determination of cyanide

Cyanide standards (10–1000 μ*M*), were analysed under the IER system and under the normal suppressed IC system. The calibration curve obtained for the height data and similarly for the area data of the cyanide standards were very linear (50–1000 μ*M*, r^2>99%). The lowest concentration of cyanide detected was 50 μ*M*, using the IER system. Fig. 1 shows the peaks, at approximately 3.07 min, obtained for 50, 250 and 500 μ*M* cyanide standards as their conjugate salts. For the normal IC system, no peaks were observed for cyanide for all concentrations 10 to 1000 μ*M* highlighting the difference between the cyanide being detected as its conjugate salt or as its conjugate acid. The two small peaks, with retention times at 1.86 and 2.54 min, indicate impurities of fluoride and chloride, respectively. Overall results for the IER system show a significant increase in the detection of cyanide as its conjugate salt.

4. Conclusions

The determination of cyanide using the IER system, proved to be very advantageous, not only is it a simple system to set up, it also gives a significant increase in sensitivity of at least 250-fold. Using the IER system it was possible to detect cyanide at the 50 μ*M*, and it may be feasible to detect cyanide

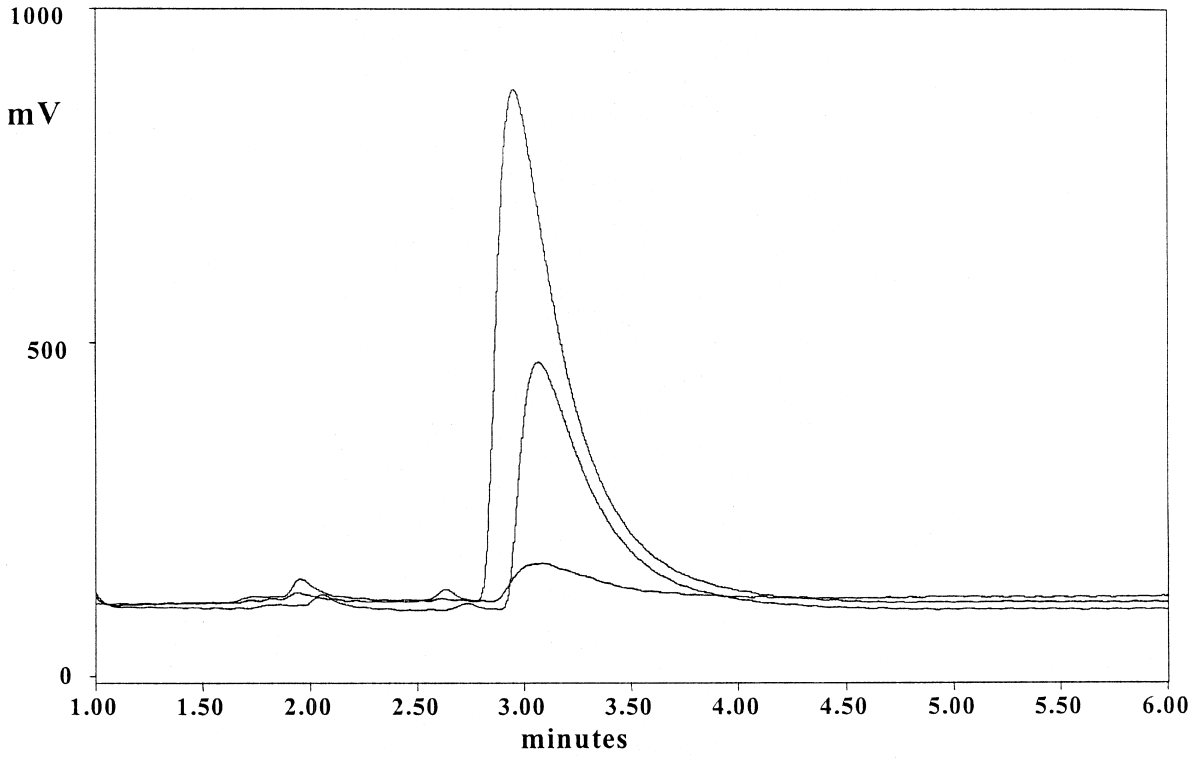

Fig. 1. Chromatograms of cyanide peaks, 50, 250 and 500 μ*M*, prepared in 5 m*M* NaOH and analysed using the IER system, at 1 μS output range. Peaks at 1.86 and 2.54 min indicate impurities of fluoride and chloride, respectively.

down to approximately 25 μ*M*. However care will be needed during calibration to take account of significant but manageable losses of HCN during the analysis.

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