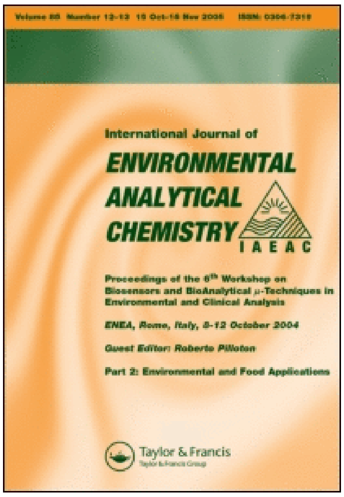

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Direct Determination of Cyanide in Seawater

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A rapid and precise method is presented for the direct determination of cyanide in otherwise unpolluted seawater using a cyanide ion-selective electrode. Although chloride interferes significantly at low cyanide levels its effect can be almost completely eliminated by appropriate selectivity corrections allowing determination of cyanide to less than 20 μg/l. The cyanide electrode can also be used for continuous monitoring at levels of interest in toxicological research.

KEY WORDS: Cyanide, seawater, ion-selective electrode analysis, toxicology.

INTRODUCTION

Because of its widespread industrial use[1] and its potent toxicity to both marine and freshwater animals (concentrations as low as 200 μg/l are fatal to many species of fish)[2] cyanide has attracted considerable interest in environmental and toxicological studies.[2–4] Adequate methods exist for the determination of cyanide in fresh and waste waters[1] and in biological material[5] but little work has been reported on its determination in seawater.[1] Although some of the existing methods could (at least in principle) be adapted to seawater analysis they are often time consuming or insufficiently sensitive, or involve the loss of sample integrity.[6] As marine waters are the ultimate sink for most cyanide waste there is a general need

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for a fast, sensitive, and simple method for determining cyanide in seawater.

The methods which appear to be most satisfactory for the determination of low levels of cyanide are spectrophotometric[7] and electrochemical.[8] Among the latter group probably the most popular is the cyanide ion-selective electrode (ISE). This electrode is easy to operate, relatively free from interferences, reasonably accurate and sensitive, and also offers the possibility of continuous *in situ* monitoring. This last feature is of special relevance to toxicity testing of marine species. This is because at the pH of natural seawater most cyanide will be present as undissociated HCN. Not only is HCN volatile under normal test conditions (especially for "static" tests)[9] but it is also thought to be the most toxic form of cyanide.[2] Thus in order to avoid serious errors in the dose-response curve, cyanide losses should always be measured.

This paper reports an investigation of the use of a cyanide ISE for the direct determination and continuous monitoring of cyanide in otherwise unpolluted seawater at levels of environmental and toxicological interest.

EXPERIMENTAL

Analytical grade reagents were used throughout. Water was distilled and deionized (Millipore "Milli-Q" system). Artificial seawater was a 3.5% w/v NaCl solution. Natural seawater was a surface sample collected from a pristine environment 5 km offshore in Bass Strait, Victoria. A stock solution of 500 mg/l cyanide was prepared by dissolving 0.9418 g of NaCN in one litre of 0.1 M NaOH. Potential measurements were made in plastic beakers stirred magnetically on a thermally isolated stirrer in a constant temperature room at 20 ± 1°C. 5 M NaOH was added to each sample to give a pH of 13.0 to ensure all the cyanide would be present as free CN^- (the species detected by the electrode) and to act as an ionic strength buffer. For the interference studies all cations were added as chlorides except for lead nitrate. The potential of the ISE (HNU, model 30-13-00) was measured against a saturated calomel reference electrode with a quartz fibre liquid junction (Beckman model 39069) to ±0.1 mV using an Orion model 811 digital voltmeter.

RESULTS AND DISCUSSION

1. Response of the cyanide ISE in $NaNO_3$, NaCl and seawater

The potential, E of a cyanide ISE is given by[10]

$$E = E' + \frac{RT}{Z_{CN^-}F} \ln \left[a_{CN^-} + \sum_{i=2}^{n} \left(k_{CN^-,i}^{Pot} (a_i)^{Z_{CN^-}/Z_i} \right) \right] \tag{1}$$

where E' is a constant which includes the standard electrode potentials of the ISE and reference electrode and the liquid junction potential, $k_{CN^-,i}^{Pot}$ is the potentiometric selectivity coefficient CN^- over interferent ion i, and the other symbols have their usual meanings.[10]

Equation (1) shows that the extent of interference of the species i is governed by the product of the selectivity coefficient and the interferent activity. The major interferents for the cyanide ISE include some heavy metal ions, sulphide, iodide and chloride.[10] However, in the absence of gross pollution the levels of all of these species in well oxygenated seawater will (with the exception of chloride) usually be too low to provide significant errors.[11,12]

Although the ability of the cyanide ISE to discriminate against the chloride ion is good[10,13] (the selectivity coefficient for Cl^- over CN^- is $\sim 10^{-5}$), the high concentration of Cl^- in sewater ($\sim$0.5 M) presents a problem for the determination of CN^- at low (<1 mg/l) levels. Considering Cl^- as the only interferent, Eq. (1) reduces to

$$E = E' - \frac{RT}{F} \ln (a_{CN^-} + k_{CN^-,Cl^-}^{Pot} a_{Cl^-}) \tag{2}$$

Figure 1 shows the response of the cyanide ISE in 0.7 M $NaNO_3$, 3.5% w/v NaCl and surface seawater and clearly demonstrates the deleterious effect of chloride ions on the Nernstian response of the electrode. In the presence of typical seawater chloride concentrations the limit of detection for cyanide is raised from $\sim$20 to $\sim$200 μg/l.

2. Allowance for chloride interference

In order to achieve satisfactory detection limits in chloride

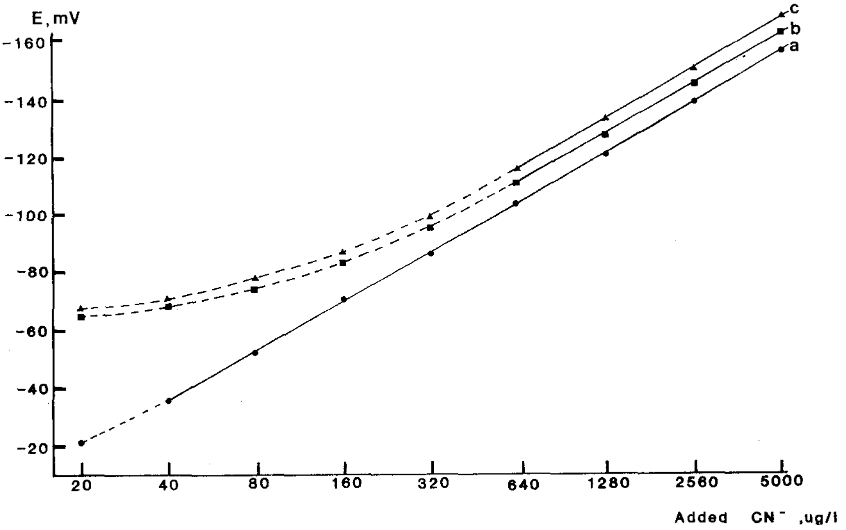

FIGURE 1 Calibration curves for cyanide in: (a) 0.7 M $NaNO_3$, (b) 3.5% w/v NaCl and (c) seawater.

matrices it is clearly necessary to correct for the interference to the electrode response. In principle this can be done via Eq. (2) providing the appropriate values of the potentiometric selectivity coefficient and the chloride activity are known. The former was measured for the present electrode by two independent methods (ref. 10, p. 32, method IID, and ref. 12) to be $(9.8 \pm 0.2) \times 10^{-6}$ in good agreement with the manufacturer's stated approximate value of 1×10^{-5}. The chloride activity ($a_{Cl^-} = \gamma_{Cl^-}[Cl^-]$) was calculated using concentration and activity coefficient data from standard sources.[14] Thus, for example, in natural seawater, assuming $\gamma_{Cl^-} = 0.66$ and $[Cl^-] = 0.536$ M,[14] Eq. (2) reduces to

$$E = E' - \frac{RT}{F} \ln(a_{CN^-} + 123) \qquad (3)$$

where a_{CN^-} is in μg/l. That is, for the present electrode, the chloride interference in natural seawater corresponds to an effective "blank" of 123 μg/l of cyanide. Calibration in a chloride matrix therefore involves plotting E *vs* the log of the *effective* cyanide activity (i.e. true

+“blank”) in that matrix. Since the measurements are performed at (relatively high) constant ionic strength γ_{CN^-} will be effectively constant and concentration can replace activity in Eq. (3) with little loss of accuracy.

After making this correction, the calibration curves obtained in artificial and natural seawater have slopes almost identical to those obtained in non-chloride containing solutions, remaining Nernstian down to approximately 20 μg/l (Fig. 2a, b). Although this limit is probably too high for surveillance of relatively unpolluted seawaters it is quite low enough for toxicological studies of cyanide, being far below the reported minimum lethal concentrations found for most species of fish[1] and well within the levels of interest for sub-lethal work.[4]

It is important to note that although the electrode has essentially the same Nernstian range in artificial and natural seawater, calibration curves should always be prepared in the particular

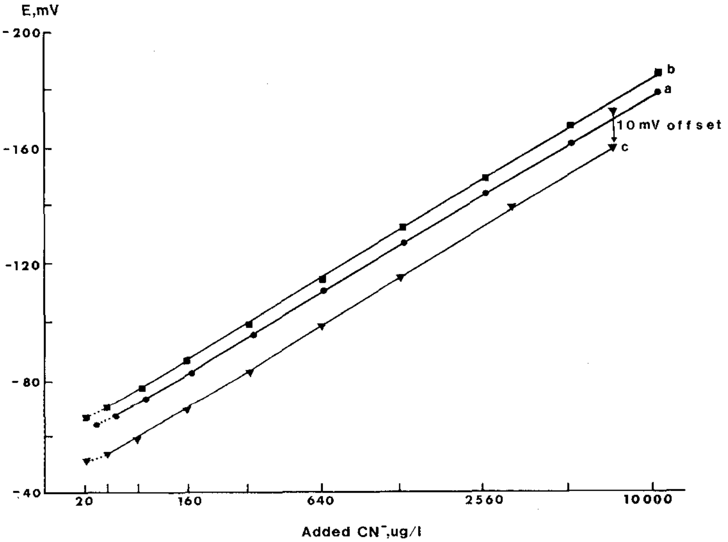

FIGURE 2 Calibration curves corrected for chloride interference, for cyanide in (a) 3.5% w/v NaCl, pH 13.0; (b) natural seawater, pH 13.0; (c) natural seawater, pH 11.5, (potential offset by 10 mV for clarity).

medium of interest, since there are slight differences between seawater and NaCl curves (~6 mV in Figure 2) presumably as a result of minor liquid junction, membrane and activity differences.

3. Effect of pH

It has been reported by Sekerka and Lechner[13] that hydroxide interferes with the cyanide ISE in freshwater and wastewater analyses, raising the lower level of linear response from ~26 μg/l at pH 11.5 to ~2600 μg/l at pH 13. It was therefore thought necessary to see if the limit of detection in seawater (Figure 2b) could be improved by lowering the pH. Curves b and c in Figure 2 show that no effect was apparent in seawater solutions, with essentially identical response being obtained at pH 11.5 and 13.0. It should also be noted that the calibration curve obtained in $NaNO_3$ (Figure 1a) is fully Nerstian down to ~20 μg/l at pH 13 in direct contradiction to Sekerka and Lechner's findings. The reasons for this discrepancy are unclear at present. However, it should be noted that Sekerka and Lechner studied the effect of pH using iodide solutions (I^- was assumed to be a 1:1 interferent) to avoid complications due to protonation of CN^-; and there may be some fundamental difference in the response of the cyanide ISE to CN^- and I^-. Alternatively, differences in buffer solutions[15] or in manufacture may influence electrode response. At any rate the findings of Sekerka and Lechner do not appear applicable to the present work.

4. Other interferences

Other documented interferents for the cyanide ISE include copper and a number of other ions forming sparingly soluble sulphides.[10, 13] As these interferences may be strongly modified under the present conditions of high pH and $[Cl^-]$ because of complexation and/or precipitation a brief study was undertaken. Concentrations of 1 mg/l of Fe(III), Zn(II), Cr(VI), Mn(II), Cu(II), Pb(II), Cd(II), Ni(II) and VO_4^{3-} were added to separate solutions of 1 mg/l CN^-. Only nickel (53%) and copper (55%) interfered by more than 4% (≃1 mV) at this level.

Comparison of the present direct method with a standard reference method[6] involving distillation gave results agreeing to within ±5% for 150 μg/l of cyanide added to a saline refinery effluent containing a variety of pollutants. On the other hand the direct method is not suitable when cyanide is very strongly complexed. Thus, for ferrocyanide, ferricyanide and nitroprusside, at concentrations equivalent to 200 μg CN^-/l, the direct method responded to the extent of 14%, 5% and 77% respectively of the distillation values.

5. Precision and detection limits

Precision was estimated by six determinations of a natural seawater sample spiked with cyanide, using both standard addition and calibration curve techniques. Standard additions have the advantage of minimizing matrix effects and also may be more accurate at low concentrations,[16] but are slower than calibration curve techniques when large numbers of samples are involved.

Using a calibration curve, precision was ±2% at 150 μg/l of added CN^- (well within the Nernstian region), decreasing to ±14% at the lower limit of Nernstian response (20 μg/l). Computer-fitted standard additions[17] gave a value of 21 ± 3 μg/l for a 20 μg/l CN^- spiked seawater solution, after correction for the chloride interference. Seawater samples taken for analysis from duplicate tanks during acute toxicity response studies[18] with the marine amphipod *Allorchestes* were reproducible to within ±3% over the range 1–10 mg/l when analysed by calibration curve.

In seawater, the elctrode response drops away rapidly at cyanide concentrations below ~20 μg/l, and the limit of detection by this method is estimated to be ~10 μg/l.

6. Response time and continuous monitoring

Electrode response time varied with cyanide concentration from about 15 min at 20 μg/l to less than 2 min at 2 mg/l. For the determination of low levels (<50 μg/l) of cyanide, ten potential readings at 1 min intervals were used to construct an E *vs* $\log t$ plot to extrapolate the response to an "equilibrium" potential[19] ($t =$ 60 min). Response was identical in seawater and NaCl solutions, despite the turbidity that results from the precipitation of Ca and Mg hydroxides in seawater at pH 13.

In order to establish the usefulness of the CN^- ISE for continuous monitoring, a series of seawater samples was monitored over a 16 hour period. At pH 8 (where most cyanide will be present as the volatile HCN) about 85% of the cyanide was lost from a sample initially 500 μg/l in CN^- in an open, stirred vessel, (Figure 3a). This effect was greatly reduced by covering the vessel (Figure 3d). No loss was observed from an uncovered 500 μg/l sample at pH 13 (Figure 3b). It is interesting that the cyanide ISE is quite stable even in unspiked seawater (Figure 3c) because of the selective response to chloride (cf. Eq. (2)).

Continuous monitoring of cyanide concentrations over extended periods is thus quite straightforward, although for very long periods, as with all ISEs, the cyanide electrode should be checked for drift occasionally.

As selectivity coefficients may vary between electrodes, it is recommended that the selectivity coefficient of the particular electrode to be used be determined before attempts are made to

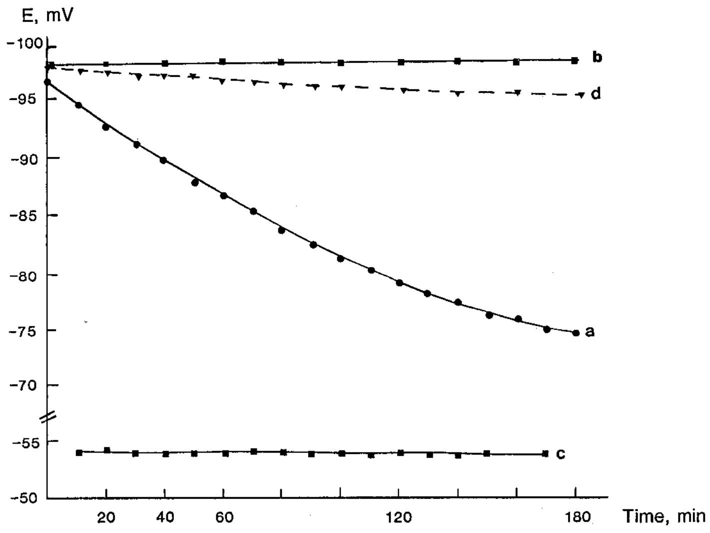

FIGURE 3 Continuous monitoring in open stirred vessels of (a) seawater plus 500 μg/l CN^- at pH 8; (b) seawater plus 500 μg/l CN^- at pH 13; (c) unspiked seawater at pH 13; (d) seawater plus 500 μg/l CN^- at pH 8 in a covered, stirred vessel.

monitor cyanide in seawater. In estuarine waters, where the chlorinity differs significantly from seawater, the chlorinity will need to be determined (and γ_{Cl} estimated)[14] before accurate corrections can be made, however, this involves very little extra experimental effort.

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References

1. M. S. Shuman, *J. Water Pollut. Contr. Fed.* **52,** 1083 (1980).
2. *Quality Criteria for Water* (USEPA, 1976) NTIS Report No. EPA-440/9-76-023, p. 133.
3. J. E. Germain, *J. Water Pollut. Contr. Fed.* **45,** 1192 (1973).
4. L. A. Klapow and R. H. Lewis, *J. Water Pollut. Contr. Fed.* **51,** 2054 (1979).
5. J. O. Egekeze and F. W. Oehme, *J. Anal. Toxicol.* **3,** 119 (1979).
6. *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association, Washington, D.C. 1975), 14th ed.
7. D. Owerbach, *J. Water Pollut. Contr. Fed.* **52,** 2647 (1981).
8. R. A. Durst, *Anal. Lett.* **10,** 961 (1977).
9. D. M. Gillespie, J. D. Eldredge and C. K. Thompson, *Water Res.* **9,** 817 (1975).
10. J. Veselý, D. Weiss and K. Stulík, *Analysis with Ion-Selective Electrodes* (Ellis Horwood, Chichester, U.K., 1978) pp. 152–156.
11. G. T. F. Wong and P. G. Brewer, *Anal. Chim. Acta* **81,** 81 (1976).
12. M. Whitfield, *Ion Selective Electrodes for the Analysis of Natural Waters* (Australian Marine Sciences Association, Sydney, 1971) pp. 73–74.
13. I. Sekerka and J. F. Lechner, *Water Res.* **10,** 479 (1976).
14. M. Whitfield, in J. P. Riley and G. Skirrow, Eds. *Chemical Oceanography* (Academic Press, London, 1975) 2nd ed. Vol. 1, p. 141.
15. M. Gratzl, *Anal. Chim. Acta* **102,** 85 (1978).
16. C. J. Rix, A. M. Bond and J. D. Smith, *Anal. Chem.* **48,** 1236 (1976).
17. M. J. D. Brand and G. A. Rechnitz, *Anal. Chem.* **42,** 1172 (1970).
18. G. W. Brand and B. Errey, unpublished observations, Marine Science Laboratories, Queenscliff, 1982.
19. *Handbook of Electrode Technology,* Orion Research, p. T-2 (1982).