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DETERMINATION OF CYANIDES AND THIOCYANATES IN WATER BY GAS CHROMATOGRAPHY

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SUMMARY

A simple method for the determination of trace amounts of CN^- and/or SCN^- in water is suggested. The method is based on the prior transformation of CN^- or SCN^- into BrCN by treating the sample with bromine; the water sample is then analyzed by gas–solid chromatography and the BrCN is selectively detected by an electron capture detector.

Cyanides and/or thiocyanates at concentrations as low as 0.01 p.p.m. can be detected.

INTRODUCTION

The determination of cyanides and thiocyanates in water at trace levels is a difficult analytical problem owing to the difficulty of removing many interfering components.

Nowadays, the determination of cyanides is of great importance in water quality measurements. The recommended method[1] for the detection of cyanide in water is essentially a modification[2] of the Aldridge[3] colorimetric procedure. This method, however, is time-consuming and tedious, particularly when a large number of samples must be examined, and it does not permit quantitative recoveries at levels below 0.1 p.p.m. (ref. 4). Recently, an automated modification, which should permit the detection of cyanides at levels below 0.1 p.p.m., has been proposed[4].

Colorimetric methods based on the use of Fe^{3+} (ref. 5) or Cu^{2+} and pyridine[6] have been suggested for the determination of thiocyanates at the level of 1 p.p.m., but they are subject to several interferences.

Similar difficulties also arise when the elegant electrochemical methods based on the use of selective electrodes are used.

This paper reports a simple and sensitive procedure that enables cyanides and thiocyanates to be detected in water at levels as low as 0.01 p.p.m. The procedure is based on two stages. The first stage is the well known reaction described by Schulek[7]:

$$CN^- + Br_2 \rightarrow BrCN + Br^- \qquad (1)$$

$$SCN^- + 4Br_2 + 4H_2O \rightarrow BrCN + SO_4{}^{2-} + 7Br^- + 8H^+ \qquad (2)$$

The second stage consists of the gas chromatographic separation of cyanogen bromide, which is then selectively detected by an electron capture detector.

Thiocyanates in the presence of cyanides can be determined as suggested by Lang[8], by treating the cyanides with an excess of formaldehyde to give the unreactive cyanohydrin.

EXPERIMENTAL

Reagents

KCN, KSCN, diisopropyl ether and $K_3[Fe(CN)_6]$ were pure products obtained from Carlo Erba (Milan, Italy); BrCN was obtained from Fluka (Buchs, Switzerland). Bromine water was prepared as a saturated solution of bromine (Carlo Erba) in distilled water. $[Co(CN)_6]^{3-}$ was obtained by adding an excess of HCN to a Co^{2+} solution under a stream of oxygen for 24 h.

Gas chromatograph

A Fractovap Model GI gas chromatograph (Carlo Erba), equipped with an electron capture detector (tritium source), was used. The column was made from borosilicate glass (1 m × 0.3 cm I.D.) and packed with Porapak Q, 80–100 mesh, supplied by Waters Ass. (Framingham, Mass., U.S.A.). Nitrogen was used as the carrier gas at a flow-rate of 50 ml/min. The injector and detector temperatures were maintained at 120° and 150°, respectively. Retention times for BrCN were 2 and 5 min with oven temperatures of 130° and 90°, respectively.

Preparation of the sample

To 3-ml samples of clear* water containing up to 1 p.p.m. of cyanide or thiocyanate 0.5 ml of 20% (w/w) H_3PO_4 is added in a 5-ml flask. Bromine water is then added, drop by drop, until a deep yellow colour persists. The flask is shaken occasionally and after 5 min the excess of bromine is removed by adding 0.2 ml of a 5% aqueous solution of phenol. The solution is made up to the 5-ml mark with distilled water and samples of up to 5 μl are removed with a 10-μl Hamilton syringe and injected into the gas chromatograph.

Standard curves

Standard curves are obtained from an aqueous thiocyanate solution, which is much easier to prepare and more stable than a cyanide solution.

A standard curve covering the 0.05–0.5 p.p.m. range is obtained by diluting a 1.0 m*M* KSCN stock solution, equivalent to 26.02 p.p.m. of CN^- and submitting the dilute solutions to the sample preparation procedure described above.

As the peak shape of BrCN is symmetrical, peak heights can be conveniently used instead of peak areas in calculations.

Detection of thiocyanates in the presence of cyanides

The water sample containing CN^- and SCN^- is neutralized and an excess

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* The water sample to be analyzed must be clear; suspended solid material, if present, must be removed by centrifugation.

of a 40% solution of formaldehyde is added (volume ratio 1:50). The sample is then treated as in the sample preparation procedure described on p. 38.

RESULTS AND DISCUSSION

Fig. 1a shows a typical recorder trace obtained by injecting a 5-μl sample of a solution containing 0.16 p.p.m. of CN^- and oxidized with bromine as described on p. 38.

The optimum gas chromatographic conditions were obtained by trials with an aqueous BrCN solution. Peaks of very poor quality, with a lack of reproducibility, were observed when liquid phases such as Carbowax and Triton were used. Better results were obtained by using a solid adsorbent such as Porapak Q. The column was conditioned before use by a preliminary treatment with BrCN (two 10-μl injections of a 5-p.p.m. solution of BrCN); the reproducibility was within the limits of experimental error.

A calibration graph is shown in Fig. 2, in which the points represent the average results from five different injections of a single standard solution.

Analyses of water samples spiked with known amounts of CN^- or SCN^-

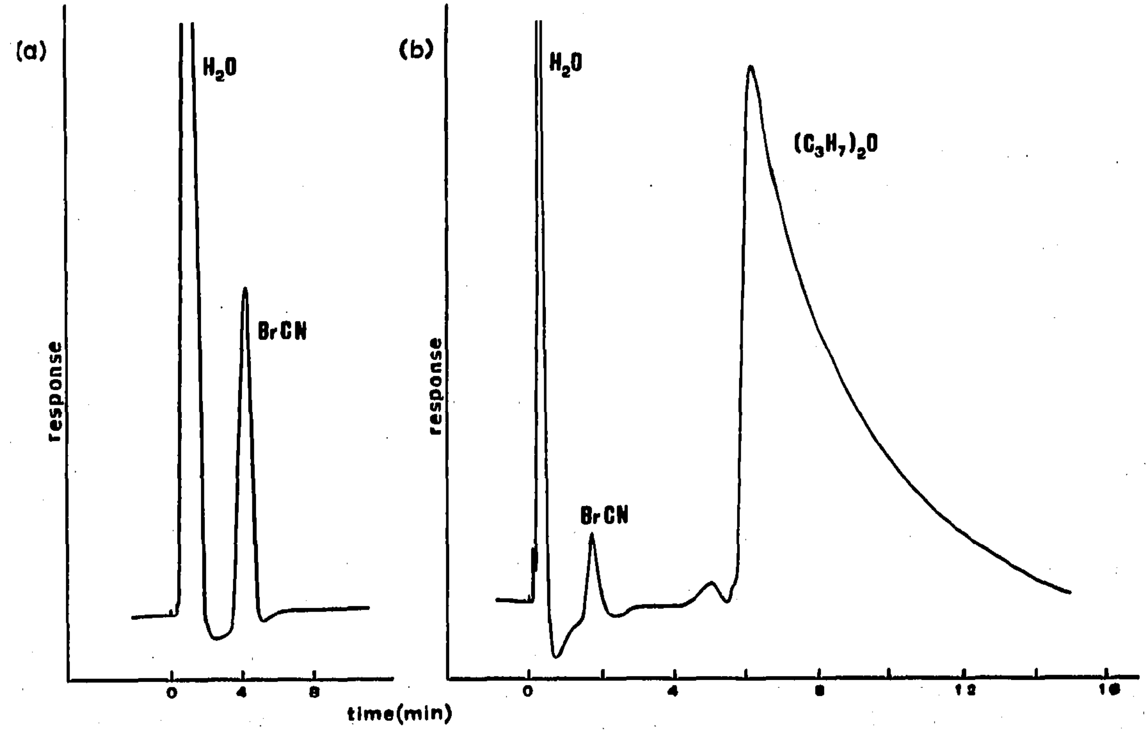

Fig. 1. (a) Gas chromatogram of BrCN obtained from an aqueous cyanide solution (0.16 p.p.m.). Oven temperature, 90°; sample injected, 5μl. (b) Gas chromatogram of BrCN recovered from an aqueous cyanide solution (0.002 p.p.m.) by diisopropyl ether extraction. Oven temperature, 130°; sample injected, 20 μl.

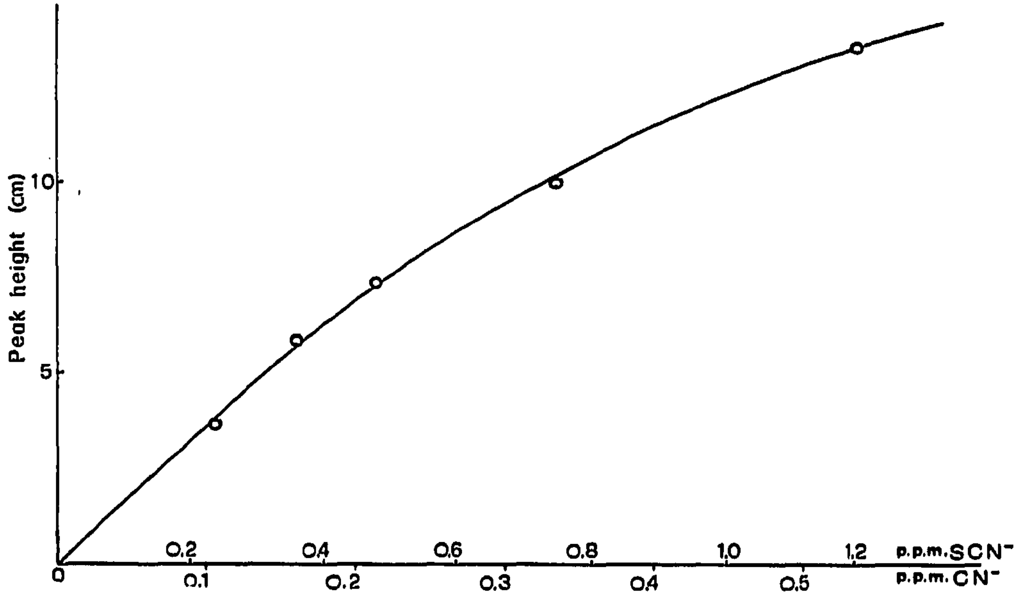

Fig. 2. Calibration graph for BrCN obtained from a standard aqueous solution of thiocyanate. Each point represents the mean of five determinations. Oven temperature, 90°; sample injected, 5 μl.

in the concentration range 0.02–0.5 p.p.m. confirmed that the method is sensitive and reproducible. The limit of sensitivity (0.01 p.p.m.) seems to be related to two distinct factors: (1) the amount of water (5 μl) that can be safely injected without interfering with the detector response for BrCN; and (2) the peak shape, which is not very sharp at an oven temperature of 90°.

These two factors can be alleviated by extracting BrCN quantitatively from the oxidized solution so that a larger amount of BrCN can be injected into the gas chromatograph and by using a higher oven temperature in order to obtain sharper peaks.

We have found that a good extraction solvent that satisfies the required physical (good partition coefficient), chemical (stability towards BrCN) and chromatographic properties (not very sensitive to the electron capture detector), is diisopropyl ether. A water sample containing $2 \cdot 10^{-3}$ p.p.m. of CN^- was oxidized as described above, then extracted with diisopropyl ether; a 20-μl volume was removed from the organic layer and injected into the gas chromatograph, with the oven at 130°. The recorder trace obtained is shown in Fig. 1b. The limit of sensitivity that can be reached is 0.001 p.p.m.

As far as the detection of simple cyanides in the presence of complex cyanides is concerned, we have observed that hexacyanocobaltate(III) up to 100 p.p.m. and hexacyanoferrate(III) up to 20 p.p.m. are not oxidized by bromine to any significant extent; therefore, provided that their respective concentrations are lower than the above limits, they do not seem to interfere in the detection of simple cyanides. The total amount of cyanide can be obtained by destroying complex cyanides by ultraviolet irradiation as described by Goulden *et al.*[4].

The proposed method can also be used for determining the amount of thiocyanates in the presence of cyanides, if the analyses are performed on solutions that have previously been treated under neutral conditions with 40% formaldehyde solution[8]. We have, in fact, observed that BrCN is not detected when aqueous solutions of cyanide in the range 0.05–1 p.p.m. were previously treated with formaldehyde. The amount of thiocyanate in the presence of cyanides could be easily obtained by difference.

In conclusion the method described seems to be more rapid, simple and sensitive than the methods that have previously been reported in the literature for the detection of cyanides and thiocyanates in water. A particular advantage of this method consists in its easy automation: the bromine oxidation can be carried out in a manifold unit connected to an automatic sampler; the gas chromatographic response can be fed into an automatic data aquisition system which expresses the results directly in terms of cyanide and/or thiocyanate concentration.

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