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Note

Determination of cyanides and thiocyanates in water as cyanogen bromide by headspace gas chromatography

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In 1973 Nota and Palombari[1] proposed a gas chromatographic procedure for the determination of cyanide and thiocyanate that was much simpler, more sensitive and subject to fewer interferences than previous commonly used methods[2–4]. We found that this method can be improved with respect to sensitivity and reproducibility and can also be automated by using the headspace technique.

The procedure is based on the prior conversion of CN^- and/or SCN^- into cyanogen bromide (BrCN) by treating the sample with bromine, according to the reactions

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

The BrCN is separated from the aqueous sample by the headspace technique, analysed by gas–solid chromatography and selectively detected by an electron-capture detector.

EXPERIMENTAL

Potassium cyanide, potassium thiocyanate, 85% orthophosphoric acid, 40% formaldehyde and phenol were obtained from Carlo Erba (Milan, Italy); bromine water was prepared as a saturated solution of bromine (Carlo Erba) in distilled water.

Gas chromatograph

A Perkin-Elmer F42 gas chromatograph equipped with a headspace device and a nickel-63 electron-capture detector was used. The column (2 m × 0.3 cm I.D.) was made of borosilicate glass and packed with Porapak Q (80–100 mesh), supplied by Waters Assoc. (Milford, MA, U.S.A.). Nitrogen was used as the carrier gas at a flow-rate of 50 ml/min. The injector and detector temperatures were 130 and 150°C, respectively, and the oven temperature was 120°C. The headspace conditions were as follows: needle temperature, 100°C; flushing of sampling capillary, 15 sec; pressurization of sample vial, 60 sec; sample withdrawal from headspace, 3 sec; 20-ml vials thermostated at 70°C for 10 min were used. Under these conditions the retention time of BrCN was 2 min.

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Analysis of CN^- or SCN^-

A 5.0-ml volume of an aqueous sample containing between 0.005 and 0.1 ppm of CN^- or SCN^-, 2 drops of 85% orthophosphoric acid (to give a pH of 2) and 2 drops of bromine water (to obtain a persistent yellow colour) are introduced into a 20 ml vial; the excess of bromine is removed after 5 min by the addition of two drops of 5% phenol solution. The vial is closed with a PTFE plug (rubber must be avoided) and the sample is then analysed under the conditions given above.

Analysis of SCN^- in the presence of CN^-

Two procedures are suggested for eliminating the interference of CN^-.

Removal of CN^- by heating. A 50.0-ml volume of the sample, to which 1 ml of 85% orthophosphoric acid has been added, is boiled for 20 min in a beaker. After cooling, distilled water is added to the 50-ml mark; a 5.0-ml volume of this solution is treated as described in the previous section.

Treatment of the sample with formaldehyde. To 4.00 ml of sample in a 10-ml flask, 0.2 ml of phosphate buffer (pH 7) and 0.1 ml of 4.0% (w/v) formaldehyde are added. After 5 min, 0.5 ml of 85% orthophosphoric acid and bromine water are added dropwise until a persistent yellow colour is formed. The solution is allowed to stand for 15 min (it must still be yellow), then the excess of bromine is removed by the addition of 0.5 ml of 5% phenol solution. The solution is diluted to 10 ml with distilled water and 5.0 ml are introduced into a 20-ml headspace vial and analysed as described above.

Analysis of CN^- in the presence of SCN^-

An aliquot of the sample is used for the determination of the total amount of CN^- and SCN^-, as described under *Analysis of CN^- or SCN^-*. Another aliquot is used for the determination of SCN^- as described under *Analysis of SCN^- in the presence of CN^-*. The concentration of CN^- is obtained by difference.

Calibration graphs

Calibration graphs for both CN^- and SCN^- can be obtained by diluting solutions containing known concentrations of SCN^- according to the method described above and plotting peak height against concentration.

RESULTS AND DISCUSSION

The chromatogram in Fig. 1 shows that BrCN gives a symmetrical peak, so the peak height can conveniently be used instead of peak area in the calculation. Under our experimental conditions, the peak height is proportional to the concentration of CN^- or SCN^- in the concentration range 0.005–0.1 ppm (Fig. 2).

Table I gives some results for a series of measurements of CN^-.

For the determination of SCN^- in the presence of CN^- it is sufficient to boil the sample for 20 min, after acidifying at pH 2, in order to remove CN^- completely. No loss of SCN^- was observed because of the heating. Similar results were obtained by adopting the procedure that involves the use of formaldehyde. The response of BrCN does not vary appreciably when volumes of solutions between 3 and 10 ml are used in the headspace vial. Table II shows the effect of the salt concentration on the

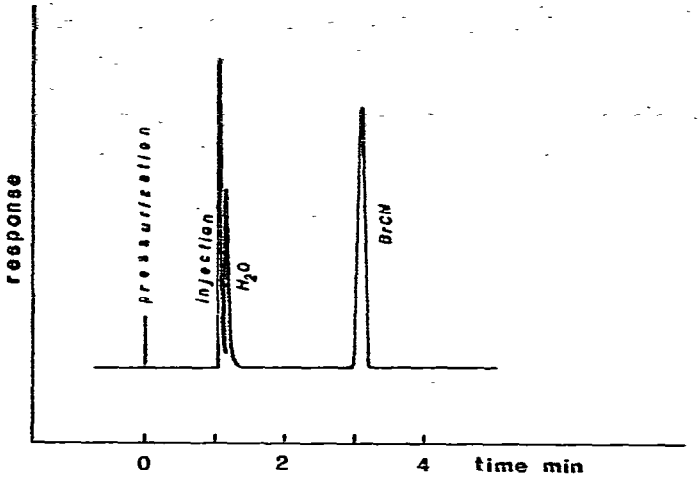

Fig. 1. Gas chromatogram of BrCN obtained from an aqueous cyanide solution (0.05 ppm).

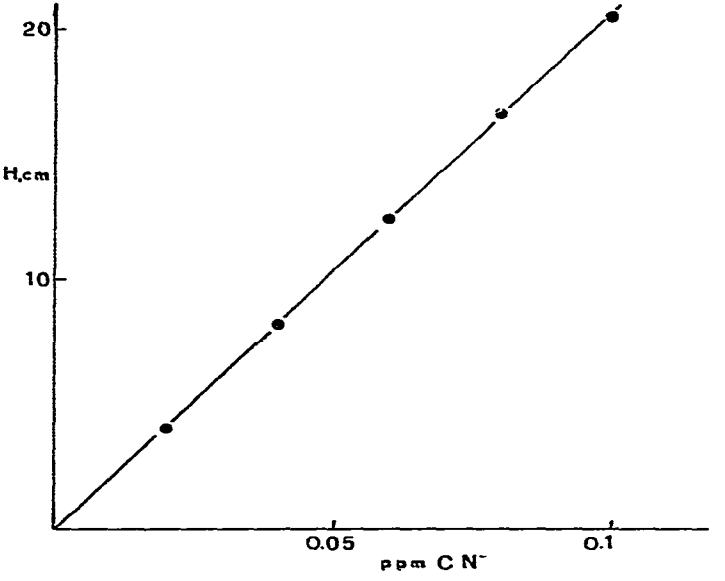

Fig. 2. Calibration graph for BrCN obtained from a standard aqueous solution of thiocyanate.

TABLE I

RESULTS OF SOME TEST MEASUREMENTS

Amount of CN^- (ppm)	*No. of measurements*	*Average peak height (cm)*	*Standard deviation (cm)*	*Relative standard deviation (%)*
0.05	4	5.85	0.10	1.7
0.5	4	9.4	0.1	1.1

response of BrCN. The matrix effect can be avoided by making use of the method of standard additions, as illustrated by the results in Table III and Fig. 3 for a solution containing 0.06 ppm of CN^-.

The use of headspace technique in the determination of CN^- and/or SCN^- as BrCN allows better reproducibility and sensitivity, avoiding extraction procedures[1] and internal standardization[5]. Moreover, sampling into the chromatographic column of volatile fractions only improves the stability of the standing cour rent and increases the column life.

TABLE II

INFLUENCE OF SODIUM CHLORIDE CONCENTRATION ON THE BrCN RESPONSE

Amount of BrCN (ppm)	*NaCl added (%)*	*Peak height (cm)*	*Increase (%)*
0.05	0	10.0	0
0.05	10	10.8	8
0.05	30	11.6	16

TABLE III

STANDARD ADDITIONS METHOD APPLIED TO A 0.06-ppm CN^- SAMPLE

Aliquot No.	*Amount of CN^- present (μg)*	*Sample volume (ml)*	*CN^- added (μg)*	*Peak height (cm)*
1	0.30	5.00	0.00	5.0
2	0.30	5.00	0.20	8.2
3	0.30	5.00	0.40	11.4
4	0.30	5.00	0.50	12.9
5	0.30	5.00	0.60	14.5

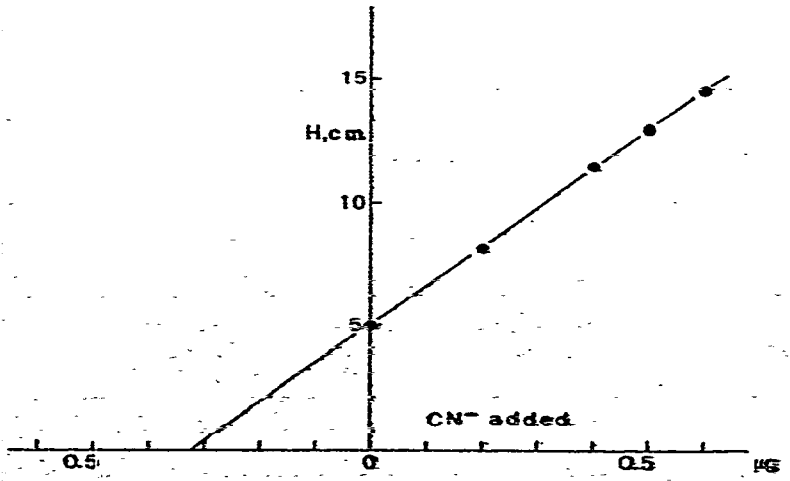

Fig. 3. Standard additions plot for the results in Table III.

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