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DETERMINATION OF CYANIDES AND THIOCYANATES IN WATER BY HEADSPACE GAS CHROMATOGRAPHY WITH A NITROGEN-PHOSPHORUS DETECTOR

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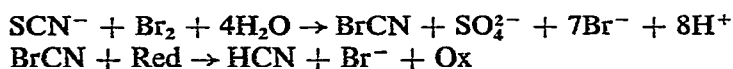
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SUMMARY

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 HCN ; the HCN is separated from the aqueous sample by the headspace technique, analysed by gas-solid chromatography and selectively detected with a nitrogen-phosphorus detector. Cyanides and/or thiocyanates at concentrations between 0.01 and 100 ppm can be detected with a linear response. The procedure has been used for the determination of CN^- in coke-oven water and in coke-oven waste effluent.

INTRODUCTION

In 1973 we proposed a gas chromatographic procedure for the determination of cyanide and thiocyanate¹ that was much simpler, more sensitive and freer from interferences than previous commonly used methods²⁻⁴. The availability of the headspace technique and of the selective nitrogen-phosphorus detector prompted us to develop a selective and sensitive procedure for the determination of cyanide and/or thiocyanate in water. The procedure for the determination of CN^- is based on three stages; first, transformation into HCN by acidification; second, removal of HCN by the headspace technique; and third, gas chromatographic separation of HCN and selective detection with a nitrogen-phosphorus detector. A similar procedure is adopted for the determination of thiocyanate, the only difference being the quantitative transformation of thiocyanate into HCN according to the reactions:



(where Red = SO_2 or I^- and Ox = SO_4^{2-} or I_3^-). If cyanide is present prior to the oxidation step, it must be transformed into unreactive cyanohydrin by an excess of formaldehyde or removed by boiling the solution previously acidified to pH 2.

EXPERIMENTAL

Reagents

KCN, KSCN, 85% H_3PO_4 , 40% HCHO, Na_2SO_3 , KI and phenol were pure products obtained from Carlo Erba (Milan, Italy). Bromine water was prepared as a saturated solution of bromine (Carlo Erba) in distilled water.

Gas chromatograph

An F4% gas chromatograph (Perkin-Elmer) equipped with a headspace device and a nitrogen-phosphorus detector was used. The column (2 m \times 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 40 ml/min; the flow-rates of hydrogen and air were 4 and 150 ml/min, respectively. The injector and detector temperatures were 120 and 150°C, respectively, and the oven temperature was 100°C. The detector wire was heated as recommended by the manufacturer (Perkin-Elmer).

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, 5 sec; 20-ml vials thermostated at 80°C for 10 min were used. Under these conditions the retention time of HCN was 5 min.

Analysis of CN^-

The procedure described below can be adopted regardless of the presence of SCN^- in the sample. A 5.0-ml volume of aqueous sample containing between 0.01 and 100 ppm of CN^- and 2 drops of 85% H_3PO_4 (to give a pH of 2) are introduced into a 20-ml vial. The sample is then analysed under the conditions given above. Any oxidizing agents present in the sample must be reduced with Na_2SO_3 prior to heating of the vial.

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

A 5.0-ml volume of aqueous sample containing between 0.02 and 200 ppm of SCN^- and 2–3 drops of 85% H_3PO_4 (to give a pH of 2) are introduced into a 10-ml volumetric flask. Bromine water is added dropwise until a persistent yellow colour is obtained, and the excess of bromine is removed after 5 min by the addition of 0.5 ml of 5% phenol solution. The quantitative removal of the excess of bromine is indicated by the attainment of a colourless solution.

BrCN is reduced by means of 0.5 ml of 0.1 M Na_2SO_3 solution or a few crystals of KI. Distilled water is added to the 10-ml mark. A 5.0-ml volume of this solution is introduced into the headspace vial and 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% H_3PO_4 has been added is boiled for 20 min in a beaker. After cooling, the sample 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) HCHO are added. After 5 min, 0.5 ml of 85% H_3PO_4 and 3–4 drops of bromine water are added. The solution is allowed to stand 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 BrCN formed is reduced by adding 0.5 ml of 0.1 M Na_2SO_3 solution or some crystals of KI. 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.

Calibration graphs

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

RESULTS AND DISCUSSION

The chromatogram in Fig. 1 shows that HCN gives a symmetrical peak, so the peak height can be conveniently used instead of peak area in the calculation. The peak height is proportional to the concentration of HCN or SCN^- , at least in the concentration range between 0.01 and 100 ppm. More concentrated solutions have not yet been tested. The plot in Fig. 2, obtained by using a solution containing known concentrations of HCN and SCN^- (transformed into HCN by the previously described procedure) shows the linearity of the response and the quantitiveness of the transformation of SCN^- into CN^- . Table I gives some results for a series of measure-

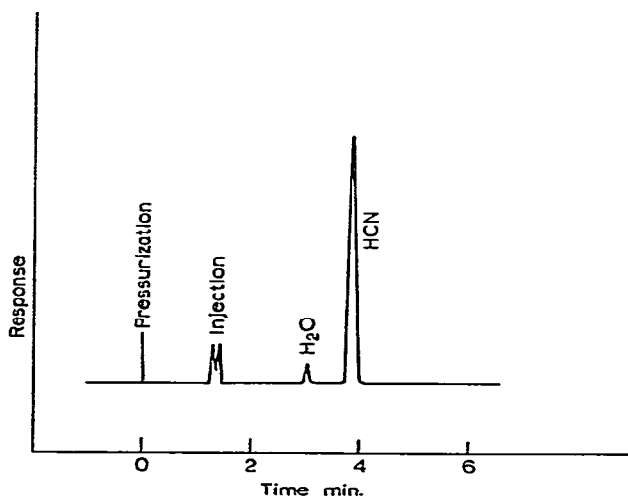


Fig. 1. Gas chromatogram obtained from a 0.10 ppm aqueous solution of cyanide.

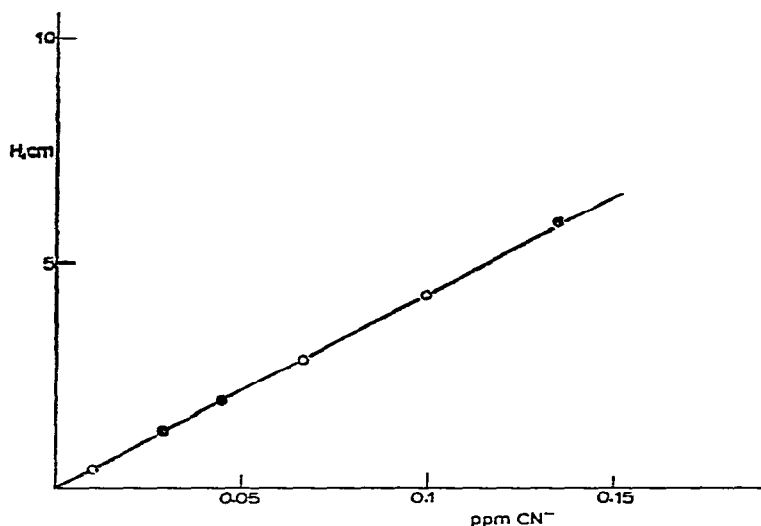


Fig. 2. Calibration graph obtained from standard aqueous solutions of (○) cyanide and (●) thiocyanate as cyanide.

ments on CN^- . The precision and accuracy of the method are indicated in the last two columns in Table I.

The determination of CN^- under the conditions described is not affected by the presence of SCN^- . No response was shown by solutions containing up to 100 ppm of SCN^- .

TABLE I
RESULTS OF SOME TEST MEASUREMENTS

Amount of CN^- (ppm)	No. of measurements	Average peak height (cm)	Standard deviation (cm)	Relative standard deviation (%)
50.0	4	7.6	0.12	1.6
3.00	5	10.7	0.10	0.93
0.05	4	8.2	0.12	1.5

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 completely CN^- . No loss of SCN^- was observed because of the heating. Similar results were obtained by adopting the procedure that involves the use of formaldehyde. Tables II and III gives the results of a series of measurements carried out to demonstrate the quantitative recovery of SCN^- after both thermal and formaldehyde treatment for the removal of HCN. The response for HCN does not vary appreciably when volumes of solutions between 3 and 10 ml are used in the headspace vial.

Table IV shows the effect of the salt concentration on the response for HCN. The matrix effect can be avoided by making use of the method of standard additions, as illustrated by the results in Table V and the plot in Fig. 3 for a solution containing 2 ppm of CN^- .

TABLE II
COMPARISON BETWEEN BOILED AND UNBOILED SCN^- SOLUTIONS

<i>Unboiled samples</i>		<i>Boiled samples</i>	
CN^- (ppm)	Peak height (cm)	CN^- (ppm)	Peak height (cm)
100	11.1	100	11.1
10	14.1	10	14.2
1	7.2	1	7.1

TABLE III
RECOVERY OF SCN^- IN SAMPLES TREATED WITH FORMALDEHYDE AFTER OXIDATION BY BROMINE

<i>Samples containing HCHO</i>			<i>Peak height of 2 ppm SCN^- sample without HCHO (cm)</i>
SCN^- (ppm)	Reaction time (min)	Peak height (cm)	
2	5	10.6	11.0
2	10	10.8	
2	15	11.1	
2	20	11.0	

TABLE IV
INFLUENCE OF SODIUM CHLORIDE CONCENTRATION ON THE HCN RESPONSE

<i>Amount of CN^- (ppm)</i>	<i>NaCl added (%)</i>	<i>Peak height (cm)</i>	<i>Increase (%)</i>
1.00	0	7.4	—
1.00	10	8.2	11
1.00	20	8.8	19
1.00	30	9.4	27

TABLE V
STANDARD ADDITIONS METHOD APPLIED TO A 2 ppm CN^- SAMPLE

<i>Aliquot No.</i>	<i>Amount of CN^- present (μg)</i>	<i>Sample volume (ml)</i>	<i>CN^- added (μg)</i>	<i>Peak height (cm)</i>
1	10	5.00	0.00	5.5
2	10	5.00	1.00	6.1
3	10	5.00	2.00	6.5
4	10	5.00	4.00	7.7
5	10	5.00	5.00	8.3

The presence of Fe^{2+} , Fe^{3+} and Cu^{2+} in the sample decreases the response for HCN. The results in Table VI indicate that the greatest effect is caused by Cu^{2+} .

Reducing agents do not interfere in the analysis of CN^- , but oxidizing substances have to be reduced prior to heating of the sample. Oxidants and reducing agents do not interfere in the determination of SCN^- .

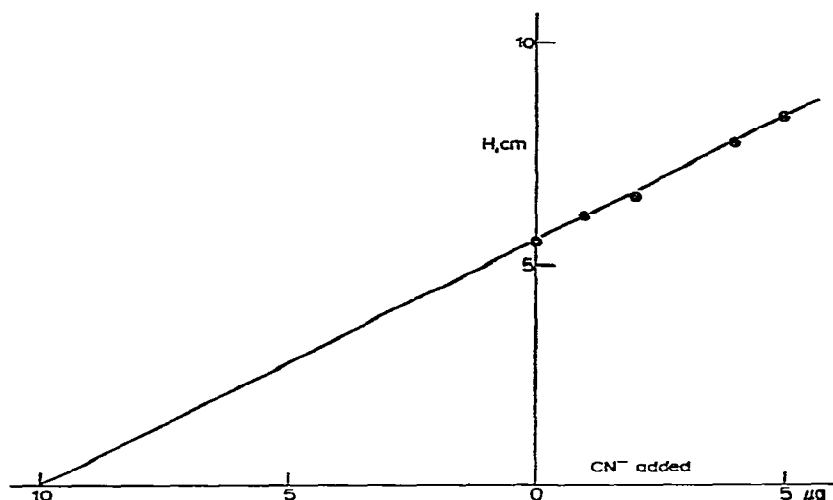


Fig. 3. Standard additions plot for the results in Table V.

TABLE VI

INFLUENCE OF SOME IONS ON THE RESPONSE OF HCN

Amount of CN^- (ppm)	Amount of Fe^{2+} (ppm)	Peak height (cm)	Amount of Fe^{3+} (ppm)	Peak height (cm)	Amount of Cu^{2+} (ppm)	Peak height (cm)
1	0	12.8	0	12.8	0	12.8
1	10	11.7	10	11.0	10	8.4
1	50	11.3	50	9.9	50	8.2
1	100	11.1	100	8.8	100	8.0

For comparable amounts of CN^- and SCN^- , the time of analysis can be considerably decreased by determining CN^- and the sum of CN^- and SCN^- on two different aliquots of the sample, SCN^- being obtained by difference.

The use of the headspace technique is likely to make the proposed method extremely selective (*i.e.*, free from interferences).

The procedure described, indicated as the "HS method", has been used for the determination of CN^- in coke-oven water and in coke-oven waste effluent for disposal in the sea. The same samples were also analysed by the previous procedure^{1,5}, indicated as "BrCN method".

Analysis of CN^- in coke-oven water and waste effluent

Analysis of CN^- in coke-oven water. A 1.00-ml volume of aqueous sample containing between 25 and 5000 μg of CN^- and 5 ml of 20% H_3PO_4 (to give a pH of 2) are introduced into a 50-ml flask and the solution is made up to 50 ml with distilled water. A 5.00-ml volume of the solution is introduced into a 20-ml vial and analysed under the conditions given under Experimental. Any oxidizing agents present in the sample must be reduced with Na_2SO_3 prior to analysis.

The calibration graph for CN^- can be obtained by diluting solutions containing known concentrations of CN^- according to the method described above. The peak heights are plotted against amount of CN^- .

Analysis of CN^- in coke-oven waste effluent for disposal in the sea: method of standard additions. Into four 10-ml flasks, are introduced 5.0 ml of aqueous sample containing between 0.1 and 1000 μg of CN^- , 1.0 ml of 20% H_3PO_4 and 0.0, 1.0, 3.0 and 5.00 μg of CN^- . The solutions are made up to 10 ml with distilled water and 5.00 ml of each solution are introduced into four 20-ml vials and analysed under the conditions given under Experimental. The peak heights are plotted against amount of CN^- . The points give a straight line and the intercept with the abscissa represents the amount of CN^- present in a particular sample. Any oxidizing agents present in the sample must be reduced with Na_2SO_3 prior to analysis.

As the HCN content in coke-oven water is of the order of 50–100 ppm, it is convenient to dilute the sample 50-fold in order to avoid matrix effects without any decrease in accuracy. In such a case it is possible to use the calibration graph directly. In the samples of coke-oven waste effluent for disposal in the sea, the HCN concentration is between 0.2 and 0.5 ppm so that it is not possible to avoid matrix effects by dilution. For these samples the results obtained by a calibration graph method have poor accuracy; matrix effects are avoided by using the standard additions method and the results are accurate.

Typical results for the analysis of CN^- in some coke-oven waste waters and coke-oven waste effluents for disposal in the sea are reported in Table VII.

The results for samples A–D analysed by the HS method and the BrCN method are in good agreement. Samples E–H show good agreement when analysed by the HS method and the standard additions method; the results obtained by using a calibration graph are appreciably higher owing to the different matrix of the standards and the samples.

The accuracy of the procedure was tested by spiking samples A–H with a known amount of CN^- ; the recoveries, reported in the last two columns in Table VII, are excellent.

TABLE VII

COMPARISON WITH BrCN METHOD AND ACCURACY OF PROPOSED PROCEDURE

Sample	CN^- determined (ppm)			CN^- added (ppm)	CN^- recovered by HS method (ppm)	
	BrCN method	HS method			By calibration graph	By standard additions method
		By calibration graph	By standard additions method			
A	53	52	—	25.0	25.1	—
B	65	65	—	20.0	20.0	—
C	42	43	—	20.0	25.2	—
D	58	57	—	5.00	5.04	—
E	0.20	0.23	0.21	0.150	—	0.150
F	0.37	0.41	0.38	0.150	—	0.150
G	0.25	0.28	0.25	0.150	—	0.149
H	0.30	0.34	0.30	0.020	—	0.021

In contrast to the BrCN method, the procedure suggested here allows CN^- to be determined regardless of the presence of SCN^- , which is always present in the samples studied; in addition, the linearity range is wider and the procedure is easily automated.

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