Journal of Chromatography, 262 (1983) 360–363
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 15,756

Note

Determination of cyanide, as cyanohydrin, in water by gas chromatography

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(Received February 8th, 1983)

Methods for the determination of CN^- in water by gas chromatography have been suggested by our research group over the last few years[1,2] and have been applied successfully in several cases[3–5]. However, they suffer from marginal limitations. In the case of the BrCN method[1] only the sum of the CN^- and SCN^- concentrations is obtained; thus the analysis of samples containing SCN^- requires an independent determination of the thiocyanate concentration. In addition, it has been reported that BrCN is also formed by the direct treatment of protein solutions with bromine water, so that a prior deproteinization of the sample is needed[3].

On the other hand, the head-space technique[2], while extremely sensitive and accurate, cannot be applied in the presence of metal cations (Fe^{2+}, Fe^{3+}, *etc.*) which strongly complex the cyanide ion.

The method suggested in this paper is based on the reaction

$$CN^- + RCHO \rightarrow \underset{\underset{CN}{|}}{\overset{\overset{O^-}{|}}{RCH}} \xrightarrow{H^+} \underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{RCH}} \quad (R = H, CH_3) \qquad (1)$$

and on the determination of the cyanohydrin obtained by gas–solid chromatography. It will be shown that this procedure allows the determination of CN^- concentrations, even when relatively high amounts of proteins and metal cations are present, thus representing an advance on the methods previously suggested.

EXPERIMENTAL

Reagents

Sodium cyanide, 40% formaldehyde, acetaldehyde and 85% orthophosporic acid were pure products supplied by Carlo Erba (Milano, Italy).

Apparatus

The gas chromatograph used was a Perkin-Elmer Model Sigma 3B equipped with a nitrogen–phosphorus detector.

0021-9673/83/$03.00

The UV irradiator consisted of a Hanovia high-pressure quartz mercury vapour lamp (450 W), without sleeves, in a water-cooled immersion well.

Chromatographic conditions

The column was made of borosilicate glass (70 cm × 0.3 cm I.D.) packed with Porapak Q-S, 80–100 mesh (Waters Assoc., Milford, MA, U.S.A.). Nitrogen was used as carrier gas at a flow-rate of 40 ml/min; the flow-rates of hydrogen and air were 4 and 100 ml/min, respectively. The injector and detector temperatures were 140 and 170°C, respectively, and the oven temperature was 160°C. Under these conditions, the retention times of hydrogen cyanide–formaldehyde and hydrogen cyanide–acetaldehyde were 6 and 8 min, respectively. The use of a glass column and injector is recommended.

Analysis of CN^-

A 9.5-ml volume of the neutral or weakly alkaline solution to be tested was poured into a 10-ml volumetric flask. One drop of 8% formaldehyde or 80% acetaldehyde, solution and one drop of 85% orthophosphoric acid solution and distilled water to volume were added. Reaction was allowed to proceed to completeness in a few minutes under stirring. If the sample contained a not-negligible amount of metal cations, the solution was transferred to a quartz vessel through which was passed a beam of UV radiation during 10 min.

A known volume (at most 2 μl) was then sampled, injected into the gas chromatograph, and the unknown CN^- concentration deduced from the peak height using a calibration graph constructed as described below.

Calibration graphs

Calibration graphs were constructed by reporting peak heights against concentration of samples containing known concentrations of CN^-, treated according to the procedure described above.

RESULTS AND DISCUSSION

Concentrations of CN^- ranging from 0.05 to 50 ppm were determined. In order to obtain accurate results, it was necessary that the reaction proceeded quantitatively: it was found that concentrations of 500 ppm of formaldehyde or 5000 ppm of acetaldehyde and a pH lower than 3 must be realized to ensure such conditions. However, when not-negligible amounts of metal cations which are strongly complexed by CN^- (Fe^{3+}, Fe^{2+}, Ni^{2+}, etc.) are present it is advisable to pass an intense beam of UV radiation through the sample; UV irradiation, in fact, catalyses the decomposition of the cyanide complexes and ensures the quantitativeness of the reaction[1–4]. We expect that reaction 1 is not disturbed by the presence of SCN^- anions and proteins, as demonstrated by experimental evidence in samples containing as much as 100 ppm of SCN^- and 1000 ppm of bovine serum albumin.

Fig. 1 shows that the gas chromatograms of formaldehyde and acetaldehyde cyanohydrins give symmetrical peaks: thus peak heights can be used instead of peak areas. Furthermore, Fig. 2 shows that the calibration graphs are practically straight lines for CN^- concentrations in the range 0.05 50 ppm, so that, strictly speaking, only

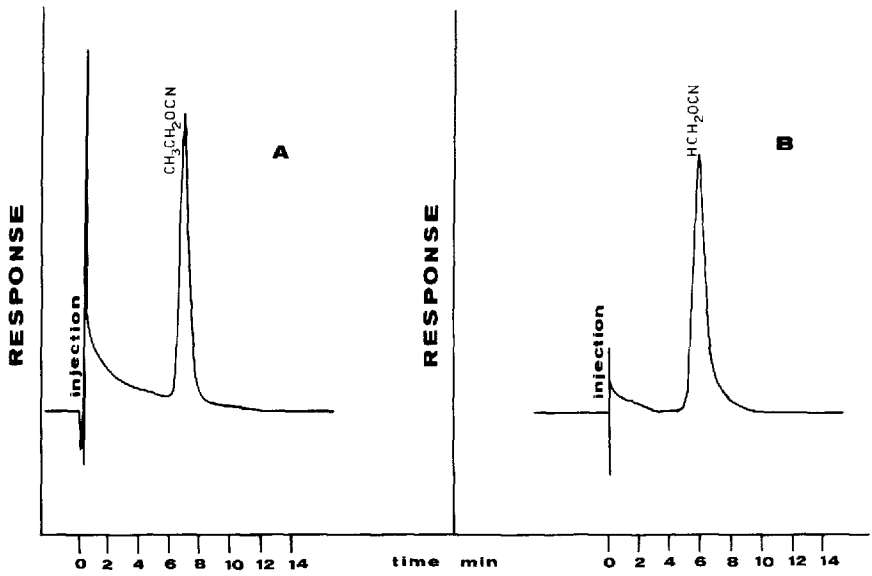

Fig. 1. Gas chromatograms obtained from a 1 ppm aqueous solution of cyanide with acetaldehyde (5000 ppm) (A) and with formaldehyde (500 ppm) (B).

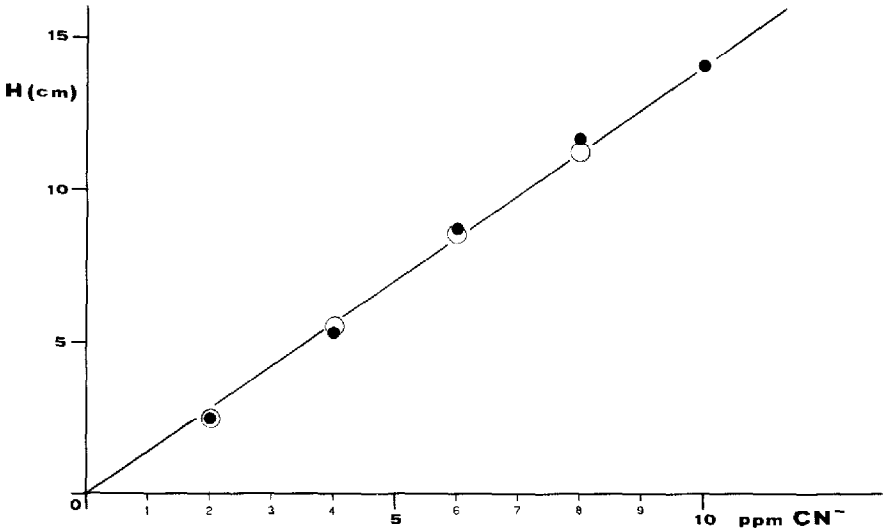

Fig. 2. Calibration graph obtained from aqueous solutions of cyanide with formaldehyde (○) and acetaldehyde (●).

a single calibration point is needed if these limits are not exceeded. The results for a set of determinations are reported in Table I.

CONCLUSIONS

A few additional remarks on the practical importance of the method outlined are needed. First, we notice that a method which does not suffer interference from

TABLE I

RESULTS OF SOME TEST MEASUREMENTS FOR CN^-.

Amount of CN^- (ppm)	*No. of measurements*	*Average peak height (cm)*	*Standard deviation (cm)*	*Relative standard deviation (%)*
HCHO method				
25	5	9.28	0.22	2.41
6	4	8.50	0.20	2.35
0.5	4	9.35	0.30	3.21
CH_3CHO method				
30	4	9.09	0.12	1.29
6	4	8.68	0.05	0.58
0.7	4	7.25	0.15	2.07

proteins and thiocyanate will prove useful for determining the CN^- concentration in most biological materials. On the other hand, interference from metal cations, which are encountered in a variety of cases, can be easily eliminated by irradiating the sample.

In addition, the method, when compared with the head-space technique[2], even if intrinsically less sensitive, does not require special equipment and hence will prove more widely applicable.

ACKNOWLEDGEMENT

This work was supported by a grant from the Ministry of Education (Rome) (to Professor G. Nota).

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