

CHROM. 9063

Note

Determination of complex cyanides in water by gas chromatography

GIORGIO NOTA, ROBERTO PALOMBARI and CARLO IMPROTA

Istituto Chimico, Università di Napoli, Via Mezzocannone, 4, 80134 Naples (Italy)

(First received December 18th, 1975; revised manuscript received January 23rd, 1976)

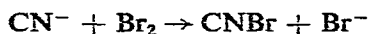
The determination of Fe(II), Fe(III) and Co(III) complex cyanides is currently accomplished by means of rather laborious procedures. A possible method is the distillation of these complexes in a strongly acidic medium, with absorption of the liberated hydrogen cyanide in an alkali solution followed by its colorimetric determination. This method permits free or weakly complexed cyanides to be distinguished from the very stable Fe(II), Fe(III) and Co(III) complexes, which decompose only in strongly acidic media. For the determination of the cyanide absorbed in an alkali solution the pyridine-pyrazolone method described by Epstein¹ is most commonly used. This procedure, which is also recommended in a standard method² is, however, time consuming, particularly when a large number of samples are to be examined; furthermore, it does not permit quantitative recoveries at levels below 0.1 ppm (ref. 3).

Recently Goulden *et al.*³ have described an improved technique of recovery; they also reported a faster automated method in which the breakdown of complex cyanides (cobalticyanide included) is obtained by irradiation with UV light.

These methods are liable to interference, the most serious being caused by thiocyanate, which produces hydrogen cyanide during the distillation and/or the UV irradiation step.

We also think that the determination of small amounts of cyanide complexes in the presence of large amounts of free cyanide will not be very accurate by the automatic method³ as the complexed cyanide is obtained by difference from the total.

The present paper reports a simple method that permits the detection of complex cyanides at levels as low as 0.01 ppm (the complex cyanides and thiocyanate concentrations are expressed as ppm of CN⁻). The procedure consists of three stages. The first stage is the breakdown of complex cyanides by irradiation with UV light. The second is based on the well known Schulek's reaction⁴:



In the last step the cyanogen bromide formed is separated by gas chromatography and selectively determined by use of an electron capture detector⁵.

EXPERIMENTAL

Reagents

All chemicals were analytical-grade reagents and were used without further purification.

Apparatus

The gas chromatograph used was a Carlo Erba Fractovap Model GI equipped with an electron capture detector (^{63}Ni source). The UV irradiator was a Hanovia high-pressure quartz mercury vapour lamp (450 W), without absorption sleeves, in a water-cooled immersion well.

Sample preparation

To 150 ml* of aqueous solution containing up to 0.7 ppm of complex cyanides, 5.0 ml of 60% (w/w) orthophosphoric acid solution and 5 ml of 0.15 M sodium sulphite solution are added. The solution is made up to 200 ml and irradiated with UV light for 10 min. After this treatment, 40 ml are transferred into a 50-ml flask and bromine water is added dropwise until a deep yellow colour persists. The flask is occasionally shaken, and, after 5 min, the excess of bromine is removed by adding 2 ml of 5% aqueous phenol. The solution is then made up to the mark and 3- μl portions are injected into the gas chromatograph.

If the water sample contains free CN^- or CNS^- the procedure is modified as follows: to 150 ml of sample, containing up to 50 ppm of CN^- and/or SCN^- , neutralized if necessary. 6 ml of pH 6.5 buffer solution [5% disodium hydrogen orthophosphate adjusted to pH 6.5 with 20% (w/w) orthophosphoric acid] are added. The solution is then treated with 5 ml of 0.3 M sodium hypochlorite solution, and, after a few minutes, 15 ml of 0.15 M sodium sulphite solution and 5 ml of 60% (w/w) orthophosphoric acid are added and the solution is made up to 200 ml. The sample is then treated as described above.

Chromatographic conditions

The column used was a borosilicate glass tube (1 m \times 0.3 cm I.D.) packed with Porapak Q, 80–100 mesh, supplied by Waters Assoc. (Milford, Mass., U.S.A.). Nitrogen was used as carrier gas at a flow-rate of 50 ml/min. The oven, injector and detector temperatures were 100, 120 and 150°, respectively. The retention time of cyanogen bromide under these conditions is about 4 min.

Standard curves

Standard curves are obtained by using an aqueous thiocyanate solution, which is much easier to prepare and more stable than cyanide solutions. A standard curve covering the 0.05–0.7 ppm range is obtained by diluting a 1.0 mM potassium thiocyanate stock solution, equivalent to 26.02 ppm of CN^- ; the dilute solutions are submitted to the sample preparation procedure without the irradiation treatment. As the peak shape of cyanogen bromide is symmetrical, peak heights can conveniently be used instead of peak areas in calculations.

RESULTS AND DISCUSSION

Our procedure, based on the decomposition of complex cyanides by means of ultraviolet light, is analogous to that proposed by Goulden *et al.*³. The main difference is that we add sulphite in order to obtain a quantitative recovery of hydrogen cy-

* This sample size may seem excessive but such was the volume of our irradiation apparatus.

anide produced by the complex cyanides. The test to establish that the recovery was quantitative was made by comparing the peak heights due to cyanogen bromide in solutions containing known amounts of complex cyanides and thiocyanate.

Experimental tests have also shown that 10 min of irradiation are sufficient to break down as much as 0.7 ppm of complex cyanides.

In the proposed method the common interferences are easily removed. Cyanides and thiocyanates, the latter of which is particularly troublesome, are transformed by hypochlorite into cyanogen chlorides, which are stable to UV light.

Ions such as sulphides, sulphites, etc., which usually have to be removed do not interfere. Moreover, some ions commonly found in industrial waste such as Fe^{3+} , Cu^{2+} , Zn^{2+} and other potential cyanide-forming materials such as cyanate, glycine and urea do not interfere in our method³.

In conclusion a very simple and sensitive method for trace determination of Fe(II), Fe(III) and Co(III) complex cyanides is suggested.

REFERENCES

- 1 J. Epstein, *Anal. Chem.*, 19 (1947) 272.
- 2 *Standard Methods for the Examination of Water and Waste-Water*, American Public Health Association, American Water Association and Water Pollution Control Federation, New York, 13th ed., 1971, p. 397.
- 3 P. D. Goulden, B. Afghan and P. Brookshank, *Anal. Chem.*, 44 (1972) 1845.
- 4 E. Schulek, *Z. Anal. Chem.*, 62 (1923) 337.
- 5 G. Nota and R. Palombari, *J. Chromatogr.*, 84 (1973) 37.