Quality of Groundwater, Proceedings of an International Symposium, Noordwijkerhout, The Netherlands, 23–27 March 1981, W. van Duijvenbooden, P. Glasbergen and H. van Lelyveld (Eds.),
Studies in Environmental Science, Volume 17

DETERMINATION OF CYANIDE IN SOIL AND GROUNDWATER

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ABSTRACT

An automated photometric determination of cyanide is described based on the König reaction with chloramine-T and isonicotinic acid-barbituric acid reagent. The method includes ultra-violet irradiation and phosphoric acid distillation to liberate cyanide from the sample. With this procedure stable cyanide compounds like iron(III)cyanide and thiocyanate are completely converted. In the range of 0-100 µg/l CN 20 samples per hour can be analyzed with a standard deviation of 1.3 µg/l.

Also a procedure is described to release cyanide from solid samples. The samples are distilled from hydrochloric acid medium in the presence of Cu(I)ions. The distilled cyanide is then measured photometrically. Thiocyanate is not measured in this procedure.

INTRODUCTION

Several methods exist for the determination of cyanide (1). Most of them include a distillation/digestion stage, in which the cyanide is liberated from the sample. The aim of this procedure is to avoid possible interferences from other substances present in the sample. The distilled cyanide is collected in an alkaline absorption solution and can be determined titrimetrically, potentiometrically or photometrically. Because of the greater sensitivity the latter method was chosen.

The photometric procedures, which are generally used are all based on the König (2) reaction, where cyanide reacts as cyanogen halide with pyridine or pyridine derivates to form a conjugated dialdehyde, glutonic aldehyde.

The latter is then coupled with a primary amine or a compound containing reactive methylene groups (RH_2) to yield a polymethine dye.

Nagashima (3) recently described a procedure in which chloramine-T is used to form cyanogen chloride which reacts with isonicotinic acid and barbituric acid.

The use of pyridine, which is unpleasant and noxious in routine work, is unneccesary in this approach, giving preference to this procedure over established methods like the pyridine-barbituric acid method and the pyridine-pyrazolone method. A slight decrease in sensitivity and a somewhat cumbrous preparation of the isonicotinic acid-barbituric acid reagent must be considered.

Nevertheless experiments were carried out to evaluate an automated determination of cyanide based on the method described by Nagashima. The determination should be able to detect cyanide concentrations in the range from 0 to 100 µg/l in order to be used for intended routine determination in groundwater and surface water.

The suitability of ultra-violet irradiation as a means to release cyanide from stable cyanide compounds was also investigated (4).

In addition, a wet-chemical digestion procedure for the liberation of cyanide from solid samples was tested (5,6).

MATERIAL

A Technicon Auto Analyser-II system consisting of a sampler pump, a distillation unit, a manifold, a colorimeter and a recorder was used (fig. 1). The manifold incorporated an ultra-violet digestor and a heating bath (G-coil, 37°C). The sampler was equipped with a 20 HR-2/1 cam. The distillation unit was operated at a temperature of 125°C. The colorimeter was fitted with a 50 mm flow cell and a 600 nm filter.

For the liberation of cyanide from solid samples a reflux/distillation apparatus was used. The liberated cyanide was trapped under suction in an absorption vessel containing a solution of sodium hydroxide.

REAGENTS

All chemicals were of analytical grade. Solutions were prepared with deionized water.

- Cadmium sulphate solution by dissolving 1 g of $CdSO_4.8H_2O$ in 100 ml water.
- Copper(II)sulphate solution by dissolving 50 g of $CuSO_4\ 5H_2O$ in 250 ml water.
- Sodium hydroxide 0.1 N.
- Hydrochloric acid concentrated.
- Tin(II) chloride solution by dissolving 50 g of $SnCl_2 5H_2O$ in 100 ml 0.5 N hydrochloric acid.
- Isonicotinic acid - barbituric acid reagent by dissolving 1.7 g of isonicotinic acid $C_6H_5NO_2$, 1.7 g of barbituric acid, $C_4H_4N_2O_3$ and 1.2 g of sodium hydroxide in 250 ml water. Adjustment of the pH to approx. 6.5 with 2 N HCl. Storage of the solution in an amber coloured bottle.
- Chloramine - T solution by dissolving 0.5 g of $C_7H_7ClNNaO_2S.3H_2O$ in 250 ml water. A fresh solution of this reagent has to be prepared daily.

- Phosphate buffer by dissolving 13.6 g of KH_2PO_4 and 0.34 g of $K_2HPO_4 \cdot 3H_2O$ in 1000 ml of 1 l water (this solution should have a pH of 5.2). Add 0.5 ml of Brij-35 detergent and mix.
- Phosphoric acid 50%.

PROCEDURE

Photometric determination of cyanide.

Build up the Auto Analyser system according to the flow scheme presented in fig. 1. Start the analysis by feeding water at first and then the reagents through the system. Let the system stabilize for approx. 20 minutes before adjusting the baseline. Calibrate the colorimeter for the heighest scale reading with a standard solution of 100 µg/l CN. Set up a calibration curve by measuring standard solutions of 10, 20, 40, 60, 80 and 100 µg/l CN respectively.

Pretreatment of solid samples.

Make use of a reflux/distillation apparatus of the dimensions shown in fig. 2. Pipet 15 ml 0,1 N sodium hydroxide into the absorption vessel before connecting it to the distillation bridge. Weigh 1-10 g sample into the roundbottom and add 100 ml water. Connect the condensor, the tap funnel and the gas inlet tube; apply heating and suction. Add through the tap funnel resp. 15 ml concentrated HCl, 10 ml copper sulphate solution and 2 ml tin chloride solution. If the sample contains sulphide, 1 ml cadmium sulphate solution should be added. Reflux the mixture for 1½ hour. Determine the cyanide content of the sodium hydroxide solution in the absorption vessel photometrically. It is then unneccesary to use the ultra-violet digestor.

RESULTS

The procedure as proposed by Nagashima has been amenable to automation. However we had to make some alterations in the original procedure. Instead of using sodium isonicotinate and sodium barbiturate as recommended by the author, the isonicotic acid - barbituric acid reagent was prepared by dissolving the acids in a slight excess of sodium hydroxide. Maximum absorbance was measured at 598 nm after addition of the resulting reagent.

Contrary however to the results reported in the original paper it was found that colour formation was rather slow, which is undesirable in automation. Hence a temperature increase was applied to speed up the reaction; a temperature of 37° proved to be satisfactory.

After establishing the optimum concentration ratios of the required reagents an Auto Analyser System was built up. The final flow scheme is presented in Fig. 1. The duration of the ultra-violet irradiation was optimized. Standard solutions of thiocyanate and iron(III)cyanide were analyzed with irradiation times of 7, 9, 12 and 15 minutes respectively. It was found that cyanide was optimally released from thiocyanate after an irradiation time of 12 minutes; iron(III)cyanide was completely converted to CN^- by irradiation during 7 minutes. Hence for the determination of the total cyanide content an irradiation time of 12 minutes seemed appropriate. It should be noted however that the classification total cyanide means those cyanide compounds which are converted to CN^- after ultra-violet irradiation and acid distillation. In practice this will be the case with most of the occuring inorganic cyanide compounds. No sufficient data were available about organic cyanide compounds. With the evaluated procedure 20 samples per hour can be analyzed in the proposed range of 0 to 100 g/l CN^-. After finishing the research on the determination of cyanides in solution a digestion procedure for the liberation of cyanide from solid samples was tested. The procedure implied refluxing for 1 hour with excess hydrochloric acid in the presence of Cu(I)ions. The liberated cyanide was trapped under suction in an absorption vessel containing a known volume of sodium hydroxide. Under these conditions standard solutions of free cyanide, thiocyanate and iron(III)cyanide were analyzed. It was found that both free cyanide and iron(III)cyanide were recovered with an average of 94%. As can be expected thiocyanate did not release any CN^- due to the formation of the slightly soluble Cu(I)SCN.

Hence the cyanide content determined by this procedure should be classified as total cyanide minus thiocyanate. Because the procedure was to be employed for solid samples in which the presence of thiocyanate was not expected this procedure was approved.

CONCLUSIONS

The methods descibed here which are based on the liberation of cyanides by ultra-violet irradiation and distillation or distillation only gave reliable results with both water and soil samples.

The colour reagent isonicotinic acid-barbituric acid used in these methods appeared to be a good alternative for the unpleasant and noxious pyridine-barbituric acid reagent.

The cyanide content of the soil samples can be determined with a mean recovery of 94%.

The reproducibility of the photometric appeared to be quite good.

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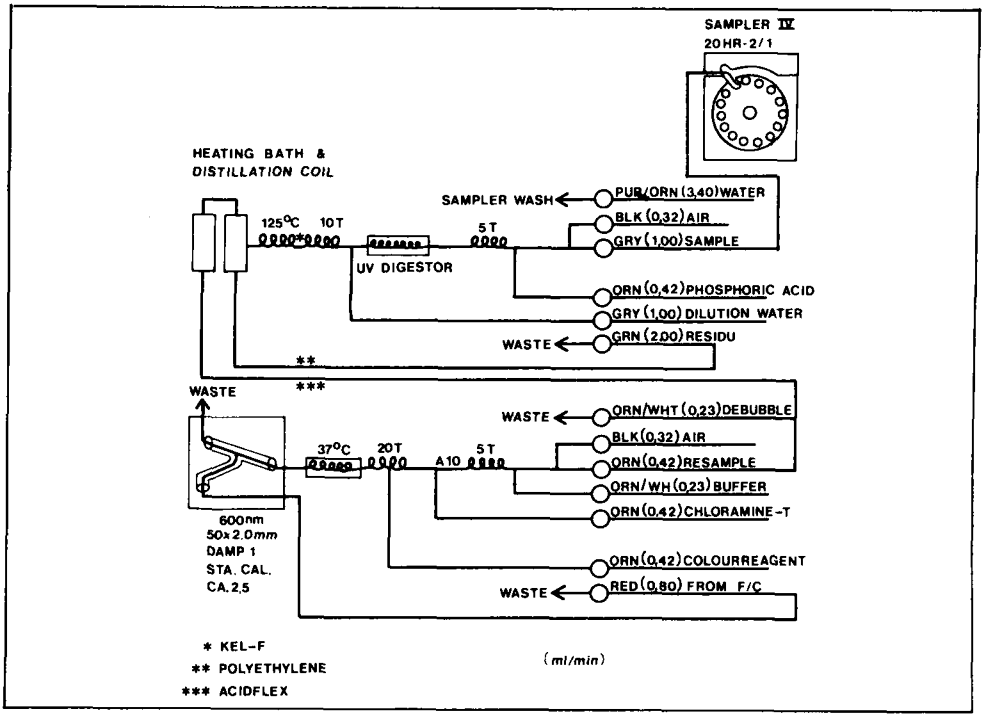

Figure 1. Flow scheme cyanide determination; 0 - 100 µg/l

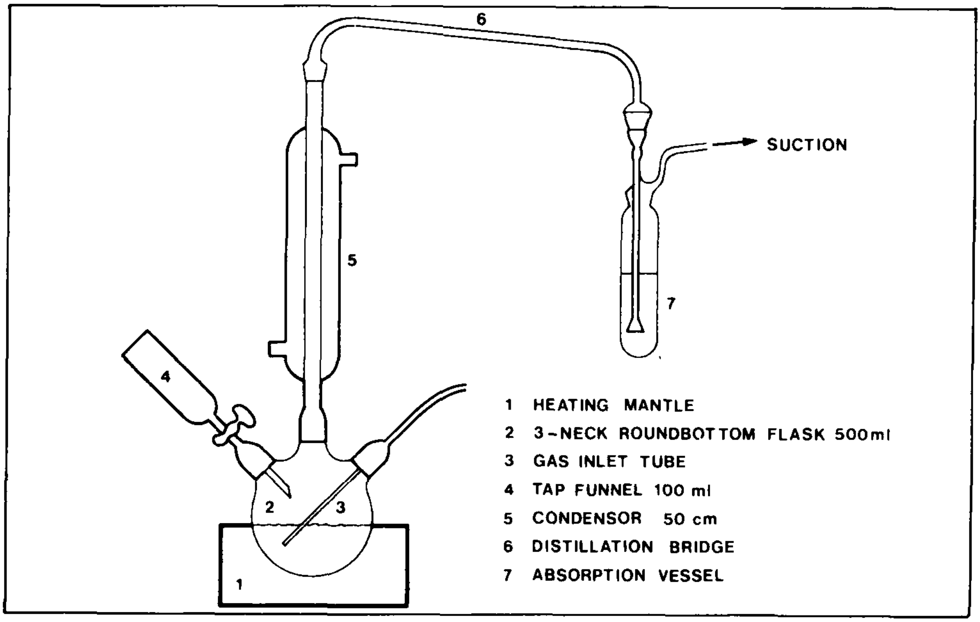

Figure 2. Reflux / distillation apparatus