

Improved automated colorimetric determination of dicyandiamide in water

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Abstract

A previously described automated segmented analytical procedure for the determination of dicyandiamide was improved through the on-line treatment of samples with an ethylenediamine tetra-acetic acid (EDTA)/mannitol reagent. At a sample frequency of 30 samples-h⁻¹ with the sample:wash ratio at 1:2, response was accurate, reliable and linear between 2 and 30 mg-l⁻¹ dicyandiamide-N, with the sample interaction limited to below 2.50%. Interference from a number of substances was evaluated and the results given.

Introduction

The automated segmented flow analytical procedure, developed for the routine analysis of dicyandiamide (cyanoguanidine or DCD) in surface- and groundwaters (Pretorius et al., 1991) is accurate, linear between 2 and 30 mg-l⁻¹ with a negligible sample interaction at a sampling frequency of 30 samples-h⁻¹ and reliable. However, even though the problem of interferences has been solved to a great extent, the procedure described to ascertain interference-free results is still unsatisfactory. For the commercial uses of dicyandiamide see Pretorius et al., 1991.

Extensive problems in determining DCD were experienced when the sample pH was low. Sample pH itself, ranging between 1.40 and 11.50, did not impair the reaction rate. In this pH range, the buffer could maintain a constant pH of 13.3. However, secondary interference effects, namely dicyandiamide decomposition, with extended exposure, as well as interference experienced from high concentrations of metal ions, especially Fe⁺⁺, Mn⁺⁺, Ca⁺⁺, Mg⁺⁺ and Zn⁺⁺ ions, resulted in erroneous results being obtained. Acidic water is not uncommon in coal mining areas and will bring about desorption of metal ions from the soil matrix through displacement with hydrogen ions. These ions can be dissolved in the groundwater. Interference was experienced in determining DCD in such samples due to metal hydroxide precipitations. This negative interference was previously described (Vilsmeier, 1982) as: "the incorporation of dicyandiamide into the metal hydroxide precipitations". It is important to note the difference between the two interference mechanisms. Firstly, the acidic decomposition takes place before determination, and therefore the DCD content will diminish with time. Secondly, the metal-ion complexation of DCD will lessen the concentration at the time of analysis and is the most important interference to be eliminated.

The addition of EDTA did relieve the interference from Ca⁺⁺ and Mg⁺⁺ ions. However, at high concentration levels these ions still precipitated; calcium with a white colour and magnesium with a purple-blue colour. Interference from other ions was resolved through NaOH (pH ± 11) and filtration after the precipitate had formed. Garby (1925) focused attention on the use of mannitol to prevent the precipitation of metal hydroxides in alkaline solutions. Preliminary studies furnished excellent results which justified its incorporation into the method.

This paper describes and evaluates an automated colorimetric procedure, improved through the on-line treatment of samples with an EDTA/mannitol reagent, for the determination of DCD in surface- and groundwaters. The effect of the EDTA/mannitol reagent on sensitivity, reliability, linearity, sample interaction and the detection limit was evaluated and the interference from a number of ionic and uncharged compounds verified.

Experimental

Apparatus

The apparatus and lay-out of the analytical flow system were previously described (Pretorius et al., 1991).

Reagents

Except for the EDTA reagent, all the reagents were constituted as before (Pretorius et al., 1991). Mannitol was now combined with EDTA and named the EDTA/mannitol reagent. It was added to the sample at the rate of 0.42 ml-min⁻¹ to ensure that the formation of EDTA-metal-ion-complexes was not affected. Furthermore, the working buffer was not diluted and need not be re-optimised. Similarly, the concentration levels of all the other reagents in the reaction mixture were unaffected as the ionic strength of the reaction mixture stayed approximately the same ($K_{a(MANNITOL)} = 4.6 \times 10^{-14}$, Merck Index, 1976).

EDTA/mannitol reagent (1.678 x W/3.280 x 10³ moW)

Dissolve 31.24 g EDTA dihydrate (disodium salt) in 400 ml deionised water. Add 29.88 g mannitol and dissolve. Dilute quantitatively to 500 ml with distilled water in a standard volumetric flask, and filter through Whatman No. 2^V filter paper.

Procedure

- The effect of mannitol on colour development was determined by varying the mannitol content of the EDTA/mannitol reagent between 1.093×10^{-1} and 3.280×10^{-1} mol-l⁻¹ and comparing the sensitivity obtained with the method as described by Pretorius et al. (1991), with an EDTA-only reagent. Optimised reagents and reaction conditions were used in this study.
- The same procedure was used to determine the effect of an increased EDTA concentration on sensitivity. The EDTA

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