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The Improvement of Accuracy of Some Photocolorimetric Methods for the Determination of Fluorides in Water

S. Janković

Laboratory for Sanitary Engineering, Faculty of Civil Engineering
University of Belgrade, Serbia, Yugoslavia

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In the tenth edition of the American Standard Methods for the Examination of Water[1] and in the International Standards for Drinking Water[2], there is only one universally accepted method for the colorimetric determination of fluorides in water, the zirconium-alizarin method, which is in use in several modifications, the Scott-Sanchis one being the most widely used.

The zirconium-alizarin colorimetric method is based on the reaction between fluoride ion and the red zirconium-alizarin lake. In the Scott-Sanchis method this coloured reagent is prepared by dissolving separately 0.3 g of zirconium oxychloride octahydrate in 50 ml of distilled water and 0.07 g of alizarin sodium monosulfonate (Alizarin Red S) in the same volume of distilled water, with subsequent mixing of these two solutions. The weight ratio of the two substances in the zirconium-alizarin solution is 4.28. To obtain the final acid zirconium-alizarin reagent a mixed solution of concentrated hydrochloric acid and concentrated sulfuric acid is prepared, in which the volume ratio of HCl/H_2SO_4 is 3.

J. P. Boonstra[3] has studied the relation between the weight ratio Zr/alizarin and the accuracy of this colorimetric method, and has found that the differentiation of tints becomes more difficult when zirconium is present in the reagent in larger quantities than alizarin. The same author concluded that for spectrophotometric analysis greater extinction values and better differentiations could be obtained using larger quantities of alizarin than zirconium oxychloride octahydrate.

We studied this problem and prepared several coloured complexes of Zr-alizarin in which the weight ratios of components were in favour of the second component, and used them for the photocolorimetric determination of the fluoride ion in water. We noticed that using the acid zirconium-alizarin reagent whose weight ratio Alizarin Red S/zirconium oxychloride octadydrate is 7, a better accuracy of the method can be achieved. Instead of the mixture of H_2SO_4 and HCl proposed by Scott and Sanchis, we used 1.35 N H_2SO_4 as was recommended by B. Visintin and S. Monteriolo[4], by reason of a greater stability of the reagent.

Our results are in good agreement with the results of a recent study made by Acuña[5], who found that for the spectrophotometric determination of fluorides in drinking water the alizarin/zirconium oxychloride octahydrate weight ratio should be 7.5—9.5 for the interval of 0—3 ppm F^-.

The above conclusions were used as a basis for the application of the same principle to the thorium-alizarin colorimetric method.

The determination of fluorides by this method was first described by N. A. Talvitie[6]. In recent works there is a tendency of substituting the Zr-alizarin method by the Th-alizarin one[7, 8, 9 and 10].

The improved thorium-alizarin method

J. Icken and B. Blank[7] have proposed a spectrophotometric and a photocolorimetric method based on the reaction between fluoride ion and the thorium-alizarin reagent. The weight ratio Alizarin Red S/thorium nitrate tetrahydrate in their reagent used for the photocolorimetric determination was 2.

We prepared new acid Th-alizarin reagents in which the above mentioned weight ratio was greater than 2. The reagents were used for the photocolorimetric determinations of fluorides in water for the interval 0.05—2.5 ppm F^-.

The extinction was measured on the Fisher Nefluoro-Photometer using original cells and the light filter 525 mμ; the same instrument was used for the photocolorimetric determination of fluorides by the improved Zr--alizarin method.

We noticed that when using the reagent whose weight ratio Alizarin Red S/thorium nitrate tetrahydrate is 3.4, a greater accuracy of the method is achieved (see Fig. 1).

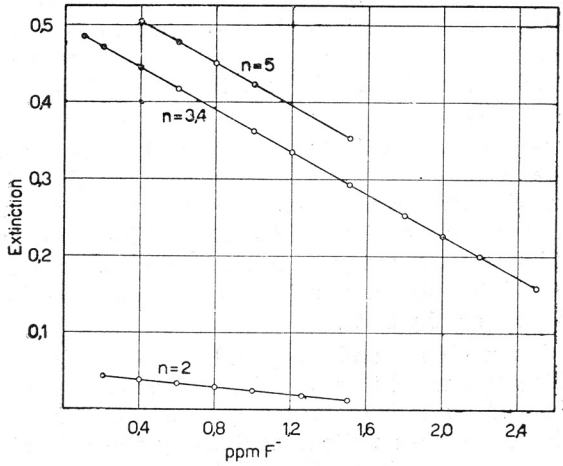

Fig. 1. Influence of the weight ratio Alizarin Red S/Th $(NO_3)_4 . 4 H_2O$ on the accuracy of the colorimetric method of fluoride determination

We propose therefore the following procedure for the photocolorimetric determination of fluorides in water by the Th- alizarin method:

Reagents:

To 10 ml. of 0.2 *N* HCl add 10 ml of 2% aqueous solution of hydroxylamine hydrochloride and 40 ml. of 0.17% aqueous solution of Alizarin Red S. Pour slowly into this mixture, contained in a 100 ml. glass stoppered flask, 40 ml. of a 0.05% aqueous solution of thorium nitrate tetrahydrate, while swirling the flask. The reagent is within an hour ready for use. It should be stored in a refrigerator.

Procedure:

To 80 ml. of the distillate, contained in a 100 ml. volumetric flask, add 10 ml. of the colour reagent. The flask is made to volume with distilled water, stoppered, shaken, and allowed to stand for two hours. Then pour the sample into the cell of the Fisher Nefluoro-Photometer and determine the extinction at 525 mμ. (The instrument is first adjusted with distilled water to 100% transmission). Read on the calibration curve the concentration of fluorides.

Our conclusion is that this improved method seems to have advantage as photocolorimetric method in comparison with the zirconium-alizarin method.

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IZVOD

Povećanje tačnosti nekih fotokolorimetričkih metoda za određivanje fluorida u vodi

Predložene su dvije usavršene metode za fotokolorimetričko određivanje fluorida u vodi. Prva od tih metoda predstavlja potvrdu rezultata, do kojih je došla Sofia Acuna[5] i temelji se na novom uteznom omjeru komponenata reagensa (alizarinsko crvenilo S: oktahidrat cirkonijeva oksiklorida = 7), koji pripravljen sa 1,35 *N* H_2SO_4, kako su predložili Visintin i Monteriolo[4], u cilju povećanja stabilnosti reagensa na četiri mjeseca.

Druga metoda pretstavlja primjenu principa novih uteznih omjera komponenata reagensa na Th- alizarin metodu za fotokolorimetričko određivanje fluorida, pri čemu je konstatovano, da je pri uteznom omjeru (alizarinsko crvenilo S: tetrahidrat torijeva nitrata = 3,4, povećana točnost ove metode.

LABORATORIJA SANITARNE TEHNIKE,
GRAĐEVINSKI FAKULTET,
UNIVERZITET U BEOGRADU

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