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TESTING OF WATER FOR EVALUATION OF ITS FLUORIDE CONTENT

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10 Claims

ABSTRACT OF THE DISCLOSURE

A control or reference amount of water is taken from the water to be tested, and thereto is added an amount of aluminum salt, such as aluminum sulphate to provide a blank being substantially free of reactive fluoride ions; zirconium salt and a dye are then added to the now ion-free blank, and to a separate water sample, and the fluoride content is determined by colorimetric comparison; obtaining the blank from the same water to be tested obviates necessity for precise timing and temperature control of standard samples.

This invention relates to an improved method for testing water for evaluation of its fluoride content.

In connection with the fluoridation of water as a public health measure it is desirable to know the fluoride content of the treated water since the effectiveness and safety of the procedure is dependent upon the maintenance of a substantially constant fluoride concentration.

Among the methods available for the determination of fluoride ion in water it is believed, according to "Standard Methods for the Examination of Water and Waste-water" American Public Health Association, 11th edition 1960, that the colorimetric methods based on the reaction between fluoride and zirconium-dye lake, are the most satisfactory at the present time.

Previous colorimetric methods using permanent standards have not been entirely satisfactory because variations in results are introduced by lack of uniformity in the quality of different batches of the alizarin and by deterioration of reagent solutions on keeping. In an attempt to avoid these disadvantages work elsewhere has been directed towards producing a standard material by repeated filtration and recrystallization from selected solvents (Lewis, D. T., 1963, Jour. R. I. C., vol. 88, p. 335, "Chemistry and the Fluoridation of Water Supplies"). There would appear to be no certainty, however, that despite the use of such specially purified alizarin the ageing effect of the mixed solution will be overcome. The method now proposed is substantially free from errors caused both by variations, within reasonable limits, of the reagent quality and by the effects of ageing.

According to the invention a method for testing water for evaluation of its fluoride content comprises adding, both to a sample of the water and to a control or reference amount (hereinafter called "a blank") of water treated to contain substantially no residual reactive fluoride ions, predetermined proportions of a zirconium salt and a dye capable of reacting with the zirconium salt to produce a lake or colour complex which undergoes a colour modification in the presence of fluoride and comparing the colour developed in the sample with that developed in the blank in a colorimetric test for the fluoride content based upon the substantially constant difference in colour intensity between the blank containing no fluoride. The method is applicable with samples containing fluoride subject to a sufficiently wide range of time and temperature to obviate the necessity for a precise time of standing for

colour development and/or a precise temperature of solution so long as both blank and sample be at or about the same temperature.

The blank may be water in which an amount of an aluminum salt, such as ammonium aluminum sulphate sufficient to complex all the fluoride ions or phosphates is present. To enable the test to be independent of interference from aluminum or phosphates, a predetermined standard amount of fluoride, such as 1 mg./l., is added to a sample of water concerned in a fluoridation treatment and taken before the addition of the fluoride, the amount of which is to be determined. This sample is then employed as the blank, the amount of fluoride therein being determined by comparison and algebraic correction—e.g. addition to 1 mg./l. if the sample reading is above 1 mg./l. and subtraction if it is below. By comparison of the test sample with the pre-treated blank, a measure of interference caused by aluminum salts present naturally or added in the course of treatment is provided. The fluoride added in fluoridation treatment can be determined substantially free from aluminum interference and from interference by any phosphates.

A reagent such as sodium borate or sodium chloride is usually added to the sample for preventing interference from the acid radical of an aluminum salt; preferably all the reagents are added in prepacked capsule or tablet form.

An advantage of the present invention of particular value from the practical point of view especially in works-control and field testing lies in the fact that rigid standardization of temperature and of standing time for colour formation which hitherto has been associated with all versions of the zirconium-alizarin method using permanent standards is not now required. Previously it has been the practice to specify a fixed temperature of say $20 \pm 2^\circ \text{C}$. and a fixed waiting period of say 60 ± 2 min. Procedures requiring such strict control are scarcely suitable for works use. Furthermore even when all instructions relating to reaction time and temperature have been strictly observed an accuracy of only about 0.2 mg./l. at the 1.0 mg./l. F level is, according to Franz J. Maier of the U.S. Public Health Service ("Manual of Water Fluoridation Practice," New York, 1963) the most that can be expected from permanent colour standard instruments. That there is considerable scope for improvements in fluoride testing is quite evident; ideally the tests should be as simple and accurate as those currently used for the control of water chlorination.

In considering the advantages claimed for the new procedure it will be apparent from the technique later described that almost all the errors caused by the presence of listed interfering substances which include alkalinity, chloride, iron, sulphate, colour, turbidity and residual chlorine are cancelled out.

In the case of aluminum its presence in water results in a proportion of any added fluoride or of fluoride naturally present becoming complexed and so prevented from reacting with the alizarin-zirconium lake. To complex all fluoride ions up to concentrations of about 2 mg./l. F requires concentrations of aluminum approaching 100 mg./l. But even the traces of residual alum that are sometimes encountered in waters after alum coagulation and filtration do combine with a significant proportion of the fluoride whether added or naturally present. The procedure recommended, for instance in the American Standard Methods above cited, for overcoming such interference consists in subjecting the sample to a preliminary steam distillation in order to separate the fluoride from the interfering constituents.

It will be appreciated, therefore, that up to now the presence of aluminum in samples of water whose fluoride content is being determined has always been regarded

as undesirable because of its complexing effect upon the fluoride ions. A novel feature of the method herein described, however, lies in the fact that deliberate use is made of this complexing effect by adding a sufficient excess of aluminum to a portion of the water sample so that all fluoride is complexed and this portion may then be regarded as a "fluoride-free" blank. Since the concentrations of other interfering constituents, with the exception of sulphate to which later reference is made, remain the same in both the "blank" and "sample" colour mixtures any resultant effects upon colour development and the associated errors are cancelled out.

The general principle of the new method is based upon the finding that within quite wide limits of time and temperature the difference in optical density, determined photometrically, or in colour intensity, as estimated by visual matching against permanent standards, between a blank containing no fluoride and a sample containing fluoride remains practically constant. This relation has not previously been made use of in the way now proposed.

Depending upon the strength of the particular reagent used it may be necessary to allow a rather longer standing period for the higher fluoride concentrations in order that the desired relation shall operate. To guard against premature measurement in these cases the range of the colour standards is so chosen that these higher concentrations cannot be measured until the corresponding colour intensities have increased to such an extent that they fall within the selected range by which time the correct conditions will have been attained. A similar safeguard can be incorporated in photometric procedures by calibrating the apparatus over a restricted range of say 0.0 to 1.6 mg./l. F at an arbitrary temperature and time, say 20° C. and 60 minutes respectively. Thereafter samples may be tested within a wide range of temperature and time it being necessary only to take readings when both sample and blank fall within the prescribed range.

Instead of using distilled water for the reagent blank the preferred method is to "defluoridate" a further portion of the sample by the addition of excess aluminum so that the effect of interfering substances may, as previously indicated, be largely or entirely overcome. The aluminum may be added for example in the form of aluminum ammonium sulphate the slight effect on colour formation of the sulphate ion itself being corrected by the simultaneous addition of a proportion of sodium borate or sodium chloride or other substance capable of influencing the colour formation in the desired way.

While the procedure as now developed enables satisfactory results to be obtained within as short a time as 10 minutes or so subject to both "blank" and "sample" colour intensities falling within the selected range as aforementioned, it is clearly advantageous to allow as long as possible within the said range since in the early stages colour values are changing rapidly with time which necessitates fairly rapid colour matching or measurement. In addition it is generally better to work with the rather more intense colours obtained by allowing reasonably full lake formation.

The invention will be illustrated by reference to the following examples:

EXAMPLE 1

The method is applicable to both photometric and visual techniques of colorimetric analysis. The following example indicates how the method may be used in a procedure employing a colorimeter, for example the Lovibond Nessleriser manufactured by The Tintometer Ltd., Salisbury, England, designed for visual matching against permanent glass colour standards. The standards are first prepared to match the colours produced by added the acid-alizarin-zirconium reagents to appropriate volumes of water containing known amounts of fluoride and allowing to stand for say 60 minutes at 20° C. or

other predetermined time and/or temperature. A convenient range would consist, for example, of nine standards 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4 and 1.6 mg./l. of fluoride calculated as Fluorine F.

Reagents

(1) Aluminum ammonium sulphate-sodium borate mixture (84 g. $\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$; 16 g. $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$).

(2) Acid-zirconium-alizarin mixture (0.7 g. Alizarin Red S, 0.45 g. zirconyl chloride, 260 sodium bisulphate).

Where the mixtures are used in prepared form which for the above reagents is recommended the prescribed quantities may be dispensed by means of suitable measures or added more conveniently in capsule or tablet form.

Method

Place 50 ml. of sample containing not more than 1.6 mg./l. F in a 50 ml. Nessler cylinder and add 0.10 g. of reagent No. 1. Mix until completely dissolved. Development of a turbidity in hard waters is of no consequence since it later redissolves. Place a further 50 ml. of the same sample in a second Nessler cylinder. To each cylinder then add 0.27 g. of reagent No. 2 and mix rapidly to dissolve. A third cylinder containing 50 ml. of the untreated sample is placed in the left-hand compartment of the Nessleriser. Stand Nessleriser before a uniform source of white light, preferably a north window. Allow the two treated cylinders to stand for any period between say 20 minutes and 60 minutes and then place in turn in the right-hand compartment of the Nessleriser. The colours produced are matched against the standard disc which is rotated so as to bring the standard colours in turn over the left-hand compartment thus to obtain the corresponding colour values in terms of F. The difference between the two results gives the fluoride content of the sample in milligrams per litre (mg./l.) F.

If the "Excess-Al" is found to be deeper than the 0.0 standard of the disc this will indicate that too long a waiting period has been allowed. On the other hand if the colours corresponding to the higher values of fluoride have not developed sufficiently to come within the disc range a further period of standing time is required.

EXAMPLE 2

The following example indicates how the method may be used in a photometric procedure employing, for example, the EEL photoelectric absorptiometer manufactured by Evans Electroselenium Ltd., of Harlow, Essex, England. A convenient cell depth is 4 cm. Sensitivity may be improved by using an optical colour filter, for example, a green filter to give incident light of peak wavelength 5200 Angstrom units.

The instrument is first calibrated by measuring the optical densities of a series of standard colours prepared in a manner similar to that of Example 1. In the subsequent determination of the fluoride content of a sample of water it is necessary to measure the optical densities of a blank and of the sample after the colours have been developed therein by means of the procedures earlier described.

The following readings were obtained, for example, in the calibration of an EEL photoelectric absorptiometer using standards in which the colours were allowed to develop for 60 mins. at a temperature of 18° C. Cell depth was 4 cm. and a green light filter was used.

Fluoride mg./l. F 0.0 .2 .4 .6 .8 1.0 1.2 1.4 1.6
Optical density 0.44 .41 .38 .34 .29 .25 .21 .17 .14

The reagents were similar to those used in Example 1 except that in the subsequent determination of fluoride in an unknown sample the alum-borate mixture was replaced by the following alum-sodium chloride mixture—

80 g. $\text{Al}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$; 20 g. NaCl

Two 50 ml. portions of the sample of fluoridated water were taken and in the first was dissolved 0.10 g. of the

alum-chloride mixture. By that means the fluoride ions present were complexed thus providing a blank containing no reactive fluoride ions. Both portions were then treated with the acid-zirconium-alizarin reagent as before. After standing for 30 mins. at a temperature of 10° C. the following optical density readings were obtained by inserting the blank and sample in turn into the photoelectric absorptiometer using cell depth 4 cm. and green filter as in the calibration procedure—Blank 0.34, Sample 0.16.

By reference to a calibration curve in which the fluoride concentrations corresponding to the above standard colours were related to the corresponding optical densities it was possible to arrive by interpolation at the following values for blank and sample respectively—Blank 0.63 mg./l. F, Sample 1.48 mg./l. F. The difference figure indicated that the sample of water undergoing examination contained 0.85 mg./l. of fluoride in terms of Fluorine F.

Interference

Any traces of aluminum, in the form, for example of "residual alum" originally present in the water being tested will interfere to give low results. In these circumstances the test indicates only that proportion of the total fluoride content which remains in the form of simple fluoride ions. If the test is used for the purpose of controlling water fluoridation processes it is usually possible to obtain a sample blank of the water just before the point of fluoride injection in which case proceed as follows:

Place a 50 ml. sample blank of the "before-fluoridation" water in a 50 ml. Nessler cylinder and add sufficient sodium fluoride, preferably for convenience in the form of a standardized tablet, to give a concentration of 1 mg./l. F. Call this the "F-dosed" cylinder. Place 50 ml. of the "after-fluoridation" sample in a second Nessler cylinder. Call this the "sample" cylinder. To each cylinder then add 0.27 g. of reagent No. 2 and mix rapidly to dissolve. Thereafter proceed in the manner above described to obtain the respective colour values of the "F-dosed" cylinder and the "sample" cylinder. Take the difference between these two readings and add to or subtract from 1.0, depending on whether the sample readings is above or below the "F-dosed" reading. This final result then gives "total fluoride" suitably corrected, so long as the actual concentration of fluoride is not too far removed from 1 mg./l. F, for errors caused by the presence of traces of aluminum. In this procedure any fluoride naturally present in the water is not taken into account, the primary aim being to provide a reasonably interference-free check on the applied dose in water fluoridation.

EXAMPLE 3

A moderately soft surface-derived water was found, after a coagulation process using aluminum sulphate, to contain a residual Al content of 0.35 mg./l. To this water was added sodium fluoride in a dose of 0.9 mg./l. F. A subsequent determination of the fluoride content of the water thus treated, as a check on the correctness of the applied dose gave a figure of 0.7 mg./l. F thus indicating a probable analytical error of minus 0.2 mg./l. in a total figure of 0.9 mg./l.

In repeating the determination by the procedure above described wherein a standard amount of fluoride, for example 1 mg./l. F, was added to a "before-fluoridation" sample of the water the following results were obtained by matching against permanent colour standards.

	Readings, mg./l. F.	
	1st observer	2nd observer
Prepared standard of 1.0 mg./l.-----	1.14	1.17
Sample fluoridated at 0.9 mg./l.-----	1.03	1.03
Correction to subtract from sample reading.	0.14	0.17
Corrected sample reading-----	0.89	0.91

Thus the average check reading for an applied dose of 0.9 mg./l. F was 0.9 mg./l. F.

EXAMPLE 4

Phosphates behave similarly to aluminum in that they prevent the fluoride from responding fully in the test thus giving low results. Their behaviour is different, however, in that they have a much greater effect on the reagent when fluoride is absent than when it is present. Allowance for the interference when checking fluoridation doses is provided by using an "F-dosed" before-fluoridation sample in a procedure similar to that already given for the elimination of aluminum interference.

A moderately hard underground water was found to contain 2.5 p.p.m. of phosphate calculated as PO₄. To this water was added sodium fluoride in an applied dose of 1.1 mg./l. F. A subsequent determination of the fluoride content of the water thus treated gave a figure of 0.7 mg./l. F. indicating a probable analytical error of minus 0.2 mg./l. in a total figure of 1.1 mg./l.

In repeating the determination by the procedure above described wherein a standard amount of fluoride, for example 1 mg./l. F. was added to a "before-fluoridation" sample of the water the following results were obtained by matching against permanent colour standards.

	Readings, mg./l. F.	
	1st observer	2nd observer
Prepared standard of 1.0 mg./l.-----	1.18	1.22
Sample fluoridated at 1.1 mg./l.-----	1.26	1.32
Correction to subtract from sample reading.	0.18	0.22
Corrected sample reading-----	1.08	1.10

Thus the average check reading for an applied dose of 1.1 mg./l. F. was 1.09 mg./l. F.

Where as is usually the case, the extent of aluminum or phosphate interference is not of sufficient significance to require the supplementary procedure above mentioned the "Excess-Al" technique remains as a simple direct method for the determination of both natural and added fluoride.

I claim:

1. A method for testing water for evaluation of its fluoride content comprising

preparing a blank consisting of a further portion of the water, said blank being rendered substantially free from reactive fluoride ions by the addition of an amount of an aluminum salt sufficient to complex fluoride ions therein;

adding, both to a sample of the water and to said thus prepared blank of water predetermined proportions of a zirconium salt and a dye capable of reacting with the zirconium salt to produce a color complex which undergoes a color modification in the presence of fluoride;

and comparing the color developed in the sample with that developed in the blank in a colorimetric test for the fluoride content based upon the substantially constant difference in color intensity between the blank containing no reactive fluoride and sample containing fluoride while both blank and sample are at about the same temperature whereby precise timing of standing for color development and precise temperature control is avoided.

2. A method as claimed in claim 1 in which the aluminum salt added to the blank is ammonium aluminum sulphate.

3. A method as claimed in claim 1 in which said zirconium salt added to the blank and to the sample is zirconyl chloride.

4. A method as claimed in claim 1 in which said dye added to the blank and to the sample is Alizarin Red S.

5. A method as claimed in claim 1 in which said comparison step includes photometrically comparing the color intensities of the sample and the blank.

6. A method as claimed in claim 1 in which said comparison step includes matching the color intensities of the sample and the blank against permanent color standards.

7. A method as claimed in claim 1,

including the step of adding a standard amount of fluoride to a sample of water taken prior to addition of fluoride thereto causing said fluoride content, to provide said blank;

and correcting for said standard amount of fluoride upon color comparison, so as to provide a measure of any interference caused by aluminum salts or phosphors previously present in the water whereby determination of the fluoride content of the water may be made substantially free from interference by aluminum salts or by any phosphates present in the sample.

8. A method as claimed in claim 1 in which said predetermined quantities of the zirconium salt and the dye are added in prepacked form.

9. A method as claimed in claim 1 including the step of adding a predetermined amount of reagent to the sample in sufficient amount to prevent interference from the acid radical of the aluminum salt.

10. A method as claimed in claim 9 in which the reagent added to the sample for preventing interference with the color formation by the acid radical of the aluminum salt is sodium borate or sodium chloride.

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