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(54) METHOD AND INSTRUMENT FOR AMPEROMETRIC MEASUREMENT OF
 THE FREE CHLORINE CONTENT IN A SOLUTION

(71) We, BERNARD SAUNIER of 16 avenue Gros Malhon, 35000 Rennes, France and ANTOINE DERREUMAUX of 19, Boulevard de Beausejour 75016 Paris, France, citizens of the Republic of France do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be described in and by the following statement:

This invention relates to the chemical analysis of a solution containing chlorine in the form of "free chlorine" (HOCl and OCl^-) and in combined form, in particular chloramines.

Such an analysis is carried out in particular on water treated with chlorine for disinfection and sterilisation. In the presence of ammonia and organic matter, chloramines form in proportions which are sometimes large and it is important to know accurately the residual free chlorine content, which is much more active than chloramines.

A method currently used is amperometric analysis, carried out directly on the water, by means of electrodes one of which is made for example of copper, the other of platinum, silver or carbon; the electrodes are subjected to a specific potential difference and immersed in the solution; a current is produced whose strength is in proportion to the chlorine concentration.

This method is applied to the determination of the total chlorine concentration. The addition of an iodide and a buffer at pH 4.0 before the passage between the two electrodes liberates the iodine with transformation of the various forms of chlorine into chloride. The diffusion current observed at the indicating electrode is a direct and accurate measurement of the iodine concentration, from which the chlorine content is deduced.

The instrument operates with retention of its calibration for several weeks or even several months, and no polarisation film forms on the electrodes.

If it is wished to determine the free chlorine content, a direct amperometric analysis must be made, without using an iodide as a reagent and without buffering, so that only free chlorine is involved in the formation of the diffusion current.

Unfortunately, it is found that the presence of chloramines, even at low rates, gives assay results with a large error, which is explained by the fact that some discharge of chlorine ions occurs from the chloramines. Moreover, a polarisation film forms on the surface of the electrodes, which upsets the calibration of the instrument.

At present, therefore, there is no means of making a continuous, accurate and reliable amperometric analysis of the free chlorine content in water containing chloramines, especially when the content of the latter is high.

The object of the invention is to provide a simple method making it possible to carry out such an analysis.

According to the present invention there is provided a method of measuring the free chlorine content in a solution containing chlorine in free and combined forms, comprising the steps of subjecting a first sample of the solution to a first amperometric analysis including the addition of an iodide to the said first sample, adding to a second sample of the solution a chemical compound which reacts selectively on the free chlorine contained in the said sample to convert it into a chloride, subjecting the second sample to a second amperometric analysis including the addition of an iodide to the said second sample, and determining the difference between the results of the first and second amperometric analyses.

The additional analysis measures the combined chlorine concentration, particularly as chloramines, and the free chlorine content is calculated by difference between the total chlorine and combined chlorine contents.

The invention further provides an amperometric measuring instrument which can be used for carrying out the above method, and includes means for carrying out the two analyses in parallel, means for calculating the difference between the results of said two analyses to obtain a direct indication of the free chlorine content, means for periodically interrupting the intake of solution into the instrument, and means for displaying, during each period of interruption, the indication of free chlorine content obtained at the end of the preceding measurement period.

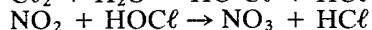
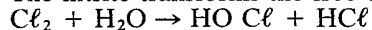
Other features and advantages of the invention will be clearly apparent from the following description of an example of implementation of the method.

This example is described with reference to the single figure of the accompanying drawing which is a skeleton diagram of an instrument in accordance with the invention.

The instrument includes an electromagnetic fluid valve 1 which controls the intake of water for analysis to two pipes 2 and 3.

In pipe 2, the water first receives, through a regulating electromagnetic fluid valve 4, a nitrite contained in a container 5.

The nitrite transforms the free chlorine into chloride as follows:-



However, it virtually does not react with the chloramines. The chlorine content in the chloramines is then measured. For this purpose, the solution may be buffered to pH 4.0 by adding a solution of acetic acid and acetate contained in a container 6, adjustment being carried out by means of an electromagnetic fluid valve 7. Potassium iodide contained in a container 8 is then introduced by means of a regulating electromagnetic fluid valve 9. The measurement is carried out by means of a standard amperometric cell 10 which supplies a current I_1 to an electronic calculating device 11.

In pipe 3, the total chlorine content in the water is analysed direct by the standard method.

The buffer, if present, is injected through an electromagnetic fluid valve 12, and the potassium iodide through an electromagnetic fluid valve 13 and the measurement is carried out by means of an amperometric cell 14, which supplies a current I_2 to device 11. The calculating device calculates from the values of I_1 and I_2 , the difference (proportional to $I_2 - I_1$) between the total chlorine and combined chlorine contents, i.e. the free chlorine content. Digital or analog display or recording of the result is effected at 15.

The two pipes end at the drain, through an electromagnetic fluid valve 16.

In some applications, e.g. for analysing the water in a swimming pool, since the concentrations evolve slowly, it is useful in order to reduce reagent consumption to operate the instrument intermittently only. For this purpose, the instrument comprises a timer 17, which controls the opening of the electromagnet fluid valves for example for one minute every two to five minutes.

The content measured just before a period when the electromagnetic fluid valves are open continues to be displayed during the ensuing closed period. At the next open period, a further measurement is made. Ten to thirty seconds are needed, at each opening, to stabilise the system. During this time, the measurements are not taken into account, the content measured just before the preceding closure continuing to be displayed or recorded.

Other chemical compounds which react selectively on free chlorine may be used and, in particular, cyanates or phenols, at the rate of 5 to 2000 mg per litre of water to be analysed and preferably of the order of 50 mg/l.

The table below permits a comparison to be made of results of analyses made respectively with diethyl-p-phenylene diamine (DPD), by means of a standard analyser and by means of the analyser described above. The chlorine contents are indicated in mg/l. The DPD measurement serves as a control. It can be seen that, in experiments 1 and 2, in the presence of chloramine contents 7 to 15 times higher than the free chlorine content, the standard-type analyser responds mainly to the combined chlorine, whereas the analyser described indicates the free chlorine content with acceptable accuracy.

Table

| 5 | | DPD | | Standard analyser | | Analyser described | | 5 |
|----|--------------|----------------------|-----------------------|----------------------|-----------------------|----------------------|-----------------------|----|
| | | Free Cl ₂ | Total Cl ₂ | Free Cl ₂ | Total Cl ₂ | Free Cl ₂ | Total Cl ₂ | |
| 10 | Experiment 1 | 0.5 | 4.0 | 2.0 | 3.6 | 0.3 | 3.6 | 10 |
| | Experiment 2 | 0.2 | 3.2 | 1.5 | 3.3 | 0.3 | 3.3 | |
| | Experiment 3 | 1.0 | 2.5 | 1.4 | 2.4 | 1.1 | 2.4 | |
| 15 | Experiment 4 | 2.4 | 2.9 | 2.5 | 2.8 | 2.4 | 2.8 | 15 |

WHAT WE CLAIM IS:

1. A method of measuring the free chlorine content in a solution containing chlorine in free and combined forms, comprising the steps of subjecting a first sample of the solution to a first amperometric analysis including the addition of an iodide to the said first sample, adding to a second sample of the solution a chemical compound which reacts selectively on the free chlorine contained in the said sample to convert it into a chloride subjecting the second sample to a second amperometric analysis including the addition of an iodide to the said second sample, and determining the difference between the results of the first and second amperometric analyses.
2. A method, according to claim 1, wherein said compound is a nitrite.
3. A method, according to claim 1, wherein said compound is a cyanate.
4. A method, according to claim 1, wherein said compound is a phenol.
5. A method, according to any one of claims 1 to 4, wherein said compound is used at the rate of 5 to 2000 mg per litre of solution.
6. A method, according to any one of claims 1 to 4, wherein said compound is used at the rate of about 50 mg/litre of solution.
7. An instrument for carrying out the method claimed in any one of claims 1 to 6, comprising means for carrying out the two analyses in parallel, means for calculating the difference between the results of said two analyses to obtain a direct indication of the free chlorine content, means for periodically interrupting the intake of solution into the instrument, and means for displaying, during each period of interruption, the indication of free chlorine content obtained at the end of the preceding measurement period.
8. A method of measuring the free chlorine content in a solution containing chlorine in free and combined forms, as claimed in claim 1, substantially as described herein.
9. An instrument, for carrying out the method claimed in any one of claims 1 - 6 and 8, substantially as described herein with reference to the accompanying drawing.

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