Water Monitoring in drinking water Plants

The Comparison Between On-Line TOC Analysis and the Permanganate Oxidation Method

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Introduction

The role of the plants providing water is not restricted to the collection of water from areas where abundantly available and then distribution to the consumer.

In reality, it involves a serious commitment to the guarantee of water which is high quality.

For this reason, drinking water facilities make use of conditioning plants which are equipped with chemical laboratories that perform all relative analyses which then allow the plant to properly treat the drinking water before distribution to the consumer.

The analyses normally made by the chemical laboratory concern parameters such as pH, conductivity, turbidity, residual chloride, and most importantly, the concentration of organic substances.

This latter analysis can be carried out by the permanganate oxidation known in Italy as the Kubel analytical method which is a typical laboratory analysis - easy to perform without the use of instruments.

Drawbacks however include the preparation time required and the resulting limit of the number of possible daily analyses.

The time period required from sample extraction to results of the analysis is considerable.

There are process instruments on the market which are able to automate the analysis of the organic substance content (TOC) in water. These instruments, if placed in strategic points within the plant, can become a very important survey network for the management of the conditioning treatment.

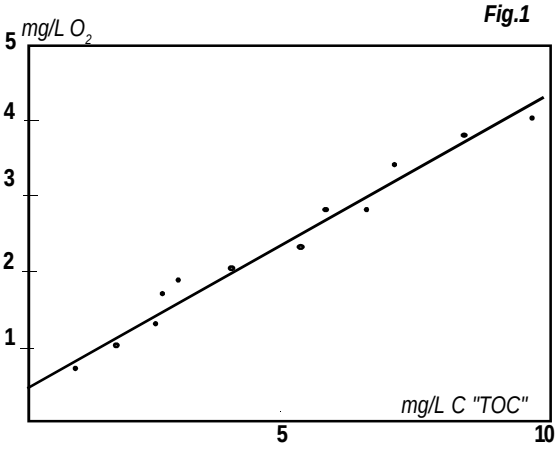

Fig.1

Comparison O_2/TOC made with TOC analyzer 0-10 mg/L

The instruments work ''on-line'' which means that they perform non-stop TOC analysis, and provide results very quickly.

In such a way it is possible to immediately recognize the presence of irregular organic loads in the water being tested. The plant can then arrange for the elimination of these irregularities.

We will now take a look in detail at the operating principle of an on-line instrument for the analysis of total organic carbon (TOC), as well as the analytical protocol of Kubel method.

Operating principles of an on-line instrument for the analysis of total organic carbon(TOC)

The operating principle of an instrument which performs the automatic analysis of TOC in water samples consists of chemical oxidation by high concentrated sodium persulfate (1,5 M), catalyzed by UV radiation.

This ensures the complete oxidation of all organic substances and thanks to the high concentration of sodium persulfate, desegregation of particles and macromolecules is also possible.

The concentration of CO_2 produced during oxidation is indicated by an infrared reading.

This output is correlated with the organic carbon content.

Analytical protocol of the Kubel method

The Kubel method consists of indirect titration.

An excess of potassium permanganate is added to the water being analyzed and this salt becomes an oxidizing agent for the organic substances present in the sample.

By means of subsequent retro-titration, the potassium permanganate which has not reacted is determined and then consequently (indirectly) the concentration of the organic substances present, (expressed as mg/l of oxygen needed for oxidation) is also determined.

Analytical protocol:

Water which does not contain organic material (usually bi-distilled water, the second distillation made in the presence of potassium permanganate) must be used for the preparation of reagents and for rinsing.

Pure sulfuric acid diluted 1:3, potassium permanganate 0,01 N and pure oxalic acid solution 0,01 N are used for the analysis.

TOC	O_2	TOC	O_2
1	0,85	1,35	0,85
1,90	1,1	2,70	1,40
3,10	1,80	3,50	2
4,50	2,20	6,10	2,60
6,25	2,90	6,90	3
7,45	3,50	8,75	3,90
9,60	4		

table 1

5 ml of sulfuric acid and 10 ml (or more) of permanganate must be added to 100 ml of water sample.

After 7 minutes of boiling a violet color will appear, indicating the excess permanganate.

A volume of oxalic acid equal to the amount of the permanganate is added.

Part of the acid in excess will remain in the solution (an amount which is analogous to the permanganate used by organic substances).

The liquid fades. The oxalic acid in excess is then hot titrated by a potassium permanganate solution until a persistent pink color occurs. According to the volume of permanganate used, the mg/l of O_2, typical to the present organic substances, are known.

In fact 1 ml of 0,01 N permanganate equals 0,00008 gr of oxygen. The ml used in the reaction are multiplied by 0,08 and thus obtaining the concentration expressed as Kubel.

This analytical protocol is interfered with by water containing manganese substances or non organic reducing agents.

EXPERIMENT

TOC analysis in parallel to the Kubel method was performed on different water samples for a period of six months.

The purpose was to assess correlation between the two methods. TOC values were regularly taken and contemporary laboratory tests using the Kubel method were effected.

The TOC analyzer was set for different measurement ranges: 0-10 mg/l and 0-20 mg/l in order to evaluate different contents of organic carbon.

Results

Table 1 shows the TOC and Kubel oxygen values measured. They were used to draw the correlation curve shown in *figure 1*.

The measurement range of the TOC analyzer was set at 0-10 mg/l:

The equation for this curve is:

$$Y = 0,437 + 0,386\ X$$

with a standard deviation of 0,1378 and R= 0,9859.

A numerical value was verified which is the ratio of the O_2 Kubel and TOC which is approximately the calculated average:

$$O_2\ KUBEL\ /\ TOC\ =\ 0,47$$

During the analysis period, the water samples were heterogeneous - raw, treated, filtered or drinking water.

To verify whether this ratio is always valid and linear, a 0-20 mg/l TOC configuration of the analyzer was chosen for those water samples with a higher content of organic substances.

Table 2 indicates the TOC and O_2 Kubel values measured. These have been used to draw the correlation curve shown in *figure 2*.

table 2

TOC	O_2	TOC	O_2
1,37	0,90	1,70	1,30
2,05	1,40	3,70	1,90
4,80	2,25	5,40	3,30
6	4	7,38	4,30
7,50	4,60	8,40	5,80
8,80	6,20	9	6,20
9,90	7,60	12,60	8,10
14,90	9,70		

In this case as well the results are satisfactory.

The related curve equation is:

$$Y = - 0,058 + 0,674\ X$$

The standard deviation is 0,464 and R = 0,9859.

The ratio of O_2 Kubel and TOC verified is:

$$O_2\ KUBEL\ /\ TOC\ =\ 0,67$$

Conclusion

Drinking water monitoring is essential as much as for public health protection as for compliance with laws.

It is widely recognized, in fact, that the organic substances present in water are the forerunners of halogen derivatives.The ratios between O_2 Kubel and TOC within 0-10 mg/l and 0-20 mg/l measurement ranges are typical for each range - linear and constant.

Therefore when the measurement range is predetermined, it is possible to carry out TOC on-line measurement and obtain, with adequate precision, an immediate reference to the corresponding Kubel oxygen value.

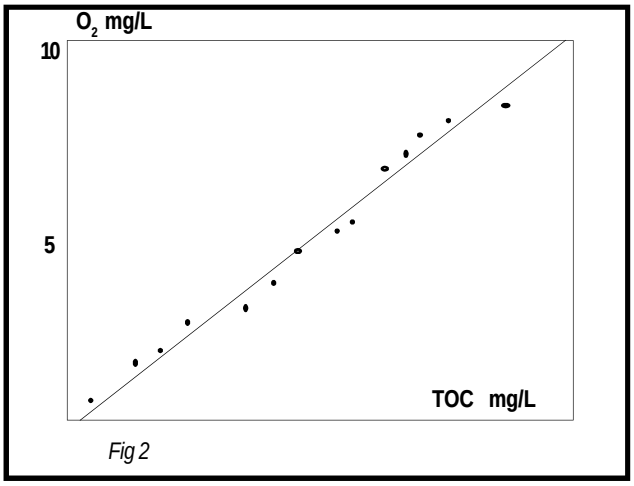

Fig 2