



DRINKING WATER CHLORINATION





Index

1.	Introduction	3
1.1	Water for human consumption	3
2.	Chlorination	7
2.1.	Chlorine and its by-products	7
2.2.	Chlorine chemistry	7
2.3.	Chlorine demand	10
2.4.	Chlorination: dose and contact	12
2.5.	Analytical methodology	14
2.6.	Determination of continuous chlorine	16
2.6.1	Colorimetry	16
2.6.2	Amperometry	17
2.7.	Chlorination protocol	19
3.	Chlorination equipment	20
3.1.	Pre-chlorination	22
3.2.	Storage- maintenance	23
3.3.	Post-chlorination	25



1. INTRODUCTION

Drinking water is a necessary but limited resource. In spite of the fact that water is the most abundant and common substance on earth – it covers 71% of its surface -, 97.3% of it is contained in the oceans. Of the 2.7% remaining water, about 2.1% is located in the polar caps and in glaciers, and only 0.61% is liquid fresh water. Of this, about 0.60% is to be found in the underground aquifers layers, difficult to reach, and only a 0.009% represents surface fresh water (rivers and lakes). Furthermore, only a 0.003% of the total is fresh water available for home use. That means that, if the total amount of water on Earth were a 100 litre container, only half a tea-spoonful water would be available for human consumption.

Water source	Water volume in cubic kilometres	Total water percentage
Oceans	1,321,000,000	97.24%
Ice layers, glaciers	29,200,000	2.14%
Underground water	8,340,000	0.61%
Fresh water lakes	125,000	0.009%
Inland seas	104,000	0.008%
Soil humidity	66,700	0.005%
Atmosphere	12,900	0.001%
Rivers	1,250	0.0001%
Total water volume	1,360,000,000	100%

Source: Nace, U.S. Geological Survey, 1967 and
 The Hydrological Cycle (leaflet), U.S. Geological Survey, 1984

From the above it can be deduced that drinking water is a very valuable and limited resource, and that it must be consumed and managed carefully. It is of the utmost importance to reduce its consumption and to try as far as possible to reuse it.

1.1 WATER FOR HUMAN CONSUMPTION

Water supply to the population can be done from two well differentiated sources:

- Surface waters: lakes, rivers, reservoirs... They are exposed to the environment and therefore they are liable to be polluted. For this reason it is necessary to have an in-depth processing before they are suitable for human consumption. This is usually carried out by the agencies in charge of operating the water resources.

- Underground waters: wells, springs... These are more difficult sources to exploit, as they are not as accessible as surface waters. Their origin is surface water which reaches the aquifer by natural filtration through the several earth layers. This system of natural filtration allows the purification of water to take place. However, in order to be considered drinking water, it must meet certain physical, chemical and microbiological conditions. Besides, on the long term the aquifer layers may also become polluted and because of this often it is necessary to process these waters (even if not so intensively as in the case of surface waters).

The pollution sources of water may be natural (rain, rotten vegetable material, soil erosion...) or man-made (cattle farming, sub-products of industrial activity, home waste...), but both give as a result water which does not comply with the necessary requirements to be considered drinking water.

The basic processes in the treatment of water involve several stages: coagulation, flocculation, particle separation (sedimentation/floatation), filtration and disinfection (chlorination/ozonisation). In several of these stages chemical products are added to the water flow to be treated, and it is at this point that ITC, S.L. can help you to do the correct dosage and control with its wide range of pumps and components.

In the case of waters whose quality has been checked and found to be apt for human consumption, such as many underground waters, and some surface waters which comply with Annex II of *Ministerial Order of 11 May 1998 of the Spanish Government, on basic quality features which must be present in the running surface waters meant for the production of drinking water*, in order to be classified as Type A1, their processing before human consumption consists of a simple physical treatment (such as filtration) followed by a disinfection process. In the case of Type A2, it is necessary to carry out a normal physical treatment, a chemical treatment and disinfection. For Type A3 it is necessary to make intensive physical and chemical treatments, followed by refining and disinfection.

ANNEX II

Parameter	Unit	Type A1	Type A2	Type A3
pH	-	(6.5-8.5)	(5.5-9.0)	(5.5-9.0)
Colour	Pt scale	20	100	200
Suspended solids	mg/l	(25)	-	-
Temperature	°C	25	25	25
Conductivity (20°C)	µS/cm	(1000)	(1000)	(1000)
Nitrates (*)	mg/l NO ₃ ⁻	50	50	50
Fluoride	mg/l F	1.5	(1.7)	(1.7)
Dissolved iron	mg/l Fe	0.3	2	(1)
Manganese	mg/l Mn	(0.05)	(0.1)	(1)
Copper	mg/l Cu	0.05	(0.05)	(1)
Zinc	mg/l Zn	3	5	5
Boron	mg/l B	(1)	(1)	(1)
Arsenic	mg/l As	0.05	0.05	0.1
Cadmium	mg/l Cd	0.005	0.005	0.005
Total chromium	mg/l Cr	0.05	0.05	0.05
Lead	mg/l Pb	0.05	0.05	0.05
Selenium	mg/l Se	0.01	0.01	0.01
Mercury	mg/l Hg	0.001	0.001	0.001
Barium	mg/l Ba	0.1	1	1
Cyanides	mg/l CN ⁻	0.05	0.05	0.05
Sulphate (**)	mg/l SO ₄ ²⁻	250	250	250
Chloride (**)	mg/l Cl	(200)	(200)	(200)
Surfactants	mg/l	(0.2)	(0.2)	(0.5)
Phosphate (*)	laurylsulfate mg/l P ₂ O ₅	(0.4)	(0.7)	(0.7)
Phenols	mg/l phenol	0.001	0.005	0.1
Dissolved or emulsified hydrocarbons (after extraction in petroleum ether)	mg/l	0.05	0.2	1
PAH	mg/l	0.0002	0.0002	0.001
Total pesticides	mg/l	0.001	0.0025	0.005
COD	mg/l O ₂	-	-	(30)
Dissolved oxygen	% saturation	(70)	(50)	(7)
BOD5	mg/l O ₂	(3)	(5)	(3)
Kjeldahl nitrogen	mg/l N	(1)	(2)	4
Ammonia	mg/l NH ₄ ⁺	(0.05)	1.5	(0.5)
Chloroform extractable substances	mg/l dry	(0.1)	(0.2)	(50000)
Total Coliforms (37°C)	u/100ml	(50)	(5000)	(20000)
Faecal Coliforms	u/100ml	(20)	(2000)	(10000)
Faecal Streptococci	u/100ml	(20)	(1000)	-
Salmonellae	-	None in 5l	None in 1l	

(*) In shallow lakes which renovate slowly

(**) Unless more appropriate waters are available for consumption.

Figures in parentheses are to be considered indicative desirable provisional values.

Of all the treatments we have mentioned above, in this document we shall consider disinfection only. In this process the aim is to destroy or make inactive the pathogens which are to be found in water, mainly bacteria, viruses and protozoa. In the case of water of Type A2 or Type A3, these pathogens are eliminated mainly in the process of the physicochemical treatments, but still they are not sufficient to ensure the total harmlessness of water.

The disinfection treatments may be physical (gamma rays, X-rays, UV rays, heat sterilization, etc.) or chemical (heavy metals, acids or alkalis, halogens, ozone, permanganate, etc.); the chemical means being the most used ones. Among the chemical reagents, chlorine and its by-products are the most used disinfection agents the world over, and therefore we shall study them more in-depth.

The values of residual chlorine are controlled by several bodies, and depend on the final destination of water. Therefore, the recommendation for drinking water is that the free residual chlorine be between 0.5 and 1 ppm, while in the case of swimming pools and spas it should be kept between 1.5 – 3.0 ppm. However, these values are in general, and each competent body determines its own. In the case of the Generalitat de Catalunya it is specified that the value of residual chlorine must be between 0.2 and 0.6 ppm in all the stages of the distribution network.



2. CHLORINATION

2.1 CHLORINE AND ITS BY-PRODUCTS

The use of chlorine as a disinfection agent started at the beginning of the 20th century and became the finishing process of filtration, which was already being widely used. The chlorine by-products most regularly used for the disinfection of water are: gaseous chlorine, sodium hypochlorite, calcium hypochlorite.

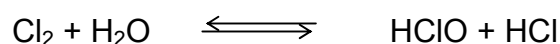
Chlorine (Cl₂) is a poisonous gas, heavier than air, yellowish green in colour. It is a very oxidizing product which reacts with quite a number of compounds. In the presence of humidity it is extremely corrosive, and for this reason the pipes and the materials in contact with it must be made up of special alloys. The chlorine vapours are irritating when inhaled and may cause serious injury to those exposed to high concentrations of the vapours. Therefore chlorine must be handled by specialized personnel and it is necessary to have very effective control and alarm systems. For this reason it is advisable to use hypochlorites in solution or in solid form.

Sodium hypochlorite (NaClO) in solution is a disinfectant used since the 18th century, and is popularly known as bleach. Industrially, it is obtained through the reaction of gaseous chlorine with a solution of sodium hydroxide. After the reaction, aqueous solutions of a greenish yellow colour are obtained, which have a given concentration of active chlorine per litre. It is sold in dissolutions with a 3 to 15% concentration in weight. Sodium hypochlorite is a very powerful and unstable oxidizing agent. So much so, that a solution of 100 grams of active chlorine per litre, after having been stored for three months, may contain 90 grams or even less.

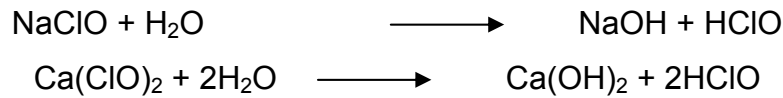
Calcium hypochlorite (Ca(ClO)₂) is a white solid with contents of 20 to 70% active chlorine. It is highly corrosive and may catch fire when in contact with some acid materials. However, it shows two advantages with respect to sodium hypochlorite: a higher chlorine contents and a greater stability. To use it, it is diluted in water to obtain a solution with an easier to handle concentration, for example 2%.

2.2 CHLORINE CHEMISTRY

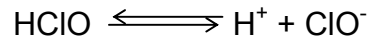
When Cl₂ is dissolved in water, it rapidly hydrolyses and produces hypochlorous acid and hydrochloric acid.



In the case of hypochlorites, there is a dissociation of both salts as per the following equations:



So, in any of the cases: chlorine, sodium hypochlorite and calcium hypochlorite, finally hypochlorous acid is produced, which is actually the disinfecting agent. However, this is dissociated according to the following equilibrium:



This equilibrium is ruled by the following constant:

$$K_a = \frac{[\text{H}^+][\text{ClO}^-]}{[\text{HCIO}]}$$

Whose approximate value is $3.2 \cdot 10^{-8}$.

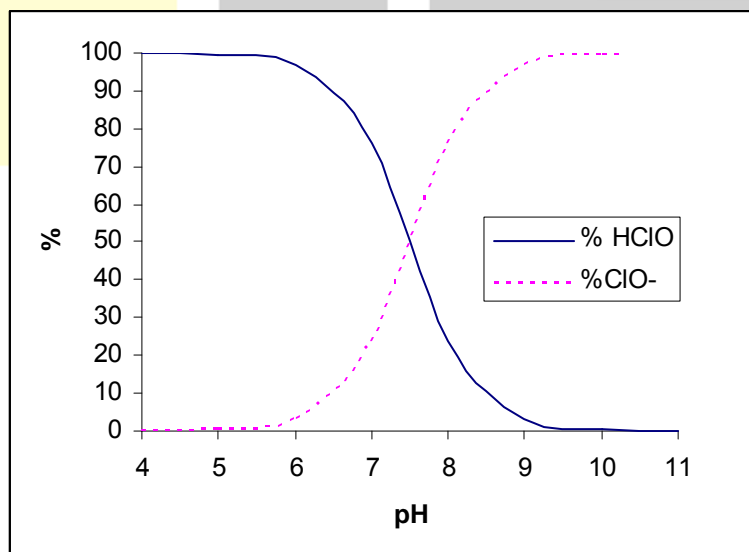
If we carry out the minus logarithm of the expression:

$$-\log K_a = -\log[\text{H}^+] - \log \frac{[\text{ClO}^-]}{[\text{HCIO}]}$$

Taking into account that $-\log X$ is known as pX , the expression will be:

$$pK_a = pH - \log \frac{[\text{ClO}^-]}{[\text{HCIO}]}$$

In the following graph the distribution of each one of the species according to their pH can be observed.



In the graph it can be clearly observed that between pH 6 and pH 9 both agents co-exist, while with pH values below 6 and above 9 it is considered that only one agent exists. With a pH value equal to the pK_a of the hypochlorous acid (pK_a ≈ 7.5), we can observe that the HClO and ClO⁻ concentrations are the same, which can be easily deduced from the previous expression.

The hypochlorous acid is a much more effective disinfectant than the hypochlorite ion. This might be related to the lack of charge in the hypochlorous acid molecule. Since it is a neutral molecule, it would be easier for it to penetrate the bacterial wall, and therefore to have a germicide activity. Under the circumstances, and taking into account what we have seen up to now, it is easy to understand the different activity of hypochlorite as a germicide agent in the presence of different pH values. So with a pH below 7.5 the amount of hypochlorite needed to disinfect water is much lower than the amount needed to disinfect that same water with a pH above 7.5.

Besides its application as a disinfectant, chlorine and its by-products have been found useful also for:

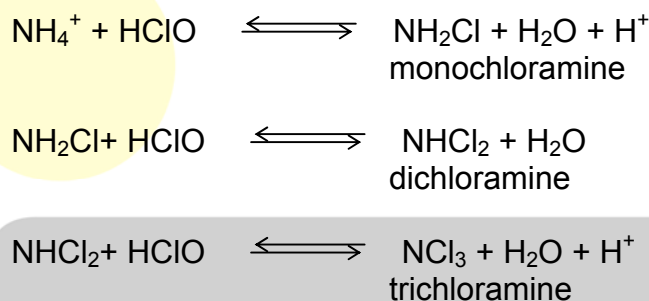
- Control of odours and tastes
- Prevention of algae growth
- Iron and manganese removal
- Destruction of hydrosulphuric acid
- Elimination of organic dyes
- Improvement of coagulation through silica

In the following table we show briefly some of these uses and their typical doses.

Application	Dose	Optimum pH	Reaction time	Effectiveness
Iron	0.62 mg/mg Fe	7.0	< 1h	Good
Manganese	0.77 mg/mg Mn	7-8 9.5	1-3 h minutes	Slow kinetics
Biological growth	1-2 mg/l	6-8		Good
Odour/taste	Variable	6-8	Variable	Variable
Colour removal	Variable	4-6.8	Minutes	Good
Zebra mussels	2-5 mg/l 0.2-0.5 mg/l		Shock level Residual level	Good
Asiatic clams	0.3-0.5 mg/l		Continuous	Good

One of the drawbacks in the use of chlorine and its by-products is that it reacts with a lot of organic matter, thus producing trihalomethanes (THM), many of which have been shown to be toxic or carcinogens. Another drawback is the production of chlorophenols in waters which contain phenols, which would give rise to bad smells.

Chlorine reacts also with ammonia dissolved in water, thus producing chloramines. These products have also a certain disinfecting power, even if about 25 times less effective than free chlorine. However, their permanence in water is long and sometimes they have been used as a reserve of residual chlorine. They have two great drawbacks: they may give rise to smells and tastes, and they are chronically potentially toxic.



Another chlorine by-product, which is used for disinfection, is the chlorine dioxide (ClO_2). It is as effective as the chlorine/hypochlorite, and not so sensitive to the changes of pH as far as its disinfecting activity is concerned. Besides, it does not combine with ammonia or with much organic matter, which prevents chloramines and other by-products with unpleasant tastes and smells to appear. However, it is a gas ten times more toxic than chlorine gas, and is explosive in the air in concentrations of 8-12%. Also, as a reagent it gives rise to chlorite, whose threat to human health is uncertain.

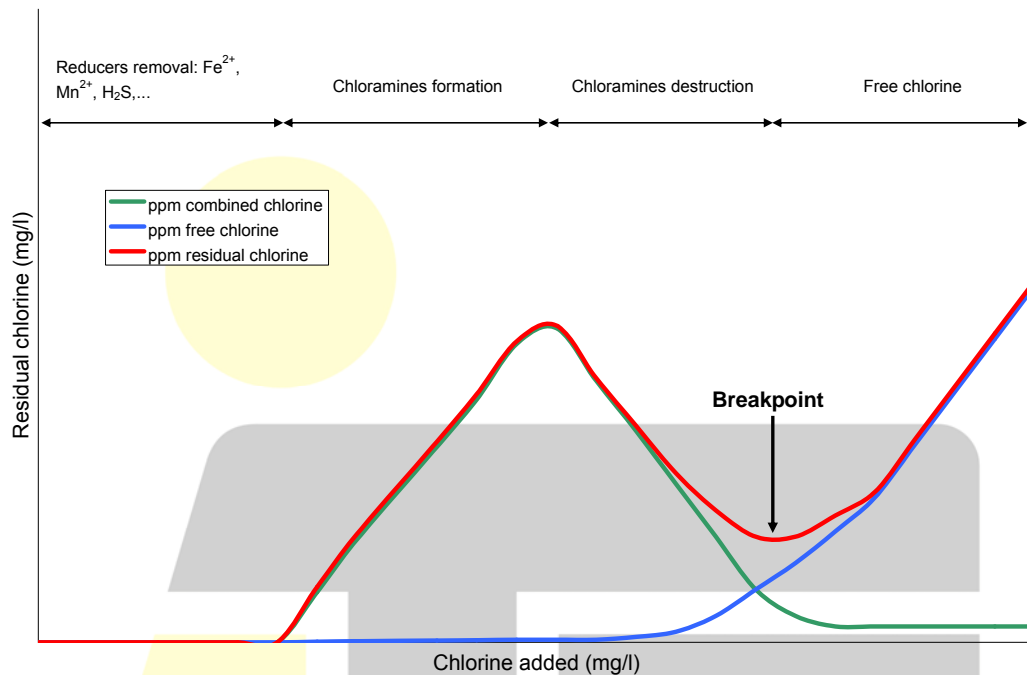
2.3 CHLORINE DEMAND

From all the above it can be deduced that chlorine (and its by-products), besides reacting with micro-organisms, it does so also with other products dissolved in the medium: organic matter, iron, manganese,... For this reason, in order to have a given level of residual chlorine, the amount which must be added is quite higher than the residual value obtained.

For all these reasons, before deciding the dose of chlorine to be used for disinfection, the chlorine demand must be determined, that is the amount of chlorine which is consumed before the residual value appears.

In the following figure we show the variation of the residual chlorine in terms of the added chlorine for a general hypothetical case:

- In the first stage, the oxidation of reducing substances, mainly inorganic ones, takes place: Fe^{2+} , Mn^{2+} , H_2S ,... All the hypochlorite added is consumed, whereby there is no available chlorine.
- After these substances have been destroyed, a stage would start in which chlorinated compounds would form, mainly chloramines, which would act as residual chlorine, thereby granting a certain disinfecting character to the system.



- When all the ammonia and the organic amines have reacted with the chlorine, after the curve reaches its maximum, there starts a stage of destruction of these chlorinated compounds produced in the previous stage. Even if more chlorine is added, no increase in the amount of available chlorine is observed, but a decrease instead, because both the existing residual chlorine and the added hypochlorite are consumed. In the following equation this effect can be observed:



Therefore, in this stage the disinfecting capacity of the system is reduced.

- After the breakpoint all the added chlorine stays as free chlorine. Therefore, it is considered that from this point on both the disinfection and the elimination of organic matter oxidable through the chlorine, have taken place and the water has a certain value of free residual chlorine.

The chlorine demand is the difference existing between the amount of chlorine applied to water and that of free available chlorine. Therefore, it can be

considered that the chlorine demand approximately fits the dose where the breakpoint is reached.

Free residual chlorine may appear as Cl_2 , HClO and/or ClO^- , depending on the working pH, and therefore it corresponds to the sum of these three compounds.

2.4 CHLORINATION DOSE AND CONTACT

Following all the above, we have already the bases to discuss more in-depth which parameters allow us to decide when water has been correctly treated. As we have seen, chlorination is right whenever we find values of residual chlorine above those of the breakpoint (they meet approximately the values of the free residual chlorine). The quantities of free chlorine recommended by the pertinent bodies for drinking water are between 0.5 and 1.0 ppm, and between 1.5 and 3.0 ppm for swimming pools.

However, it is free chlorine, that is to say, this quantity is not the added chlorine, since a part of it has been consumed by substances which are present in water (chlorine demand).

Up to now we have not taken into consideration at all the reaction speed of chlorine (hypochlorite) with micro-organisms. In this respect it is necessary to define the Ct concept, which is the product of the concentration of hypochlorite available (i.e. free chlorine) by the contact time between chlorine and the micro-organisms, in order to ensure the desired disinfection. The Ct value depends on the relevant micro-organism and the water temperature. Besides, as we have seen before, the activity of hypochlorite is highly influenced by pH, this means that, in terms of disinfection, it is not the same to have 5 ppm with pH 7 than to have them with pH 8. For this reason, Ct depends also on the water pH. In the following table we show an example of Ct. It can be observed that these values depend also on the concentration of available chlorine.

The Ct product is stated as mg·min/l, which means it has dimensions of concentration per time.

Giardia Cysts inactivation at 20°C									
Chlorine concentration (mg/l)	pH 6.5			pH 7.5			pH 8.5		
	90%	99%	99.9%	90%	99%	99.9%	90%	99%	99.9%
0.6	15	30	45	21	43	64	31	61	92
1.0	16	31	47	22	45	67	33	65	98
1.4	16	33	49	23	47	70	34	69	103
1.8	17	34	51	25	49	74	36	72	108
2.2	18	35	53	26	51	77	38	75	113
2.6	18	37	55	27	53	80	39	78	117
3.0	19	38	57	28	55	83	41	81	122

Example 1
 Water at 20°C
 pH 7.5
 99% inactivation
 Dose to be used 1 mg/l

Giardia Cysts inactivation at 20°C									
Chlorine concentration (mg/l)	pH 6.5			pH 7.5			pH 8.5		
	90%	99%	99.9%	90%	99%	99.9%	90%	99%	99.9%
0.6	15	30	45	21	43	64	31	61	92
1.0	16	31	47	22	45	67	33	65	98
1.4	16	33	49	23	47	70	34	69	103
1.8	17	34	51	25	49	74	36	72	108
2.2	18	35	53	26	51	77	38	75	113
2.6	18	37	55	27	53	80	39	78	117
3.0	19	38	57	28	55	83	41	81	122

So, the Ct = 45 mg·min/l

Therefore, the contact time recommended is obtained by dividing this value by the concentration

$$t_{\text{contact}} = 45/1 = 45 \text{ min.}$$

Example 2

We must treat the same water as in the previous example, but we use a dose of chlorine of 3 mg/l.

In this case Ct = 55, a higher value than the previous one, but

$$t_{\text{contact}} = 55/3 = 18.3 \text{ min.}$$

Example 3

We must treat the same water as in **Example 1**, but now the water pH is 8.5.

In this case Ct = 65, a higher value than the previous one, and therefore

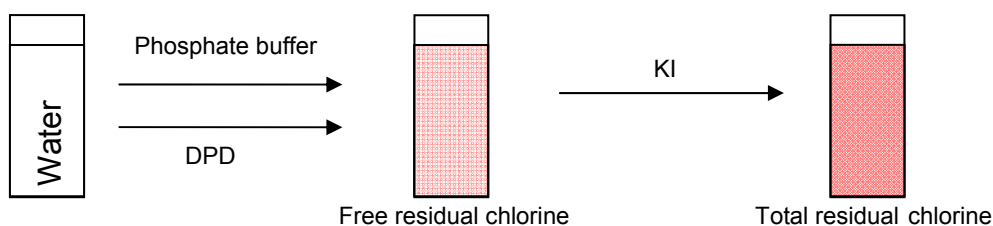
$$t_{\text{contact}} = 65/1 = 65 \text{ min.}$$

As it has been shown in the previous examples, the time for disinfection depends on many parameters and the fact of having a given concentration of free chlorine does not ensure an appropriate disinfection, if there is no strict control both of the contact time and of all the other factors: pH, temperature,...

2.5 ANALYTICAL METHODOLOGY

Usually determination of residual chlorine in water is made by reaction with o-toluidine or N,N-diethyl-p-phenylen-diamine (DPD). The first method is simple to carry out, but its disadvantage is that it does not allow a good differentiation between free residual chlorine and combined chlorine. O-toluidine reacts rapidly with free chlorine but after 5 seconds it also reacts with the combined chlorine; therefore they cannot be determined separately as it is almost impossible to carry out the analysis of each of them separately in such a short period of time. As we cannot determine if there actually is free chlorine (and its amount), we might have wrongly chlorinated water: high contents of combined chlorine but lack of free chlorine (it is to say, we would be dosing below the breakpoint). In addition, o-toluidine is a toxic product which is potentially carcinogenic.

Because of the above, it is more advisable to use DPD, which allows to differentiate between free and combined chlorine. DPD, with a pH between 6.2 and 6.5 produces a reddish colour which is proportional to the amount of free chlorine existing in the medium. Compared with a colour scale, free chlorine can be determined. On the same sample potassium iodide is added, which releases the combined chlorine and makes it react with the DPD, so finally we can get a reading of the total residual chlorine. By simple subtraction between the two figures, we may determine the combined residual chlorine.



This reaction may be monitored easily in the form of reaction kits, available through many suppliers. The use of a photometer, which is the instrument that takes the reading of colour intensity and allows relating it directly with the products concentration, is a more precise way to carry out this determination. Chlorine colorimetric determination by reaction with DPD is recognised as the standard method of EPA 4500-Cl G. There are devices in the market which allow carrying out these reactions on line, but they are not commonly used due to their cost and complexity.

As chlorine and its by-products are oxidizing substances, its presence in the medium produces a variation in the value of the water redox potential, (ORP, *oxidation-reduction potential*). Maintaining an ORP value within the assigned range ensures that the quantity of oxidant is appropriate for guaranteeing the disinfection process. However, there is not a direct relationship between the ORP value and chlorine concentration. It means that different types of water with different chlorine concentrations may have the same ORP value. In 1972 The World Health Organization adopted a value of 650mV as the appropriate value for purified water. The German Standards Agency adopted a value of 750mV for the disinfection of public swimming pools whereas the National Swimming Pool Institute proposed a value of 650mV for public spas.

The redox potential can be easily measured by means of electrodes which allow carrying out continuous readings in the treated water flow. Besides, they are very economical elements. All this makes the chlorination control through the redox potential very attractive. Nevertheless, we should be aware that the measurement of ORP can only be taken as a guidance system. Any change in the nature of water (even though maintaining constant chlorine level) leads to a change in the redox potential reading. Generally, the use of ORP is not recommended as a monitoring system for free chlorine, unless the water being treated does not change its characteristics, composition pH or temperature. Nor would it be an appropriate system in installations in which the exact level of chlorine contained in the water is important, such as drinking water chlorination.

The amperometric method is another system for chlorine determination. A sensor is introduced in the solution, in one of its electrodes the reduction of the chlorine present in the water is produced, which generates a current intensity that is proportional to the chlorine concentration. There are versions which allow determining free chlorine or total chlorine with differentiated characteristics which will be discussed in section 2.6. The great advantage of this method is that continuous readings may be carried out, which allows on-line control of chlorination with actual readings of the chlorine values.

2.6 CONTINUOUS DETERMINATION OF CHLORINE

Above, the most common analytical methodologies for the determination of free chlorine are shown. Today, the only methodologies recommended for continuous measuring are the colorimetric method with DPD and amperometric method. Next, these techniques are discussed.

2.6.1 Colorimetry

The base of the colorimetric method is the addition of reagents which produce a colour development. This method applicability at the laboratory level or as a single measurement is undeniable since the sequential addition of reagents is carried out on a static sample which is always the same. However, in continuous systems the aliquot to be analysed changes continuously.

Colorimetric systems for continuous readings are based on a timing sampling of water, and in each water sample all reagents are added. Therefore, one-time readings distributed over time are obtained, which gives us an idea of the system development but not the reading in each of the moments. This fact becomes even worse if we consider that addition and mixture of reagents and colour development takes some time, in this way reducing the sampling frequency. Another problem regarding kinetics is that the reaction speed depends on the medium salinity. Thus, in systems with considerable salinity variations it might happen that for the reaction period of time set, in some cases colour is developed and not in other cases.

For all these reasons, colorimetric equipments for continuous determinations are quite complex. Such equipments are provided with electrovalves for carrying out the sampling and pumps for adding the reagents. Automation of these components is also important as the reading accuracy depends on the correct coordination among them. Furthermore, in order to ensure correct readings, good maintenance of such components and avoiding blockage of the hydraulic circuits is required. It is obvious, but it is necessary to emphasize that there is a continuous consumption of reagents which need to be replaced at a certain frequency and whose exhaustion would produce the lack of reading.

It is considered to be a destructive method. Water samples analysed cannot be used again as reagents developing heat have been added. This is an important detail for drinking water samples.

Finally, it is worth noting that this system cannot be used with systems working under pressure as the optical part, which is the most delicate part, could be damaged.

To summarize, we could conclude that the colorimetric system is the reference system but its adaptation to continuous reading systems is not well solved.

2.6.2 Amperometry

The amperometric measuring system, despite being conceptually more complex, is easier to be installed than the colorimetric system. It is simply a sensor consisting of several electrodes on whose surface chlorine reacts producing a current flow. There are several technologies applied to this type of measurement. They are described below.

Galvanometric sensor

The electrode system consists of two electrodes Cu and Pt (Au). Between those electrodes, a voltage appropriate for chlorine reduction appears. In fact, it would be equivalent to a galvanic cell producing a voltage which corresponds to chlorine reduction. Thus, it is a voltage which is spontaneously generated and it is totally uncontrolled. Any type of change in the electrode environment such as pH, conductivity, sample composition..., may lead to changes in the voltage generated with the subsequent change in the electrical response obtained. Because the surface of the copper electrode is being continuously oxidized, changes in its composition would also lead to the modification of the voltage generated. For this reason, it is essential to always keep the surface clean and habitually cleaning abrasive systems (brushes or glass balls which are accelerated by the water speed) are used, which are not always 100% effective. Due to this operation mode, a continuous loss of the electrode mass is produced, being necessary to be replaced when they are worn. Equipments are often out of calibration because it cannot be guaranteed that the electrode system is always under optimal operating conditions.

Closed-cell potentiostatic sensor

In order to control the working voltage, it means working at constant potential (=potentiostatic), a reference electrode needs to be used to allow adjusting the voltage applied, depending on the changes observed in the medium. In this way, the measurement is much more stable than in the case of the galvanometric sensor.

To prevent soiling of working electrodes, the entire electrode system is separated from the reading media through a selective membrane which allows discriminating between different types of analytes with the same reading media. The cell, in which the electrodes are immersed, contains a support electrolyte which allows chlorine to be diffused from the water to the electrodes. Composition of such electrolyte changes continuously due to the continuous flow of matter inwards. Then, it needs to be often replaced.

A problem associated to the use of membranes is its plugging. If the membrane is plugged, the analyte cannot reach the electrode system and the correct response will not be obtained. This is the reason why it is not advisable to use this type of sensors in dirty waters.

On the other hand, resistance to pressure and depression of this type of membranes is low and frequently break.

Open-cell amperometric sensor

With the objective to solve the limitations previously described, cutting-edge sensors have been developed which allow to operate under specially complex conditions.

This type of sensor is not protected by a membrane and therefore problems arising from its use are avoided. In contrast, working electrodes are exposed to the medium at all times and therefore they are susceptible to soiling. However, the use of an electrochemical cleaning system, during which the working potential is changed in order to produce an electrochemical reaction, allows the electrode surface returning to its original state.

ITE has developed its own sensor, which is based on this technology, for the determination of free chlorine in all types of water, both drinking water and process water with a maximum concentration of 3 mg/l and a pH between 6.5 and 9.0.



2.7 CHLORINATION PROCEDURE

Generally speaking, a chlorination procedure can be established which follows several stages:

1. Estimating the chlorine demand or breakpoint. This will allow us to determine the dose of chlorine to be supplied in order to attain a full disinfection of water.
2. Fixing the Ct value needed for work. This will allow us to work out the contact time between hypochlorite and the micro-organisms so that we may obtain disinfected water. Usually, the dosage of disinfectant is carried out in a tank in the distribution network, in order to allow the highest homogenization of water. The sizes of the treatment tanks must take into account the Ct parameter in order to allow a residence time suitable for the treatment. Generally speaking, it is considered that for a pH lower than 8, a contact time of 30 minutes is sufficient. It is recommended that the residence time of the water in the tank be less than 48 hours.
If the tank was already in use before starting the chlorination and it was smaller than needed, it might happen that the residence time of water was not sufficient, which would give as a result a bad disinfection. In such cases, in order to keep the Ct parameter it would be necessary to increase the treatment dose.
3. After disinfecting the water, it must be checked that the amount of residual chlorine in the farthest point of the supply network is within the standards fixed by the qualified bodies by using a chlorine determination kit. Should it be too low, the dose of chlorine supplied should be increased after the disinfection. On the contrary, if the dose is too high – as would be the case if the tank were too small- the addition of a reducer (such as sodium bisulphite or metabisulphite) would allow the elimination of residual chlorine to the necessary level.

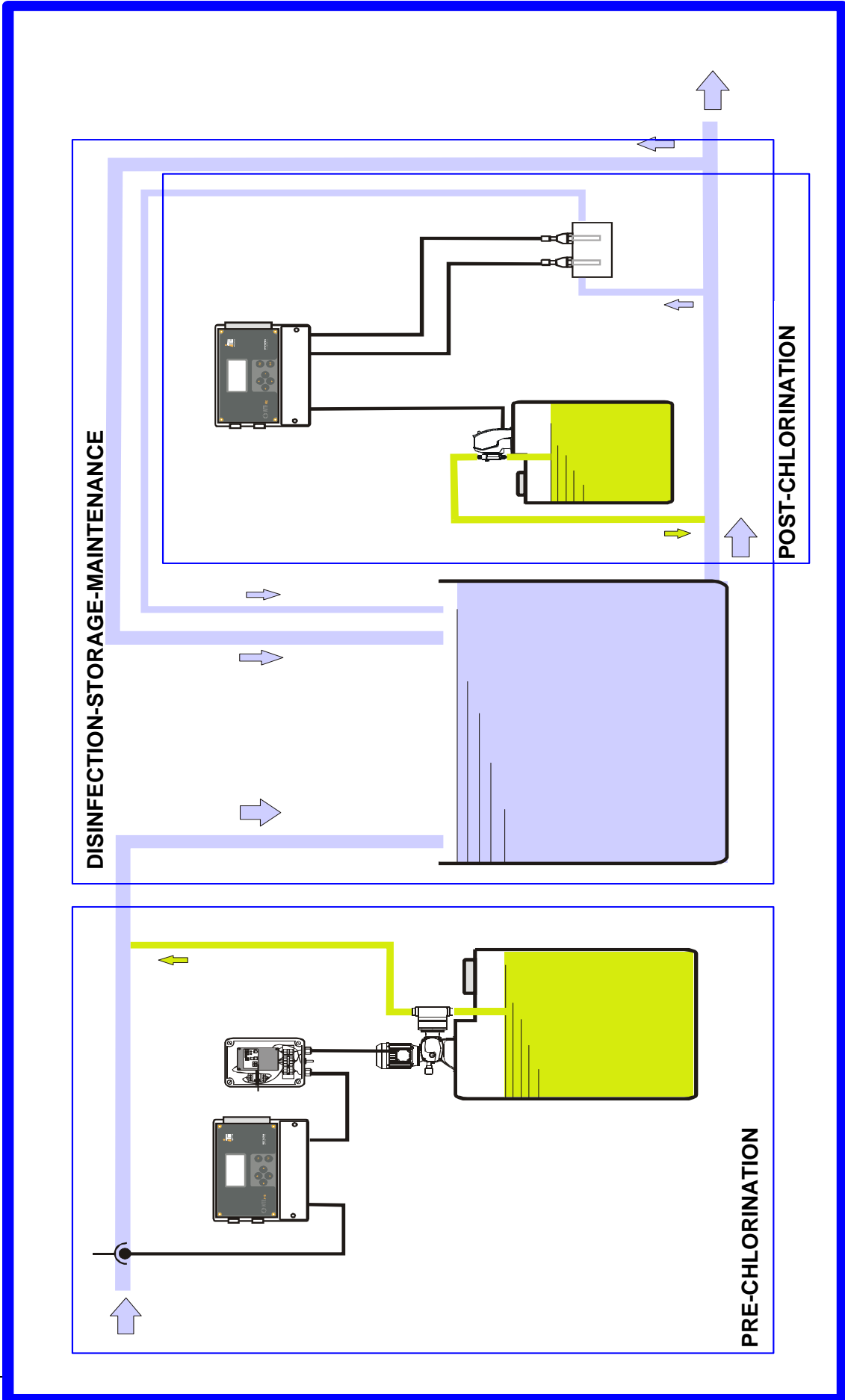
The above procedure is given only for guidance and is not to be considered as a fixed recipe to be followed. In case of doubt, we suggest to ask the advice of the pertinent Public Health bodies.

3. CHLORINATION EQUIPMENT

Over the disinfection process of water for human consumption, there are three stages, in which different procedures should be applied:

- A. **Pre-chlorination:** In this stage the amount of chlorine needed to exceed the breakpoint is added. This ensures that the level of residual chlorine is appropriate for farther disinfection. Usually, dosage of chlorine is carried out proportionally to the water flow to be treated.
- B. **Disinfection-storage-maintenance:** This stage takes place inside the tank and it is when disinfection as such is produced. If the residence time is high, it is necessary to maintain a residual level of chlorine to ensure that a possible new microbiological contamination has not been produced. To carry out the corresponding chlorine input, a monitoring and dosing system in the tank is needed. The same working methodology is applied to tanks acting as a buffer, which receive water that has already been treated or in a close system such a swimming pool.
- C. **Post-chlorination:** When water has come out from the tank and is distributed for being used, it may happen that an additional chlorine input is needed to ensure that the levels of residual chlorine are as required at the consumption points. These are re-chlorination stations in wide distribution networks. In this case, the on-line control equipment is of great importance as it will be the final responsible for maintaining the chlorine level.

Next, the nature of equipments to be used in each stage is described.



3.1 PRE-CHLORINATION

The main objective of this stage is the addition of the amount of chlorine needed to ensure that the breakpoint has been exceeded. Usually, this is the chlorination process stage in which a higher amount of chlorine is needed and therefore large pumps are used.

Chlorination is usually carried out in the line of water intake, before going into the disinfection tank. For this reason, the way water is delivered will set two different work methodologies with the objective to maintain the same proportion of chlorine in the water.

1.- Water entry at constant flow: In this case, in order to maintain the proportionality between the entry water and chlorine, it is only necessary to maintain a constant dosing flow. When water entry is produced, the dosing pump must be started up. Depending on the chlorine needs of the system, there are two types of models: **DOSITEC MD** (for flows up to 9l/h) and **DOSTEC** (for higher flows).

2.- Water entry at variable flow: If the water flow is not constant, a monitoring system, which allows adjusting the dosed flow in accordance with this variable, is needed. In this case, the system is more complex than the previous system because more elements are needed. Therefore, for chlorine flows lower than 9l/h, a water meter sending pulses to a **DOSITEC Q** pump, which works proportionally to these pulses, can be used. On the contrary, for higher flows the system consists of a flowmeter whose readings are managed by a **WTRpro Q** controller, which modifies the adjustment of the **DOSTEC** pump in order to maintain the previously set proportionality.

For correct chlorination at this stage, it is necessary that the chlorine demand (breakpoint) of the water sample is correctly determined. In installations where the water intake is carried out from a single origin, whose nature does not vary (such as a well or a spring), this parameter is clearly defined. However, if the composition of the intake water is variable (for instance, mixture of different origins), it is necessary to know the needs of each water sample and carry out the chlorination at levels exceeding the breakpoint of each sample. If not, the level of residual chlorine would be lower than needed if the intake water is rich in water with a high level of chlorine demand.

Another factor to be considered in the definition of the chlorine amount to be added is the dimensions of the disinfection/storage tank and the C.t parameter, because it will determine the needed level of residual chlorine for correct disinfection.

Thus, a general formula can be established to calculate the dimensions of the dosing pump:

$$Q_{Cl} = \frac{Q_{H_2O} \times (D + C)}{10 \times \%}$$

Where:

Q_{Cl} is the flow of hypochlorite in l/h

Q_{H_2O} is the flow of water to be treated in m³/h

D is the demand of chlorine of the water sample in ppm (mg/l)

C is the level of residual chlorine in accordance with the parameter C.t, in ppm

$\%$ is the percentage of purity of commercial hypochlorite

Example

It is necessary to chlorinate spring water with an entry flow into the treatment tank between 50 and 250 m³/h. The chlorine demand of the sample is 10 mg/l. Depending on the residence time in the tank (and according to the C.t tables), the chlorine dose needed is 1mg/l and it will be supplied from a trade product with 5% active chlorine content.

As the water flow is variable, it is necessary to estimate the pump flow at extreme conditions.

Thus, when the water flow is 50 m³/h, the calculation is

$$Q_{Cl} = \frac{50 \times (10 + 1)}{10 \times 5} = 11 \text{ l/h}$$

And for 250 m³/h

$$Q_{Cl} = \frac{250 \times (10 + 1)}{10 \times 5} = 55 \text{ l/h}$$

Therefore, to ensure the correct chlorination at this stage, a **DOSTEC** pump able to dose the 55l/h with a **WTRpro Q** is needed. This range of pumps can be adjusted up to 10% of its nominal flow. In this way, the needs in the two extreme cases would be met.

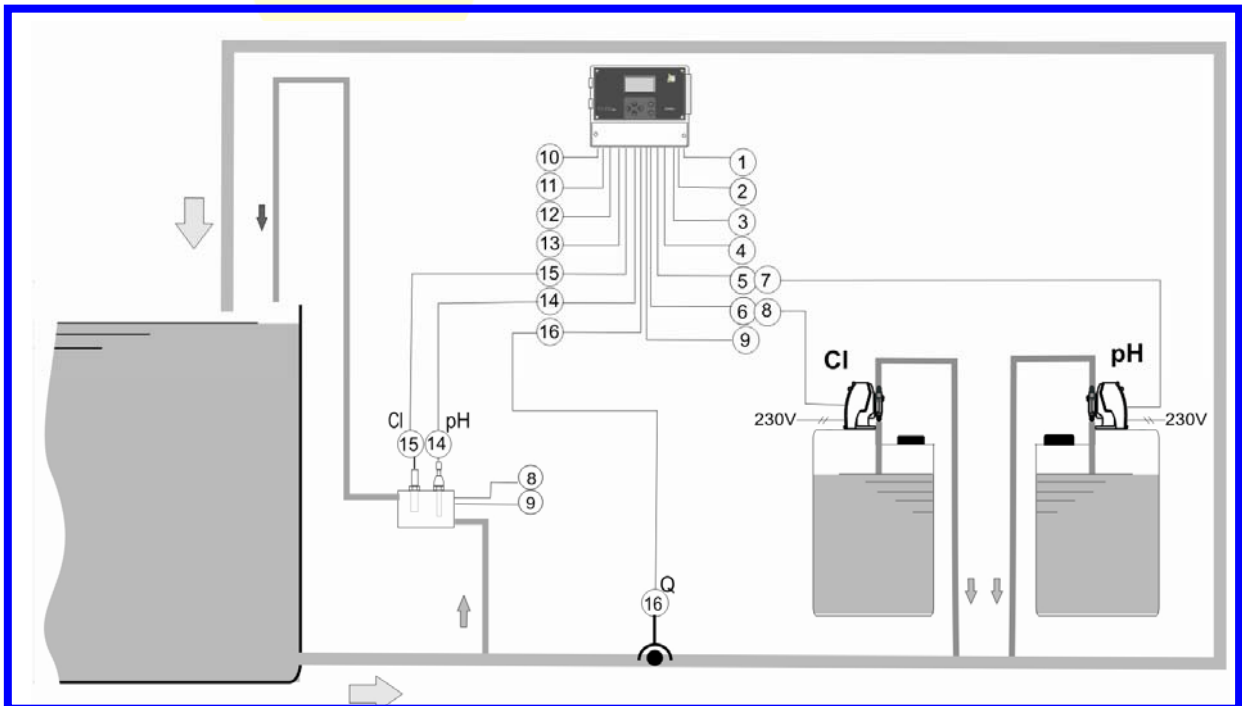
3.2 STORAGE- MAINTENANCE

When the minimum period of contact time has elapsed, it can be considered that the water has been appropriately chlorinated and therefore it is disinfected. The guarantee of this is the presence of a level of residual chlorine in the water stored in the tank. However, if the residence time is too long, chlorine losses, which endanger its disinfection, may be produced. For this reason, it is necessary to maintain a residual chlorine level not only during the disinfection process but also during storage. The chlorination process is carried out at this stage in accordance with a set point of residual free chlorine. This means that the chlorine content inside the tank is continuously monitored and chemical product additions are carried out to maintain the levels required.

This approximation is similar to the management of a water tank which acts as a buffer with the aim to supply at high demand moments, such as hotels, factories... In this case, the water feeding the tank is consumption water which is duly chlorinated, but during its storage, the chlorine existing may disappear and supplementary intakes maintaining its level in accordance with the current regulation for human consumption waters are required.

The same equipment would be used for the maintenance of the chlorine level in swimming pools or in any other installation consisting of a tank (more or less large), which contains previously treated water and where it is necessary to maintain a specified level of free chlorine.

The material needed would include a monitoring and control equipment **WTRpro pH-Cl** for the free chlorine with the corresponding **chlorine and pH sensors** and a dosing pump **DOSTEC** or **DOSITEC**, depending on the flow to be supplied.



The equipment **WTRpro pH-Cl** would carry out the measurement of the amount of chlorine existing in the water at all times. As the reading of the chlorine sensors depends on the pH of the sample, it is necessary to carry out corrections of it considering the pH value. When the chlorine reading has been carried out, if the value obtained is lower than the set point required, the equipment **WTRpro** would start the dosing pump until reaching it. The additional chlorine supply would be controlled proportionally to the difference between the actual reading and the set point. In this way, the amount added would be lower as we were reaching the set point with the aim to minimize the overdosing. The control output may be a proportional relay or a 4-20mA

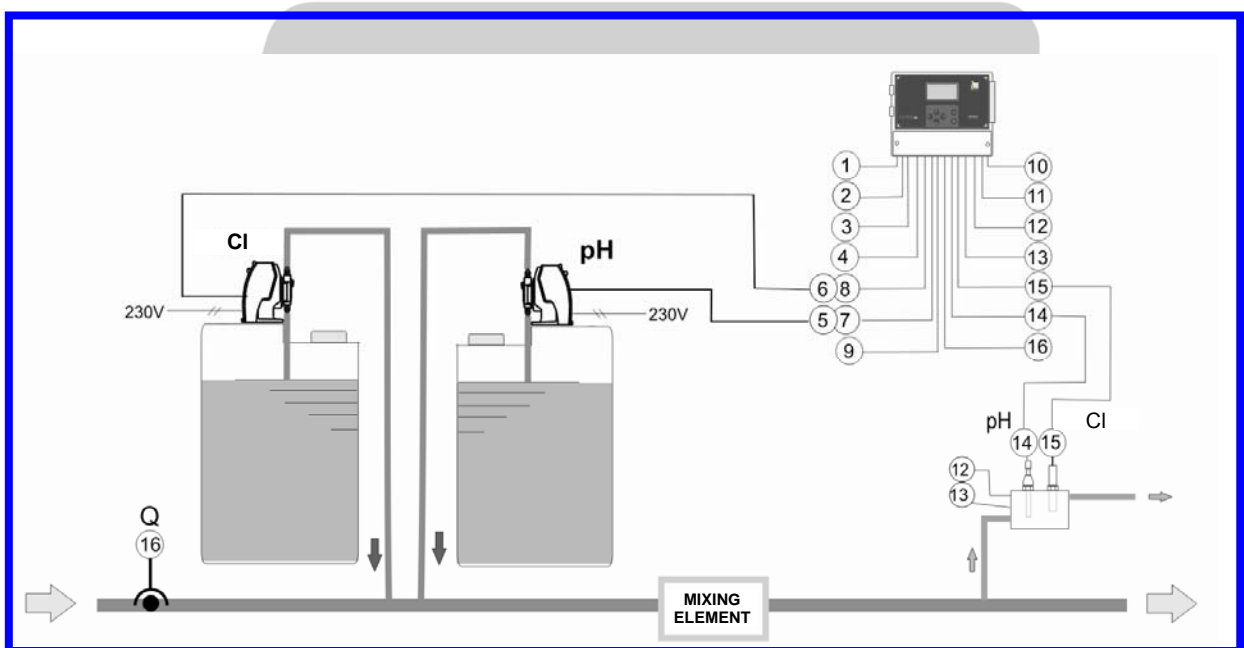
analogue signal. The first one would allow us controlling a **DOSITEC MD** pump, whereas a 4-20mA signal would be needed to control a **DOSTEC** pump.

As the chlorine supplies are always carried out on the same water sample, it is important to guarantee an appropriate homogenization of it in order to avoid wrong readings and wrong actuations which may result in overdosing.

3.3 POST-CHLORINATION

In certain occasions, an additional chlorine supply in the conduction may be necessary. It would be the case of a pumping and re-chlorination station in the main line of water distribution.

The material needed for the control and adjustment of the amount of free chlorine in an online system is exactly the same as in the case of dosing inside a tank: monitoring and control equipment for the free chlorine **WTRpro pH-Cl** with the corresponding **chlorine and pH sensors** and a dosing pump **DOSTEC** or **DOSITEC** depending on the flow to be supplied; but its starting up must be differently configured.



When dosing online, the amount of chlorine added is mixed with a specific portion of water because it flows continuously. Cumulative effect of successive additions inside a tank does not exist. Therefore, proportional approximation cannot be used to reach the set point, as it is in the case of a tank, because each portion of water treated goes only once through the treatment point. In these situations, a proportional-integral mathematical algorithmic (PI) is used, which is able to carry out on line adjustments.

The proportional-integral approximation is based on the continuous analysis of the effect of each chemical product addition. For this reason, in this case the

reading of chlorine content is carried out after the injection. In this way, the control equipment is able to analyse the effect on the level of free chlorine of the last chlorine addition and according to it, readjust the amount to be added in the next chlorine injection. For a PI process to be successful, it is necessary that all the other parameters affecting the reading (pH, water flow,...) remain constant because if not, changes in the chlorine reading due to these other parameters would be wrongly attributed to the changes in the amount dosed.

In many cases of on line post-chlorination installations, the amount of water going through the pipe is variable because it depends on the immediate consumption of water. For example, water consumption at dawn is much lower than in the early morning hours. If changes in the water flow are frequent, it may happen that the set point could not be reached at any time. In order to avoid this type of problems, ITC has developed special control equipments **WTRpro PIQ**, that in addition to the usual entries for pH and chlorine, include a connection port for a flowmeter. In this way, continuous reading of the immediate flow can be carried out and the amount of chlorine dosed immediately corrected.

Let us suppose the case of an installation with a $10\text{m}^3/\text{h}$ flow, where the free chlorine set point is 1mg/l obtained when the dosing pump is operating at 20% of its capacity. At a certain point in time, the flow circulating through the installation is instantly set at $20\text{m}^3/\text{h}$. If the control equipment is a **WTRpro pH-CI**, the change in flow is not detected and the dosing pump continues operating under the same conditions. As the circulating flow has doubled, the amount of chlorine present is set at 0.5mg/l . From this moment, the controller would start the process of approximation to the set point until reaching it again. However, if the equipment installed was a **WTRpro PIQ**, the change in flow would be detected immediately and the controller would modify the dosing pump adjustment according to it. Thus, in the example above, the pump would be automatically set at 40% and the set point maintained at 1mg/l all the time.