TECHNICAL BULLETIN

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Chlorine Testing and Terminology

Free Chlorine
Available chlorine
Free Available chlorine
Residual Chlorine
Bound Chlorine
Total Chlorine

The first three terms (**Free chlorine, Available Chlorine and Free available chlorine**) are often used interchangeably in industry because the method of determination is the same. They refer to the calculated chlorine value obtained using the normal iodometric titration procedure (add potassium iodide to the sample, acidify, and then titrate with sodium thiosulfate). For very low levels of chlorine (< 100 ppm) it is customary to use special chlorine indicator paper or swimming pool test kits.

Residual Chlorine usually refers to water which contains some available chlorine, but most of the original chlorine had been lost to the atmosphere or reacted with other materials to form either chloride ions (Cl-) or organochlorine compounds. Neither the chloride ion nor the organochlorines are detected in an iodometric titration.

Free chlorine is taken to mean either chlorine in its standard state – ie two chlorine atoms bound together and in a gaseous state (Cl2 (g)), but in Pool Chemistry technology it means the chlorine molecule surrounded by water molecules – ie Cl2 (aq).

When Chlorine dissolves in water, an equilibrium is established between chlorine in the gaseous state (Cl2(g)), chlorine surrounded by water (Cl2(aq), chlorine which has reacted with water to form hypochlorous acid (HClO (aq) and hydrochloric acid, and the hypochlorous ion (ClO-(aq). Although these are all distinctly different, they will all react in a normal titration with sodium thiosulfate solution, and the result is usually expressed as **total available chlorine**.

Bound chlorine is often used in connection with chemical compounds which can release chlorine. A typical example is chlorinated isocyanates used in swimming pools (eg SDIC, TCC). In addition, chlorine can be bound with “chlorine stabiliser” – isocyanuric acid. When free chlorine levels start to drop, this bound chlorine is converted to free chlorine fairly quickly to compensate for the consumed chlorine.

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Sometimes chlorine is bound in chemicals which only slowly release chlorine. A typical problem arises with chloramines formation from urine in swimming pools. Chloramines cause stinging eyes and some chloracne.

Excess stabiliser or chloramines present a problem in a swimming pool because the free chlorine levels are low (and less effective against bacteria) but the available chlorine (as determined by titration) indicates a higher level. **Superchlorination** will remove chloramines but excess stabiliser cannot be removed except by removing part or all the pool water.

When bound and free chlorine are present, the iodometric titration conditions are such that all of the bound chlorine (in swimming pool chemicals) is converted to free chlorine and all are measured as **Available Chlorine**. It is very difficult to distinguish in normal titrations between bound and free chlorine as these are usually rapidly inter-converted by equilibration.

Sodium hypochlorite is a solution of chlorine gas in sodium hydroxide solution and is often referred to as **liquid chlorine**. In this form, the gaseous (free) chlorine above the aqueous layer is lower in concentration and far less hazardous than the equivalent amount of chlorine in water only. The active species present is hypochlorite ion (OCl-) but the strength is customarily reported as available chlorine (Cl2).

The **iodometric titration** conditions are acidic and, regardless of whether the original species present is Cl2, HOCl or OCl-, all are converted to iodine and will react with the thiosulfate titrant.

Test Methods

Free chlorine may combine with the organic matter to produce chlorinated organics. These chlorinated organics may test positive when tested by the standard **OT** (orthotoluidine) or **DPD** (N,N-diethyl-p-phenylenediamine) chlorine test procedure. The advantage of test papers and tablets is that very low levels of chlorine can be easily detected.

A variation of the DPD method is the **DPD-FAS** method (FAS is Ferrous ammonium Sulfate). This enables both free and total chlorine to be measured, and the difference giving the combined chlorine.

The standard **iodometric titration** method is more cumbersome and less sensitive to low chlorine levels, and only gives the total available chlorine.

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A simple method for determining whether chlorine break-through readings are really chlorine or are false-positive readings.

If a positive chlorine reading is detected, take a second reading on filtered water using a 0.1-µm filter. If the filtered water is chlorine free, then the first reading was a false positive caused by chlorinated organic matter in the water.
Note: the filter should not be reactive to chlorine.

RO membranes. Naturally formed chloramines appear are in a form that is easily removed by the RO membranes. If present, it will be necessary to test the permeate and concentrate water of the RO unit.

Other Methods

Free chlorine can be measured by Colorimetric, Potentiometric and Polarographic instruments after they have been calibrated (readings are temperature and pH sensitive), but generally these only measure free chlorine.

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