Colour

An aesthetic objective of *≤15 true colour units* (TCU) has been established for colour in drinking water.

Definition and Measurement

The appearance of colour in drinking water is caused by the absorption of certain wavelengths of normal "white" light by dissolved or colloidally dispersed substances, by fluorescence in the visible wavelength region from substances that absorb "white" or ultraviolet light,(1) by the presence of coloured suspended solids, and by the preferential scattering of short wavelengths of light by the smallest suspended particles.(1,2) Colour measured in water that contains suspended matter is defined as "apparent colour"; "true colour" is measured in water samples from which particulate matter has been removed by centrifugation.(3,4) In general, the true colour of a given water sample is substantially less than its apparent colour.(4)

The colour of a water sample is measured by visual comparison with a series of standard solutions containing known amounts of potassium chloroplatinate and added cobalt (II) chloride; the amounts of the latter are varied to match the normal yellow to brown hue of the test water at a given location.(4) As the platinum–cobalt standard method was designed to analyse naturally coloured water, other methods are employed to measure colours originating predominantly from industrial wastes or coloured minerals.(4) Difficulty in comparing the colour of a public water supply with standard colour solutions may therefore be indicative of pollution. Methods based on chemical oxidation,(5) absorption spectrophotometry,(6–8) and colloid titration,(9) for example, can also be employed to estimate the concentrations of organic substances that may cause colour in water. In general, however, very poor correlations are obtained between chemical results and colour measurements for water from different locations.(1,10) This result should not be unexpected, as identical colours can be obtained by the standard method for waters containing different proportions of colouring agents(10); that is, the values obtained by the standard platinum–cobalt method are not specific.

One true colour unit (TCU), or platinum–cobalt unit, corresponds to the amount of colour exhibited under the specified test conditions by a standard solution containing 1.0 mg of platinum per litre.(4) Thus, a sample exhibiting a colour of 15 TCU has a closer colour match with a standard containing 15 mg of platinum per litre than with standards containing 14 or 16 mg/L. A colour of 15 TCU can be detected in a glass of water by most consumers, and 5 TCU will be apparent in large volumes of water, such as in a bathtub; few people can detect a colour level of 3 TCU.(11)

One major factor that affects the colour of natural surface water is pH. The increase in colour with increasing pH of the test sample is commonly referred to as the "indicator effect,"(1) and it is widely recommended that the pH of the sample be recorded together with the colour measurement to allow for this effect.(4) The alternative is that all colour measurements be done at a standard pH of 8.3.(12) Such standardization would be of value only in individual treatment plants, however, owing to the non-specific nature of the standard method.

Occurrence

Colour may occur in drinking water for any one or more of several reasons. It may be due to the presence of coloured organic substances originating in the decay or aqueous extraction of natural vegetation, such as in soil runoff(13); the presence of metals such as iron, manganese and copper, which are abundant in nature, are weathered from rock or corroded from distribution systems by water, and are naturally coloured; or the presence of highly coloured industrial wastes, the most common of which are pulp and paper and textile wastes.(14)

At least 90% of the drinking water supplied to Canadian municipalities is obtained from surface water sources.(15) The colour of surface water is predominantly due to organic substances of natural origin.(1) In general, hard surface waters are less highly coloured than soft waters,(6) and the organic:inorganic ratio in the total dissolved solids content of soft water tends to be higher than that in hard water. The colour of groundwater is usually due to its coloured mineral content. In some areas, especially those associated with limestone stratification, the colour of groundwater from both shallow(1) and deep(16) wells may be organic in nature.

Chemistry

Although much research has been performed on the nature of organic colour in water during the past 60 years,(17) important chemical information on these “colour bodies” is still lacking. The dissolved organic colouring material in water consists almost totally of humic substances,(1,18–20) and the gross characteristics of these substances are very similar in the surface waters of many different parts of the world.(1,6,18,21–23) The genesis of humic substances is still subject to conjecture.(24) Most of the humate content of water is probably derived from soil, but some of it is also produced by aquatic micro-organisms.(25,26) Dissolved humic substances isolated from water are predominantly fulvic acids(1,5,19,22); humic acid is an important constituent of sediments(27) and of the particulate matter in surface water.

Humic substances isolated from soil can strongly adsorb a variety of organic substances.(28,29) Part of this adsorption capacity is probably due to the presence of pore spaces, or voids, in these polymeric molecules(30); part may be due to the long lipophilic aliphatic side chain “building blocks” in humic substances; part is probably due to an affinity of certain adsorbates for the functional groups present in humic substances (ester, ether, carboxyl, benzene ring, etc.); and, for polar and charged adsorbates, part is probably due to the polyelectrolytic nature of the humate polymers.

The adsorption by humic substances of organic compounds — many of which are of concern because of their toxic properties — in amounts that can exceed their aqueous solubilities(31,32) is a matter of potential importance and merits further investigation. In addition, because of their polyanionic electrolytic properties, humic substances play an essential role in the dissolution, transport, and deposition of positively charged inorganic ions, the most important of which, from a public health viewpoint, are those of the heavy metals. Most metals will complex to a degree with humic substances in water. Complex formation can dramatically increase the solubility of the metal; for example, naturally occurring humic substances in water may render iron up to a billion times more soluble.(33) The detection of iron in highly coloured waters in amounts greatly in excess of its ionic solubility is probably due more to iron–organic complexes than to colloidally dispersed ferric hydroxide, as was commonly supposed. Mixed complexes with common anions are also known and include fulvic acid–iron phosphate complexes(34) and fulvic acid–copper citrate, phosphate and salicylate complexes.(35)

Some metals also form insoluble complexes with humic substances under certain circumstances. This phenomenon serves to precipitate them from natural water systems(36) and is exploited in the production of potable water from coloured surface waters.(14) In general, the order of precipitation of insoluble metal complexes decreases with the charge of the metal; thus, trivalent metals are 700 to 1000 times more efficient as coagulating agents than monovalent metals, and doubly charged metal ions are 30 to 60 times more efficient than monovalent metal ions.(14,28,29) Iron and aluminum, which are employed in drinking water purification, appear to be capable of forming insoluble bridged complexes between the metal and two or more molecules of fulvic acid; polymeric hydroxy-aquo forms of iron and aluminum may also be involved in the precipitation of humic substances from solution.(37)

The fate of complexed toxic metals during drinking water treatment is a particularly relevant question. The most prevalent view has been that, although toxic metals associated with the suspended solids content of water may be at least partially removed, dissolved trace metals are probably removed to a negligible extent during conventional treatment.(38) On the other hand, if certain toxic metals in solution are strongly complexed to coloured organic molecules, which are themselves removed during treatment, it might be the case that colour removal by precipitation could also affect the removal of toxic metals. Although a small amount of information is available that suggests that 30 to 65% removal of trace metals can be achieved by conventional water treatment plants,(39) the degree to which complexes are involved in this removal remains unknown.

Relationships with Other Water Quality Parameters

Colour is directly related to almost every other drinking water quality parameter. In general, these relationships are due to colour itself, which can interfere with the colorimetric analysis of some constituents of potable water; the formation of complexes or adsorption of some water constituents by the dissolved humic substances that colour comprises; reactions between humic substances and chemicals added during treatment; and the provision of nutrients to some micro-organisms by humic substances and their metal complexes. In addition, combinations of some of the above mechanisms are involved in the corrosion and incrustation of drinking water distribution lines.

Physical Characteristics

Although some of the older water quality literature claims that dissolved humic substances cause taste in water,(40) no recent research appears to have been done on this question. Highly coloured, polluted water will frequently have an associated objectionable taste, but the degree to which this association is causative is unknown.

In order for any substance to exhibit an odour, it must have an appreciable vapour pressure, and it is implausible that this could be the case for the polyelectrolytic, high molecular weight, dissolved humic substances. It is known, however, that the organic colouring material of water stimulates the growth of many aquatic micro-organisms,(25,26,41) some of which are directly responsible for the production of odour in water.

As humic acid and certain metal complexes of humic substances are poorly soluble at the pH of potable water, they will be responsible for a portion of the turbidity in a water sample. Another constituent of the suspended solids fraction of water is known to be a complex of clay particles with humic substances. Furthermore, as "dissolved" humic substances in water exist predominantly as colloidal dispersions, and as optical measurements of turbidity are influenced by particles in the colloidal size range,(2) the presence of colour in water will have an effect on the measurement of turbidity. It is also well known that the presence of moderate amounts of colour in certain types of raw water has an adverse effect upon the removal of turbidity by coagulation and sedimentation.(13) Laboratory studies have shown that the presence of fulvic acid lowers the optimum pH for turbidity removal and increases the amount of coagulant required to treat dilute clay suspensions(42,43); the coagulant dose and optimum pH for colour removal, however, are independent of the presence of clay.(42)

Microbiological Characteristics

Humic substances are generally regarded to be very resistant to the action of bacteria and higher micro-organisms in the environment,(28,29) and laboratory studies have confirmed this stability in water samples that were stored for months under conditions favourable to the growth of bacteria.(1,44) One recent preliminary study, however, has presented evidence for two different aquatic microbiological transformations of soluble humic substances; one of these processes appears to increase the colour of the water, whereas the other decreases it.(45) Several authors have reported that certain bacteria, fungi and higher micro-organisms are capable of utilizing humic substances as a source of energy.(44,46–48) Studies of other specific micro-organisms have shown that they are unable to utilize humic substances as a food source.(49) The most common colour problem of microbiological origin is the production of "red water." This phenomenon occurs because many genera of bacteria are capable of oxidizing iron (II) to iron (III), which precipitates from solution as the hydroxide and imparts a characteristic reddish colour to tap water. In severe cases, distribution lines have been blocked, or nearly blocked, by the action of these "iron bacteria." Similarly, a black discoloration may be imparted to drinking water by the action of bacteria that are capable of oxidizing dissolved manganese to its insoluble oxides. This colour problem occurs more frequently in groundwater than in surface water supplies.

A few investigators have reported the formation of coloured, humic-like substances by aquatic micro-organisms.(25,26) The proportion of colour in water that originates in this way is thought to be very small, however.(13)

The presence of organic colour in treated water that is disinfected by chlorination is one factor that can cause difficulty in maintaining a free available chlorine residual in distribution systems. Although this has been known since at least 1949,(40) it was not until the discovery(50,51) in 1974 of relatively large amounts of chloroform and other trihalomethanes in chlorinated water that the reaction of chlorine with dissolved humic substances was subjected to careful study. Since 1974, it has been established that the trihalomethanes are reaction products of chlorine (and adventitiously present bromine and iodine) with humic substances, and that conventional water treatment can remove most of the organic precursors from the raw water.(52,53)

Chemical Characteristics

It is well known that colour can interfere with the chemical analysis of many of the other constituents of water. It has been noted in *Standard Methods for the Examination of Water and Wastewater*, for example, that colour must be compensated for or removed in colorimetric analytical methods,(4) and the use of cupric acetate precipitation has been shown to be effective in removing the interference due to colour in standard colorimetric analyses for chloride, fluoride, nitrate (and nitrite), phosphate and sulphate.(54)

Non-colorimetric methods of analysis can be interfered with by colour because of the metal-complexing properties of humic substances. It is for this reason, for example, that samples for the determination of total hardness by the titrimetric method involving ethylenediaminetetraacetic acid (EDTA) must be ashed prior to analysis in order to completely oxidize organic material.(4) Specific-ion electrode methods for the analysis of metals in water, such as calcium and cadmium, give low results as a result of complex formation if humic substances are present.(4) Humic substances can also interfere with trace metal analysis when the sample is concentrated by extraction with an organic solvent that contains a complexing agent.(55,56)

Some of the other relationships between colour and chemical parameters include the following observations: that the bicarbonate alkalinity of water can be destroyed by humic substances(57); that total dissolved solids and organics may include humic substances; that humic substances can interfere with the analysis of methylene blue active substances(4); and that nitrilotriacetic acid (NTA) can form stable mixed complexes with several divalent metals and fulvic acids.(58) Phosphate also forms mixed complexes with fulvic acid and trace metals,(58,59) and one recent reviewer has suggested that all phosphate in water is complexed with humic substances.(60)

The relationship between corrosion and incrustation and the humic content of water is a complex and important one. Small amounts of humic substances (1 to 2 mg/L) aid in the deposition of a protective layer of calcium carbonate in distribution systems for mildly incrustive waters(14); however, larger amounts may be responsible for the deposition of flow-restrictive "humus mud" in distribution systems where lime is added as a post-treatment step for corrosive waters.(61) The presence of humic substances in water has differing effects, in kind and in degree, on the corrosion of iron, copper, aluminum and lead.(62,63) Water containing very little dissolved humic material can be more corrosive than water containing larger amounts. Distilled water at pH 7, for example, is more corrosive to lead than other types of water,(64) and activated carbon treatment, which removes humic substances from drinking water, has been related to increased corrosion problems in Germany in instances in which all of the humic substances have been removed.(64)

Severe chemical corrosion in distribution systems can also lead to the production of colour (and turbidity) at the consumer's tap. Red colours tend to be associated with iron, black colours with manganese and faint blue colours with copper corrosion.

Health Effects

Limits for colour in potable water have traditionally been based on aesthetic considerations. It has been noted, however, that provision of a supply of visibly coloured water may lead consumers to seek colourless, but possibly unsafe, alternative sources of drinking water.(65) Other health-related criteria include the previously discussed relationships between colour and trihalomethane production, removal of turbidity and interference with chlorine residuals.

Many beneficial human health effects have also been attributed over the years to the consumption of coloured water and to the use of humic preparations in the treatment of disease.(66) These beneficial uses include the treatment of rheumatic fever(67); the healing of skin defects(68); the stimulation of wound healing(69); and the prevention of swelling in battle wounds. Humic substances in water and sediments are also intimately involved with hydrotherapy and balneotherapy, which are respected and widely practised elements of European medicine.(70)

Few toxicological studies of organic colouring agents have been undertaken. The median lethal dose for intracardial application of humic acid in the rat was found to be 1127 ± 200 mg/kg bw; the lethal reaction was ascribed to the possible reaction of humic acids with serum proteins.(71) Male rats were supplied with drinking water containing 10, 100 and 1000 mg/L of a low ash preparation of soil fulvic acid for periods of up to 90 days; no significant changes in body weight, food and water intake, organ/body weight ratios or tissue histology were observed.(72) The same fulvic acid was also given daily to rats by gavage at a dosage of 1000 mg/kg for 14 days. No mortality occurred at this dose level, although the rate of weight gain was less than that in control animals, and slight changes were noted in some of the kidney enzyme concentrations.(72) In the most relevant study to date, humic material at two dose levels was fed to rats in their drinking water for periods of 19 to 35 weeks; the authors concluded that a safety factor of approximately 100 would apply to the human consumption of drinking water containing 2.5 mg of "humic acid" per litre.(66)

Very little study has been devoted to the comparative toxicities of trace metals and their humate complexes with reference to human health.(73) It has been shown that the acute mammalian toxicities of iron, lead, barium, silver, copper and zinc are substantially enhanced on intravenous injection as their humate complexes, but that orally ingested lead humate is at least 60% less toxic than lead acetate.(74) Large increases, from 50 to 100%, were found in the amounts of ionic material — calcium, magnesium, iron, manganese, zinc and sulphate — permeating the intestine in the presence of humic acid.(75) Unfortunately, the substances studied did not include toxic trace metals. No information has been published to date on the bioavailability to mammals of the humate complexes of toxic organic substances.

Rationale

1. Colour in drinking water may be due to the presence of coloured organic substances; the presence of metals such as iron, manganese and copper; or the presence of highly coloured industrial wastes, the most common of which are pulp and paper and textile wastes. Although the presence of colour in drinking water may be indirectly linked to health, its primary importance in drinking water is aesthetic. Experience has shown that consumers whose drinking water contains aesthetically displeasing levels of colour may seek alternative, possibly unsafe, sources.

2. Levels of colour above 15 TCU can be detected in a glass of water by most people.

3. The aesthetic objective for colour has therefore been set at ≤15 TCU. The provision of treated water at or below this limit will ensure rapid notification by consumers should problems leading to the formation of colour arise in the distribution system. In addition, interferences by colour in water treatment processes and analytical procedures will be diminished. The removal of excess colour prior to chlorination will also reduce

the production of trihalomethanes. Finally, limiting the colour in potable water will limit the concentrations of undesirable substances that may be complexed with or adsorbed to organic colouring agents.

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