SYMPOSIUM*
WATER

POTABLE WATER

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SOURCES

POTABLE water is obtained from a multiplicity of sources, but the ultimate source is always the sea, usually *via* evaporation, cloud formation and rainfall. The rainfall may either run off the surfaces on which it falls, giving rise to various surface water sources or may percolate into the soil, giving rise to various underground sources. Although this is the usual cycle of water supply, in some places of extreme water shortage or in emergency, potable water is obtained directly from the sea, either by distillation or by demineralisation with ion exchange compounds.

Collection of Rain

It is frequently imagined that the direct collection of rain will provide a very pure water, but this is very rarely the case. Rainfall will always collect dissolved gases and dust during its fall, particularly in industrial areas and must always be collected from a solid surface such as a roof, which even in remote country places may be a roosting place for birds and consequently be fouled by them. Such water will be very soft and probably plumbo-solvent so that lead piping, lead flashing and lead-lined tanks should be avoided. Collecting tanks should be watertight and fitted with close-fitting covers. Depending on the method of collection it may be necessary to filter and to disinfect such water.

Lakes

Lakes which may be natural or impounded in remote upland areas will vary according to the nature of the rock formation in the catchment area. Limestone areas will give rise to hard, alkaline waters, but insoluble rock formations especially if peat bogs are also present, will give rise to soft, acid waters which may be discoloured yellow or brown from the organic matter derived from the peat and are liable to be plumbo-solvent. In the absence of grazing animals, farms or villages with cess-pits or sewage systems draining into the catchment area, such sources should be bacteriologically pure. Growth of algæ is not likely to be troublesome owing to the absence of mineral salts in the water. Treatment of such waters may involve the addition of alkalis such as lime to neutralise excess acid, coagulation with alum to remove colour and treatment with chlorine primarily to remove bacteria. Elaborate filtration processes are not usually necessary as such waters are usually clear.

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Rivers and Streams

To obtain an adequate constant supply from rivers and streams it is usually necessary to abstract the water well below the source, by which time it has usually become polluted not only by natural surface drainage from the land through which the river flows, but from sewage effluents and industrial effluents. Twenty-five per cent. of the population of England and Wales now obtain water from rivers polluted in this way. Turbidity is liable to fluctuate widely with rainfall and such waters are usually hard.

This type of water cannot be used without careful treatment including storage, clarification and disinfection. Storage may serve three purposes; partial clarification due to settlement; bacterial improvement due to death of some of the polluting bacteria; and storage against drought. These advantages may be partially offset under certain conditions by some disadvantages. Water from polluted lowland sources will usually contain sufficient nitrogen compounds and dissolved salts to support the growth of algæ under suitable climatic conditions. Such growths will give rise to increased turbidity and colour with consequent filtration difficulties and to objectionable tastes derived either from the living cells or from their decomposition products. Control is facilitated by field observations and sampling to determine the best management of the reservoirs, sometimes helped by treatment with copper sulphate or, in the case of small reservoirs, with chlorine. Over suppression of one type of growth may lead to the appearance of a more objectionable type.

Under some climatic conditions thermal stratification may occur in deep reservoirs followed by de-oxygenation of the lower layers. When climatic conditions change, the de-oxygenated layers may mix with the rest of the water making the whole reservoir unusable for a time.

Clarification of stored river waters may be accomplished by filtration or chemical coagulation or a combination of the two. Filtration is frequently carried out in two stages, a rapid coarse filter followed by a slow finer filter, the rapid filter serving the purpose of prolonging the intervals between cleaning of the secondary filters and enabling a greater rate of filtration to be adopted. The rapid primary filters may take the form of coarse sand beds which are cleaned mechanically at intervals or may be rotary screens of fine stainless steel wire mesh which are automatically continually washed. Sand filtration improves the chemical quality of the water, but micro-straining is purely a physical process.

Secondary filters may take the form of large gravity-fed sand beds, where much of the filtration effect is dependent on the accumulation of an organic layer on the sand surface which may be cleaned by skimming manually or mechanically, or more recently by mechanical washing *in situ*. Secondary filters may also take the form of enclosed pressure filters containing sand, usually combined with alum coagulation, the precipitated aluminium hydroxide forming a filtering layer on the surface of the sand which is periodically washed by a scouring action or by rotation and inversion of the whole bed and container.

Clarification by coagulation with alum may be carried out without the need of a supporting sand bed. During the coagulation process

accompanied by stirring, suspended matter including some of the bacteria and algæ is trapped in the floc which then settles and is drawn off as a sludge. The process is usually a continuous one, the sludge forming a blanket through which the raw water passes, clear water overflowing at the top and sludge being drawn off at the bottom.

Sterilisation of river-derived water is usually achieved by chlorination or sometimes by ozonisation or, on a small industrial scale, by ultra-violet light. Chlorination and ozonisation will also remove some colour and taste by oxidation of the organic compounds causing these properties. The presence of much ammonia in the water will delay the disinfecting action of chlorine due to the formation of chloramines instead of free chlorine. The use of contact tanks is now usually advocated to ensure sufficient time for action between chlorine and bacteria to effect their destruction before the water passes into the distribution system. By the end of such contact time all the chlorine should have been deviated by the organic matter present, or if not, the excess can be removed with sulphur dioxide. Various types of apparatus are now available for automatic control of chlorine residuals.

Wells and Springs

Wells may be either shallow, sunk into the top pervious strata and collecting water from the immediate vicinity, or deep, sunk below an impervious stratum and collecting water possibly from considerable distances.

Shallow wells are very liable to surface pollution which may be intermittent and considerable care should be taken in siting and protective measures. Many are unsafe to use without filtration and disinfection. Various domestic types of apparatus are available for small installations.

Deep wells are usually of good bacteriological quality as the water usually has to travel considerable distances underground, being filtered on the way. Fissures and swallow holes in some rock formations may however provide access for gross pollution. Such waters are usually hard. Filtration is very rarely necessary. Disinfection with chlorine or ozone is usually carried out as a safeguard against sudden unpredictable pollution. Contact tanks are advisable to ensure adequate disinfection before distribution, but in the absence of organic pollution there will be little deviation of chlorine so that excess must be removed with sulphur dioxide before distribution.

POTABILITY

All statutory water undertakings are required to provide a supply of pure and wholesome water, but purity and wholesomeness are not precisely definable in scientific terms. Wholesomeness implies non-injury to health and absence of pathogenic organisms and toxic substances. As a chemically or physically pure water cannot occur in nature, purity implies pleasing to the senses, that is, absence of visible particles, turbidity, colour, taste and odour, and freedom from excessive amounts of substances in solution not normally detectable by the unaided senses.

Potability therefore implies physical attractiveness as well as safety. Such standards, however, are not satisfactory for all pharmaceutical purposes. All the sources described above can provide such a pure and wholesome water, but their suitability and ease of treatment for pharmaceutical purposes will vary.

BACTERIOLOGICAL QUALITIES

The most important function of the bacteriological control of potable water is to ensure freedom from the causative bacteria of so-called waterborne diseases, such as typhoid fever, paratyphoid fever, gastro-enteritis, dysentery and cholera. Cysts of amœbic dysentery and ova of intestinal helminths can also be carried by water and also presumably, the virus of poliomyelitis. All these organisms are of fæcal origin and their absence may be presumed with confidence by demonstrating the absence of the normal intestinal flora. These are the coliform group, the most important of which is *Escherichia coli* (*Bacterium coli*), the fæcal streptococci, of which the most important is *Streptococcus fæcalis* and anaerobic spore-forming organisms, of which the most characteristic is *Clostridium welchii*.

The Coliform Group

For waterworks control the organism normally sought is *E. coli* but from unknown sources or where interpretation of results is doubtful, enumeration of *Strep. fæcalis* and *Cl. welchii* is of value. Various culture media are used throughout the world for the primary detection of *E. coli*, but the one used for the standard method in Great Britain is MacConkey broth. This medium contains bile salt, which inhibits the growth of many of the common bacteria found in water, and lactose which is fermented by *E. coli* and other members of the coliform group, with the production of acid which is detected by an indicator change, and gas which collects in an inverted tube. Coliform organisms other than *E. coli* will also produce a positive result by this method. *E. coli* is much the most frequent type of coliform organism present in the human and animal intestine and is rarely found in sites free from excretal pollution. Other coliform types such as *Citrobacter freundii* (Intermediate types) and *Klebsiella aerogenes* (*Bact. aerogenes*) also occur in the intestinal canal, but in much smaller numbers. Outside the body these other coliforms have much greater powers of survival and even appear to be capable of multiplication under special conditions. In addition to being widely distributed in obviously fæcally polluted sites and in agricultural soils where their presence cannot be dissociated from manurial pollution, they can also be found in soil apparently free from fæcal pollution and in which *E. coli* is absent. The presence of *E. coli* in water denotes recent fæcal pollution; the other coliforms may indicate more remote pollution, but in some circumstances are of no epidemiological significance. *E. coli* can normally be distinguished from other coliforms by its ability to ferment lactose at 44° C.

It is usual to examine the water at all stages of purification from the raw

water before any treatment, to the final water as it reaches the consumer's tap. The frequency of examination of each stage will depend on the nature of supply, its liability to pollution and the stage in the purification process. Water passing into supply should be examined at frequent intervals, preferably daily, whereas raw or stored water need only be examined at less frequent intervals. Water sources not normally liable to pollution can be examined less frequently than those liable to pollution.

Streptococcus fæcalis

If a supply repeatedly gives a high coliform count in the absence of *E. coli* and their origin is in doubt, interpretation is facilitated by a search for *Streptococcus fæcalis* which is another organism undeniably indicative of fæcal pollution either of human or animal origin.

Clostridium welchii

Clostridium welchii, an anaerobic sporing bacillus is also a normal inhabitant in the human and animal intestine and is sometimes used as an indicator of fæcal pollution, but it has a different significance from the other fæcal organisms discussed, as its spores can survive for much longer periods and they are much more resistant to disinfection by agents such as chlorine. Their detection in a raw water in the absence of *E. coli* or *Strep. fæcalis* would be indicative of more remote fæcal pollution. It is for this reason that these organisms may still be found in a treated water derived from a polluted source, particularly at certain times of the year. It is not unusual to find them in 10 ml. quantities of water in London's river-derived supplies in winter. Their presence does not render the water unsuitable for drinking, but it does mean that it is unsuitable and dangerous to use for washing out syringes to be used for parenteral injections in the belief that it is sterile, or for the solution of tablets for hypodermic injection.

For further details of standard methods for the bacteriological examination of water, reference should be made to Report 71 of the Ministry of Health[1].

Colony Counts

In addition to examining water supplies for evidence of fæcal pollution, it is usual to attempt to obtain some information on the numbers of other bacteria present. The results will depend very considerably on the methods adopted and will be affected by the culture medium used and the time and temperature of incubation. No one combination of these conditions will be capable of permitting the growth of all the bacteria liable to be encountered.

As the method of counting depends on the ability of a bacterial cell to multiply into a visible colony in a nutrient medium, and that the bacteria initially giving rise to colonies may have occurred, singly, in pairs, chains, groups or dense clumps, not every individual cell will develop into a separate colony. It is therefore necessary when quoting colony counts to state the conditions under which they were obtained, and to express results as the number of colonies per millilitre.

An incubation temperature of 37° C. was chosen by most early workers as it was thought that organisms growing at that temperature would be of greater significance. Forty-eight hours has become recognised as the standard incubation time, although with river-derived waters there is usually little difference between 24 and 48 hours, whereas with shallow wells the difference might be considerable. The medium used as standard in Great Britain is a peptone yeastrel agar. Incubation for 3 days at 22° C. will give much higher results on river water, the ratio of the 37° C. to 22° C. counts being about 1 to 10. The ratio is often much lower on shallow well samples. The ratio is also lower after chlorination because normally only spore-forming organisms survive. A very much higher count will be obtained using various dilute nutrient agar media incubated at 22° C. for 15 days. Nutrients in such media are kept dilute to prevent colonies growing too large and interfering with each other. Such counts may be 100 to 1000 times as great as corresponding 37° C. counts.

Different types of water, all equally satisfactory for potable purposes may all have quite different colony counts. Such counts are not therefore of any direct value in themselves in assessing potability, but they are of considerable value once a series of counts has been obtained from any particular supply. Any gross variation from the normal count would then be of significance and its cause should be investigated. Water is used for many purposes other than domestic supply and for some manu-facturing, food-processing and pharmaceutical purposes, large fluctuations in colony counts are undesirable. Large numbers of chlorine resistant aerobic saprophytic sporing bacilli are liable to cause considerable nuisance in some food-processing industries although they may be of no significance for domestic purposes. For pharmaceutical purposes, the relationship between bacterial counts, extent of pollution of raw water and the presence of pyrogens needs further study.

Bacteriological Standards

Standards for the bacteriological quality of potable water have been given by the Ministry of Health[1] and the following recommendations have been obtained from the Ministry Report. Ideally all waters intended for drinking should show no coliform bacteria in 100 ml., and it should be the aim of every water undertaking to provide water of this quality. Many natural waters reach this standard and, since it is readily attainable by effective treatment, no chlorinated supply should fail to give this result. The appearance of coliform organisms in a chlorinated supply as it leaves the works should at once occasion misgivings as to the adequacy of the chlorination process.

The following classification is suggested by the Ministry of Health for non-chlorinated piped supplies.

		Coliform count per 100 ml.	E. coli count per 100 ml.
Class 1	Excellent	0	0
Class 2	Satisfactory	1–3	0
Class 3	Suspicious	4–10	0
Class 4	Unsatisfactory	>10	0 or more

Throughout the year, 50 per cent. of samples should fall into Class 1; 80 per cent. should not fall below Class 2; and the remainder should not fall below Class 3.

In view of the hazards to which the water is exposed in the distribution system, a different interpretation must be placed on the results of samples taken on consumers' premises. It is difficult to lay down standards for supplies of this type and opinions differ on the subject, but the present writers are of the opinion that the standard for non-chlorinated waters can reasonably be applied to any samples taken from the distribution system because in most cases, by the time the water reaches the consumers, there is no residual chlorine remaining in the water, or at best, it would be "stale" chloramine with very feeble bactericidal powers.

There is always a reason for the appearance of coliform organisms in a sample taken from a consumer's tap and sooner of later the source can usually be found. The degree of investigation and remedial measures considered advisable will depend on the number and type of organisms isolated, but the presence of *E. coli* should be considered as a sure indication of dangerous fæcal pollution calling for immediate action.

DETERIORATION IN DISTRIBUTION SYSTEM

Defects

Although water may be sent out from a works in a satisfactory condition, changes may occur in the distribution system before it reaches the consumer's tap. Contamination may occur through defective mains, hydrants, air valves etc. The construction of "dead ends" in distribution systems so that the water cannot freely circulate sometimes causes trouble and should be avoided wherever possible.

Service Reservoirs

Distribution systems normally also contain service reservoirs, situated in the highest parts of the district. These serve to equalise pressures and to act as a reserve against peak demands. Bacterial growth may occur to some extent in these in a river-derived water under warm conditions but the biggest danger is usually from leaks, especially in the roof, as these service reservoirs are normally covered. Defective ventilators will permit the access of small animals and birds particularly in elevated tanks. Regular bacteriological examination of these reservoirs is necessary to control these possibilities.

In some parts of Great Britain and elsewhere, service reservoirs are open and often of such a size that covering would be impracticable. Open service reservoirs would be quite impossible for a polluted river-derived supply owing to the growth of algæ which would occur, but with most upland surface supplies, no such difficulty arises. Such reservoirs often situated in built-up areas, are obviously liable to pollution of many kinds over which the water supply undertaking has little or no control. They are a feature of water supply practice which should be avoided wherever possible.

Cross Connections

Precautions must be taken to prevent cross-connections with, or to prevent back-syphonage from, various types of apparatus on consumers' premises, sewer flushing tanks, ships' ballast tanks or raw water hydraulic mains. Waterworks history has included many such accounts of un-authorised cross-connections in contravention of bye-laws, sometimes with serious consequences and more often with local minor inconvenience. Hot water and steam from neighbouring laundry boilers has issued from cold water taps, also dirty soapy water and in one case paraffin oil from a connection with a paraffin tank. In some of these cases, back-syphonage has occurred in spite of the insertion of non-return valves. What may appear to be unnecessarily strict bye-laws exist to prevent such occurrences, but instances of ignorance or deliberate flouting of them are continually being discovered.

Jointing Materials

Growth of bacteria may also occur on some of the materials such as jute yarn, used for packing joints in mains and the glands of valves or on mastic jointing materials used in concrete tanks. Tap washers particu-larly if made of leather, can also be a source of bacterial growth. Bacterial deterioration of this type in the distribution system may be revealed by increased colony counts or growth of coliform bacteria. The appearance of E. coli in the distribution system would indicate access of fæcal pollu-tion from an outside source.

Cisterns

Bacterial deterioration in distribution systems cannot be considered without some discussion on the role of cisterns. It is usual to fit a tap off the rising main for "drinking water" where the other taps in a building are off a cistern. This tends to imply that cistern water is not suitable for drinking. If this is so, then it also implies that it is permissible to distri-bute such impure and possibly unsafe water throughout a building provided that there is also somewhere in the building a tap off the rising main, whether readily accessible or not. From the public health point of view this is certainly not meant to be the case and it must be accepted that, if water is conveniently available from any tap, people will drink from it, even though there is a special tap for drinking water in another part of the building.

The agents likely to cause bacterial contamination of a cistern are human beings, rodents, birds and possibly flies. No precautions will exclude the human factor, and indeed any man has a perfect right to open and inspect his cistern if he so desires. The inadequacy of protection often originates from the practice of carrying expansion pipes above the cistern, necessi-tating the cutting of holes in the cover, which consequently usually has to be made on the site from wood. Such holes, even if the cover is other-wise well made, permit the access of animals and birds, and it is not unusual following complaints of bad tastes or repeated illnesses, to find the decomposing remains of dead rats or birds in cisterns.

Such defects in covers could be overcome by the use of standard specifications for the method of plumbing to cisterns, and to permit the provision of a close-fitting, overlapping metal lid. The only disadvantage in using water from a properly protected cistern is that its temperature is likely to be higher with the possibility of flat or even slightly musty tastes. For pharmaceutical purposes, if there is any doubt as to the adequacy of protection of cistern water, it would be advisable to use mains water.

Where cisterns are exposed to weak alcoholic atmospheres within premises such as spirit distillers and bottlers, scent manufacturers, paint and varnish manufacturers and even the spirit department of a museum, sufficient nutriment may be present for certain fungi to grow profusely, forming gelatinous masses in the cisterns and around ball valves. Numerous bacteria are also found in these zoogleal masses and protozoa and nematodes soon make their home there.

Earthy Tastes

Earthy, musty or mouldy tastes have been frequently reported from distributing systems in large buildings when no taste could be detected from hydrants in the street. These tastes have usually been associated with warm semi-stagnant conditions in the pipes in the building such as obtains in large centrally heated office blocks with cold and hot pipes carried in the same ducts and not used outside office hours or at weekends, or where cold pipes run through basement boiler rooms or bake-houses. Under these conditions strains of fungi and sometimes of actinomycetes have been isolated producing strong mouldy, musty or earthy odours. The ability of moulds and actinomycetes to grow under these conditions has been demonstrated by Silvey, Russell, Redden and McCormick[2], a minimum temperature of $17°$ C. being necessary before tastes and odours are noticed. Dissolved organic matter is necessary to initiate this growth as it occurs in organically polluted river-derived water, but not in deep well waters. Complaints of this nature in the London area are obtained only from premises supplied with river-derived water and not deep well water. Mackenzie[3] reported that fungi would only produce a taste in water when in actual contact with or growing in the water, whereas actinomycetes produce a volatile substance that would dissolve in the water without direct contact with the organisms. Growth of these on damp wooden cistern lids or materials used for lagging cisterns could therefore lead to the production of volatile products dissolving in the exposed water and producing earthy tastes. Both Windle Taylor[4] and Silvey and colleagues[2] have shown that these tastes cannot be destroyed by chlorination, unlike many of the other tastes of organic origin. In fact, the addition of chlorine often increases the taste, due probably to the production of stable chloro-derivatives.

CHEMICAL AND PHYSICAL QUALITIES

Turbidity and Colour

As explained earlier, a chemically or physically pure water cannot occur in nature, so that purity of a water supply implies, pleasing to the senses,

and lack of substances likely to give rise to trouble. A potable water should be clear and bright and colourless. Turbidity may originate from rain washings or the flow of water over or through the soil, or from insufficiently treated sewage or industrial effluents, or it may arise as the result of growth of algæ in reservoirs, lakes or filter beds. It may also arise from precipitation of metals in solution or from action of the water on metal pipes or from deposition of chemicals used in treatment. These metallic impurities will be discussed later.

Colour may be derived from the organic matter in solution or the material causing turbidity may itself have a colour such as clay or iron oxide or green algæ. There will be traces of dissolved organic matter in any water derived from a surface source, the colour being deepest in water from acid peaty sources. Colour due to dissolved organic matter is partly removed by oxidation by aeration by chlorination or more effectively with ozone. Traces of organic matter can be completely removed only by distillation. Colour is measured in a colorimeter by comparison with a standard colour. Turbidity is measured photoelectrically and allowance is made for the effect of the colour.

Taste and Odour

A potable water should also be tasteless and odourless. Natural mineral waters, especially chalybeate waters will have their own characteristic tastes. Tastes originating from decaying vegetation or from micro-organisms such as fungi and actinomycetes growing on the decaying vegetation or in association with living algæ giving rise to weedy, musty, mouldy or earthy tastes have been described by Silvey and others[2], Silvey and Roach[5], and Ferramola[6]. Tastes may also arise from the growth of algæ, some algæ in the living state having very marked characteristic tastes and odour, e.g., "cucumber" and "geranium", and in the decaying stage the tastes produced will be similar to other decaying vegetation. Certain effluents will produce objectionable oily, tarry or phenolic tastes in a water. Tastes arising in the distribution system have already been discussed. Treatment with chlorine will remove some tastes as a result of oxidation of the organic matter or it may accentuate others such as earthy tastes due to actinomycetes. Chlorine combined with phenolic substances will produce chlor-phenol tastes which are detectable in extreme dilution and are very objectionable in nearly all beverages. Such tastes are very difficult to deal with. Excess of residual chlorine will produce its own characteristic taste.

The acceptance of a chlorinous taste is dependent on the education or conditioning of the water-drinking public. In some parts of the world the absence of a chlorinous taste is viewed with some alarm, whereas in other places, even slight chlorinous tastes produce strong complaints.

Residual Chlorine

As a result of interaction with ammonia, chlorine may be present in a chlorinated water as free chlorine, monochloramine, dichloramine or nitrogen trichloride. The proportion of the chlorine dose which remains

as residual chlorine in any one of these forms depends on the relative proportions of chlorine and ammonia, the nature and quantity of other impurities, the contact time, the pH and the temperature. A pure well water containing no organic matter will deviate negligible quantities of chlorine and excess chlorine should therefore be removed with sulphur dioxide or a carbon filter before passing into supply. A polluted surface water will deviate considerable quantities of chlorine and if the dose is suitably adjusted and a sufficient contact time is allowed, satisfactory sterilisation will be achieved with a negligible chlorine residual passing into supply. A simple test is available for the quantitative estimation of residual chlorine. Addition of *ortho*-tolidine produces an immediate yellow colour if free residual chlorine is present. If the residual chlorine is due to chloramines the yellow colour takes several minutes to develop.

Ammonia

Ammonia arises in a water supply as a result of breakdown of polluting nitrogenous organic matter, particularly sewage. It may be free in solution or combined as ammonium salts. During filtration through sand beds, especially through rapid gravity sand filters, rapid bacterial nitrification occurs when *Nitrosomonas* spp. oxidise the ammonia to nitrites, and *Nitrobacter* spp. oxidise the nitrites to nitrates. These organisms build up a layer around the sand grains and so long as the water temperature remains above about 4° C. they remain active. Below this temperature they tend to die out and ammonia increases in the filtrate. When the temperature rises again, there is a time lag before the bacteria increase in sufficient numbers to oxidise all the ammonia.

Ammonia is undesirable from the waterworks point of view because it interferes with chlorination. The chloramines which are formed when chlorine reacts with ammonia are much less effective sterilising agents than free chlorine, and they persist for much longer periods giving rise to chlorinous tastes in the distribution system. This effect of ammonia on chlorination can be overcome by means of "breakpoint chlorination". In waters with a high organic demand, however, this process is found to be too slow to be practicable and some ammonia is inevitable in supply in extremely cold weather.

Organic matter

All surface-derived water supplies, no matter how efficiently treated, contain traces of organic matter in solution. This is usually measured by estimating the albuminoid ammonia content of a sample and the oxygen consumed at a given temperature in a given time from acid potassium permanganate solution. The figure for the former may be high in upland surface supplies due to the ingress of products of decayed vegetation and river-derived supplies may show high figures for both albuminoid ammonia and oxygen absorbed contents. The 1955 Addendum to the British Pharmacopœia indicates that demineralised water suitable for pharmaceutical purposes should have an albuminoid ammonia figure of less than about 0·4 mg. per litre and an oxygen absorbed figure of less than

0·8 mg. per litre when tested at the temperature of boiling water for ten minutes. Examples of corresponding figures for a potable river-derived domestic supply are 0·08 and 2·75 mg. per litre respectively. From an epidemiological point of view, a water free from undesirable bacteria is not unsafe because it contains organic matter, but it might not be entirely suitable for pharmaceutical purposes.

Free Carbon Dioxide

Well waters in some formations contain free carbon dioxide in solution which may contribute to corrosion of iron, copper and galvanised steel pipes causing solution of traces of copper, iron and zinc.

Dissolved Salts

Chlorides occur in practically all waters and may be derived either from the strata over and through which the water flows, or by infiltration of sea water or from sewage. An excess causes a brackish taste and there is considerable variation in the amount which may be tolerated. It is usually recommended that chlorides should not exceed 350 mg. per litre as Cl but some communities are drinking up to 550 mg. per litre without observed effect.

Sulphates may occur as calcium, magnesium, sodium or potassium sulphates. The calcium and magnesium salts are the cause of permanent hardness and excess of magnesium or sodium sulphates may cause intestinal disturbance. It is recommended that sulphates should not exceed 250 mg. per litre as SO_4. The base exchange system of water softening will replace calcium and magnesium sulphates with sodium sulphate.

Carbonates will not occur in more than minimal amounts in waters containing calcium salts, as calcium carbonate is relatively insoluble, but bicarbonates will be found, calcium and magnesium bicarbonates being the cause of temporary hardness. Sodium carbonate and bicarbonate may occur in some soft waters and are present in many table and medicinal waters. Sodium bicarbonate will be formed as a result of base-exchange softening of water containing calcium and magnesium bicarbonates.

Nitrates present in water are probably derived mainly from oxidation of organic matter chiefly of animal origin. In river-derived supplies sewage is the main source of nitrates. Under some circumstances the nitrates may be reduced to nitrites and ammonia. Excess nitrates in water given to a very young baby can cause infantile methæmoglobinæmia. The risk is greatest in artificially fed infants as all the feeds are made up with water. For this reason nitrates should not exceed 100 mg. per litre as NO_3.

The quantity of fluorides present in natural waters varies considerably and it is not our intention to enter here into the question as to whether fluorides should be purposely added to control dental caries. The subject should be regarded as *sub-judice* until results are available from the trial areas which have been set up in various parts of the United Kingdom, namely, Kilmarnock, Anglesey and possibly Watford and Amersham. It should suffice to say at this stage that it has been observed that fluorides

in excess of 1·5 mg. per litre as fluorine are liable to cause mottling of the dental enamel whereas in areas with supplies containing less than 1 mg. per litre the incidence of dental caries is higher than in areas with more than 1 mg. per litre.

Metals

Some well and spring waters naturally contain iron in solution in the ferrous state giving the water a chalybeate taste. On exposure to air in reservoirs or tanks the ferrous iron is oxidised and precipitated as ferric hydroxide which may cause opalescence and brown stain on sanitary ware. A similar ultimate effect may be produced by the action of aggressive waters on iron pipes. The iron can be removed by aeration and filtration or by an ion exchange process. Trouble of this nature is likely to occur only when the iron content exceeds 0·2 mg. per litre, but a water may be rendered turbid by as little as 0·1 mg./l.

Manganese often occurs in conjunction with iron, particularly in upland surface waters and is not so readily removed. Waterton[7] has investigated its liability to precipitate in mains as a black crystalline deposit of manganese dioxide which periodically gets flushed into supply leading to complaints of dirty water. Manganese deposits may set up bimetallic systems leading to corrosion of copper pipes. Manganese in solution should not exceed 0·05 mg. per litre.

Contamination with metallic salts is likely to occur through the solvent action of some aggressive waters on pipes. Low pH and high free carbon dioxide content are liable to contribute to solvency of lead, copper, iron and zinc. Solution of lead, due to its cumulative toxic action is liable to be dangerous and great care must be taken with such waters to avoid the use of lead pipes. Steps are taken on some waterworks to correct the aggressive action of such waters. Zinc is relatively harmless, but solution can be so extensive as to cause opalescence due to precipitation of zinc hydroxide. With some well waters the zinc accumulates as hard grains of zinc carbonate which occasionally get flushed through the taps leading to complaints of "sand" in the water. When this occurs deterioration of galvanised iron ware is so rapid as to make this material unsuitable for use with such waters. Zinc content of the water should not exceed 5 mg. per litre at any point in the distribution system.

Corrosion of copper also varies according to the nature of the water. Pitting corrosion may occur in either hard or soft waters. Its prevention by the presence of certain organic inhibitors in water derived from organically polluted sources such as rivers has been studied by Campbell[8]. Traces of copper derived in this way are not likely to be harmful, but if such copper-containing water subsequently passes through galvanised pipes or tanks, zinc will be dissolved causing corrosion. In the same way copper-containing waters boiled in aluminium kettles will lead to deposition of the copper with solution and corrosion of the aluminium. Bi-metal systems of this nature should therefore be avoided with waters containing no organic inhibitors. Copper piping is contra-indicated

where the water would take up more than 3 mg. per litre after standing in new pipes for sixteen hours.

Copper derived from copper sulphate treatment of algal growths in reservoirs is likely to be infinitesimal as it is nearly all precipitated as basic copper carbonate in the reservoir and settles to the bottom fairly rapidly.

Some other instances of solution of metals are difficult to explain except as a result of electrolytic action from stray electric currents originating from the practice of earthing electrical circuits to water pipes.

Toxic Elements

Toxic elements should be absent at the source and if present in greater amounts than given below should condemn the supply. The figures are low but are based on long continued ingestion.

Lead	0·1 mg. per litre and 0·3 mg. per litre after 16 hours contact with lead pipe.
Arsenic	0·2 mg. per litre.
Selenium	0·05 mg. per litre.
Chromium (hexavalent) ..	0·05 mg. per litre.
Cyanide	0·01 mg. per litre.

GENERAL CONCLUSIONS

There is considerable variation in methods of assessing purity of a water supply throughout the world, both bacteriologically and chemically and different standards are adopted. It is gratifying, therefore, to record that an International Study Group, under the auspices of the European Office of the World Health Organisation, has been investigating the standardisation of methods of analysis and standards of quality. In view of the developments which continue to take place in analytical methods it is not yet possible to specify single standard methods for each characteristic but some general principles have been agreed which will be of considerable advantage to all. The report is completed and the figures quoted here are largely derived from this document.

A summary has been given of the possible and limiting concentrations of constituents of potable water which is the "raw material" of the pharmacist for dilution purposes. With ever increasing demands for water, more impure sources have to be exploited. An increasing degree of protection is being applied to the sources and the water is efficiently purified wherever it comes from, so that it is safe to drink and palatable, but some of the characteristics remaining may be embarrassing to the pharmacist unless further treatment is given.

There will be traces of dissolved organic matter in any water derived from a surface source. Occasionally algal cells, bacteria and pyrogens may also be present. Dissolved salts may be in excess and metals may be present in traces. Residual chlorine and ammonia complete the list. Their content may in a lesser or greater degree determine the type of treatment necessary to render the public water supply suitable for specific pharmaceutical purposes.

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WATER FOR PHARMACEUTICAL PURPOSES

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DR. WINDLE-TAYLOR and Mr. Burman have described the problems involved in the supply of a pure and wholesome, potable water and have pointed out that this water can be defined only in terms of its suitability for human consumption. In consequence, potable water is a very variable commodity from the chemical point of view, the nature and concentration of the impurities remaining in it depending on the locality from which it is drawn. No national chemical standard has been imposed for potable water and indeed such a standard is unnecessary for the water to fulfil its primary function.

Without further purification, potable water is not suitable for many applications in pharmacy and in chemical work associated with pharmacy. The extent of the further treatment to which it is subjected depends on the technical requirements for the water and on the cost of the treatment.

The impurities in potable water which necessitate its further purification for pharmaceutical purposes are:

(1) Micro-organisms and their breakdown products. This form of contamination should be slight in water which is freshly drawn from a mains supply. The bacterial breakdown products are not necessarily removed when the bacteria themselves are eliminated and these substances can cause the pyrogen reaction when they are present in water used for making solutions for injection. Solutions of this kind are therefore prepared from freshly distilled water and potable water is used only for sterilising syringes by boiling. Small amounts of hard water remaining in a syringe after sterilisation in this way may yield sufficient alkali to react chemically with medicaments, for example, to cause the precipitation of insulin.

(2) Inorganic salts and dissolved gases. A comprehensive list of the anions and cations normally present in potable water has been given in the first paper and many problems arise from their presence. The divalent cations such as calcium are particularly troublesome since they may cause precipitation reactions in addition to yielding alkalinity.

Potable water is now sanctioned in the B.P.C. 1954 and in the National Formulary, for making oral and other preparations. Where incompatibilities do not occur or are unimportant, the use of potable water can be justified on the grounds of economy. However, owing to the variation in the composition and proportion of the dissolved salts in potable water in different parts of the country, differences in the properties of certain pharmaceutical preparations are found. For example, the concentration of calcium ions present in the water affects the sol viscosities and gel strengths of alginate and pectin dispersions. The use of potable water

can therefore produce problems in formulation, as will all chemically unstandardised substances.

A major use of water in pharmacy is for cleaning apparatus and containers. If potable water is used for the final rinse, a residue is left on the apparatus after drying which may be alkaline and give rise to trouble with unbuffered solutions. Water which has been softened by treatment with zeolites or other cation exchangers, is economical to use with certain types of detergents but it does not obviate the trouble from residue left on drying.

Methods of purifying water

In the light of recent developments, methods for purifying water can be divided into two classes.

(1) The traditional process of distillation in which the water is separated as vapour from the small amounts of non-volatile impurities. This is an extravagant process, the high specific heat and latent heat of evaporation causing heavy power costs.

(2) Removal of the impurities from the water at normal temperatures by means of solid reagents which are themselves insoluble in water.

The development of stable ion exchange resins which can be reactivated many hundreds of times, renders this second method of purification very much cheaper than distillation[1].

Distillation

A recent paper by Greppin[2] describes an extensive study of various methods for preparing distilled water for pharmaceutical purposes. An all-glass apparatus was found to give the best product.

It is of course essential that a still should be cleaned regularly in order to prevent the growth of bacteria and fungi in the condenser, where they would cause contamination of the distillate. Sterilisation of the condenser can be carried out daily by steaming out before turning on the condenser water. When high rates of distillation are used, there is a danger of contaminating the distillate with droplets of liquid carried over from the boiler in the form of a fine spray. These entrained droplets will pollute the distillate with the non-volatile impurities present in the feed water. Entrainment is a particular problem in preparing water for injection solutions.

Shotton and Habeeb[3] have shown that, providing liquid is not swept as a film along the walls of the stillhead, the contamination due to entrainment in a simple still, is about 1 in 10,000. At this dilution, pyrogenic effects are unlikely to be serious if fresh water is fed into the still (Todd private communication). Pyrogenic effects observed with distilled water are more likely to have arisen in a condenser which has not been cleaned and sterilised regularly, or from careless storage of the water in a non-sterile condition.

In order to reduce power costs and to improve rates of distillation, two new methods for the electrical heating of water in continuous stills have been developed. One of these is the use of a bare nichrome element immersed in the water. When a current is passed through the wire, smooth

boiling starts very quickly and a rapid rate of distillation can be achieved without formation of deposits on the wire. As a result there is none of the bumping which so often causes trouble when immersion heaters are used. After a time, the boiling water becomes coloured due to a slow dissolution of the nichrome; however, providing that there is an efficient baffle system to prevent entrainment, the distillate is quite free from traces of nickel or chromium. The nichrome element requires replacement at regular intervals.

The second new heating method uses carbon electrodes which are immersed in the water to be distilled. It may be necessary to add a salt to this water to give it sufficient conductivity to start the boiling. A heavy alternating current is passed between the electrodes and sufficient heat is produced to boil the water. Both these types of direct electrical heating can give rise to volatile electrolysis products, such as chlorine, in the distillate and tests should be made to ensure that the product is free from these impurities.

Freshly prepared distilled water from a clean, well designed still is substantially free from micro-organisms. On standing, it rapidly becomes contaminated with airborne organisms, unless precautions are taken to prevent this. The storage of distilled water in carboys over long periods may result in heavy contamination. It is odd that distilled water, which should be free from nutriments, provides a growth medium for a number of organisms.

The presence of viable bacteria in stored water can give rise to pyrogenic substances and can ultimately impart a hazy appearance which is difficult to remove, giving the water the appearance of a dilute vaccine. In addition, the organisms can cause decomposition of materials dissolved in the water; for example, the growth of micro-organisms in Injection of Mersalyl has been observed to cause a pronounced increase in the sodium sulphide reaction for mercuric salts. Thus it is essential not only to sterilise Water for Injection immediately after collection if it is to be stored, but also to minimise the time interval between exposure of the water to contamination and the sterilisation of the solution prepared with it.

Treatment of water with solid reagents

The earliest solid reagents used in the treatment of potable water were the zeolites. These are complex silicates which are insoluble in water and which exchange the cations such as calcium in the water with sodium ions contained in the zeolite. The softened water obtained after treatment with zeolites is free from divalent metal ions and is as a result, more economical to use with certain types of detergents than is untreated potable water. The total amount of non-volatile matter in the water is not however reduced by the softening process. The development of stable ion exchange resins containing strongly ionised acidic and basic groups has led to an important new method for purifying potable water, which has been recognised by both the U.S.P. XV and the B.P. Addendum, 1955, for preparing water suitable for pharmaceutical purposes other than for injection.

The resins now generally used for this method of water purification consist of hard insoluble beads of a styrene-divinylbenzene polymer. The cation exchanger has sulphonic acid groups distributed throughout its mass, while the anion exchanger contains quaternary ammonium hydroxide groups[4]. When water containing dissolved salts is passed over a mixture of these two resins, all the cations in the water are replaced by hydrogen ions from the sulphonic acid resin while the anions are replaced by hydroxyl groups from the anion exchanger. The final result is that the dissolved salts are removed completely, being replaced by hydrogen and hydroxyl ions and the resulting water has a very high specific resistance. When the resins are spent they can be regenerated by separating them by flotation (the anion exchanger is considerably less dense than the cation exchanger), the anion exchanger is regenerated with sodium hydroxide solution and the cation exchanger with hydrochloric acid. The resins are then washed and re-mixed. These operations are carried out without removing the resins from the column.

Water purified in this way is called de-mineralised or de-ionised water. The product obtained from a single column containing a mixture of the two resins has a much higher resistance and contains less non-volatile matter than does water purified by a two column process in which each exchanger is contained in a separate column[5]. This may be due to the fact that the traces of resin breakdown products imparted to the water are absorbed by the resin of opposite type in the mixed resin method. For example, the anion exchanger in the hydroxyl form tends to give traces of an amine due to the reaction,

$$(R.N^+X_3)OH^- \longrightarrow ROH + NX_3$$
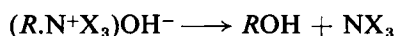
where R represents the resin and X, an alkyl group. This reaction accounts for the unpleasant fishy smell of some resins of this type. In the mixed resin column, any traces of amine dissolving in the water are immediately taken up by the cation exchanger.

At ordinary temperatures the rate of decomposition of the resins is small and although they are expensive they have a long life and can be regenerated hundreds of times. As a result the ion exchange process is a very much cheaper method for purifying water than is distillation. Details of the purification of water by this method have been given by Saunders[6] and others[7,8] and the subject was reviewed comprehensively by Professor Büchi[9] at the conference of the Federation Internationale de Pharmacie in London last year. Recently, a small laboratory apparatus suitable for laboratories or pharmacies, has been made available and has formed the subject of an equipment test report in the journal *Laboratory Practice*[10]. This apparatus supplies about eight gallons of purified water per resin charge when London tap water is used as the feed, the resins are not regenerated but the cartridge containing them is returned to the manufacturer when exhausted and is replaced by a freshly activated one.

The ion exchange treatment of potable water is more effective than distillation in removing ionised substances from potable water, de-mineralised water may however contain other contaminants.

Colloidal matter. If the feed water is a pure and wholesome potable water, it should contain only very small amounts of colloidal matter. Providing that the resins are regularly regenerated, the concentration of albuminous matter in de-mineralised water is less than that in the feed water, though the resins do not remove this impurity completely. As a precaution the B.P. Addendum monograph on purified water has specified an albuminoid nitrogen test to avoid the possibility of accepting a product which contains undesirable amounts of albuminous colloids.

Non-ionic impurities. The concentration of non-ionic materials in potable water is normally very small. Appreciable amounts of them in the feed water would lead to rejection of the demineralised water prepared from it, as a result of the non-volatile matter test.

Micro-organisms. By filtering bacteria and suspended organic matter from the feed water, an undisturbed resin column may become a breeding ground for micro-organisms and may finally give a "purified water" which passes all the chemical tests but which is more heavily contaminated with micro-organisms than the feed water. This result can be avoided by operating the de-mineralising plant under carefully controlled conditions with frequent regeneration[11] and back-washing of the column. It has been suggested that the treatment of the column with formaldehyde will reduce the bacterial population[12].

Greppin[2] has stated that "bacteriological controls (of demineralised water) indicate a contamination proportional to the length of service of the apparatus". We suggest that the same result would be obtained with any water purification apparatus, unless it is carefully cleaned and sterilised at regular intervals. Greppin reports a detailed examination of a sample of de-mineralised water drawn from an industrial apparatus which had been in service for two years but he gives no details about the way in which it had been maintained. This water had a specific resistance of 0·43 megohm. cm., a poor value for demineralised water. He found that it passed all the tests of the Pharmacopœia except the non-volatile matter test in which it gave a residue of 12 mg./l., the permitted limit being 10 mg./l., and the residue was dark coloured. He also stated that the sample was "infested with germs and pyrogenic substances" and quite correctly pointed out that specific resistance must be used cautiously as a criterion for the purity of de-mineralised water as it is greatly affected by traces of inorganic substances but is hardly changed at all by colloidal substances and micro-organisms. These results of Greppin illustrate the point that it is not good enough for pharmaceutical purposes to take an industrial water de-mineralising plant and run it for year after year without regular cleaning. The heavy contamination of Greppin's sample by micro-organisms was almost certainly due to inadequate maintenance of the ion exchange equipment.

Providing the resin column is kept free from heavy bacterial contamination, de-mineralised water can be used in place of distilled water for most purposes except for preparing injection solutions. It should be suitable for making preparations for oral and external use and for preparing

stock solutions of chemical reagents. In addition, its cheapness and freedom from non-volatile matter make it advantageous for use as the final rinse liquid in washing bottles and other containers for liquids.

Pyrogen-free water by ion exchange

Present methods for de-mineralisation of water are not suitable for preparing Water for Injection though there seems to be a reasonable possibility of developing reliable techniques for this purpose. The first problem to be settled is the sterilisation of the ion exchange column. According to the manufacturers of the Amberlite resins, the strong cation exchanger can be sterilised by heating it for 15–30 minutes with a steam pressure of 15 lb./in.^{2}, the anion exchanger in the hydroxyl form is liable to suffer degradation by this treatment though in the chloride form it can be heated for 15–20 minutes at this steam pressure (Rohm and Hass, private communication). Cold treatment with formaldehyde would appear to be a simpler method and this can be done with both the resins in their activated forms.

Removal of gaseous impurities

De-mineralised water is completely free from carbon dioxide and free ammonia, but its oxygen content will be the same as that of the feed water. On standing in air it rapidly absorbs carbon dioxide and its specific resistance falls to an equilbrium value of about 1 megohm. cm.

In distillation, the feed water is usually heated to a temperature above 95° C. before it enters a continuous still thus eliminating most of the dissolved gases, some remain however and pass over into the condensate.

It is necessary to ensure that gaseous impurities are removed from the water used for some preparations. For example, carbon dioxide precipitates certain barbiturates from solution, and the presence of oxygen will cause the destruction of materials such as ergometrine. In instances like these the dissolved gases are removed from the water immediately before it is used. Two methods frequently used for this are based on Henry's law, (i) the water is boiled for some time, and the gaseous impurities are swept out by the bubbles of water vapour, (ii) the dissolved gases can be replaced by an inert gas of low solubility, such as nitrogen, by bubbling a stream of the inert gas through the solution. Subsequent manipulations of the solution are carried out in an inert atmosphere.

Storage of purified water

Some of the problems associated with the storage of distilled water have already been mentioned. The best rule is to store small amounts and to use it as rapidly as it is produced; this applies equally to distilled water and de-mineralised water.

In storage two types of contamination can occur.

(i) Growth of micro-organisms. This can be avoided only by sterilisation followed by storage under aseptic conditions. Alternatively a preservative such as the phenyl-mercury nitrate borate as used by Greppin[2] can be used to kill micro-organisms present in the water and to prevent

subsequent growth. However the presence of compounds of this type in the water will be undesirable in many applications.

(ii) The solvent properties of purified water will lead to attack on the container and closure materials during prolonged storage. These materials are usually rubber and glass and their effects on water stored in them have been described in the Symposium of the British Pharmaceutical Conference held in London in 1953[13-15]. A variety of impurities may be introduced into the water by this means and the content of non-volatile residue will increase and in time may exceed the permitted limit of 10 mg./l.

Materials other than glass and rubber which are frequently used for storing water are metals and plastics. Metal storage tanks should always be enclosed otherwise appreciable amounts of suspended matter may appear in the water. Galvanised iron tanks are particularly objectionable because after a time when the inevitable corrosion occurs the water may be discoloured by ferruginous substances. Copper is not used for the storage of purified water since, appreciable amounts of the metal may be dissolved in pure water stored in a copper tank. Some kinds of stainless steel are suitable though expensive materials for storage tanks but traces of heavy metals are likely to be found in the water after prolonged storage. Perhaps during the discussion some disadvantages of stainless steels as storage tank materials may come to light. Large storage tanks can be made by fitting a polythene liner into a metal tank.

Silver lined condensers have been used for collecting distilled water to be used for injections[16]. The effect of the silver was probably considered an advantage in retarding the growth of micro-organisms between the time of collection and use. Whether this is a real effect when the silver is coated with a film of oxide or sulphide is not known. Presumably the object is to lessen the risk of pyrogens being formed in the water by inhibiting the growth of organisms.

De-mineralised water is so completely free from metal ions that it seems a pity to pollute it by allowing it to come into contact with metal piping or tanks. Fortunately the development of polythene "plumbing" and containers means that no metal need be used.

We have found that prolonged storage of good de-mineralised water is a polythene container causes very little change in the amount of non-volatile matter in the water. After three months this was unchanged at 2 mg./l. We have always found that the residues resulting from the evaporation of demineralised water are white, contrary to Greppin's observation[2].

The development of plastics which can withstand temperatures up to 120° C.[17] means that in the future it will be possible to sterilise water and solutions in plastic containers by means of heat treatment.

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DISCUSSION

MR. W. P. HUTCHINSON (Oxford) mentioned that large-scale sterilisation of water was possible using the gamma radiation from the spent fuel rods of atomic piles in atomic power stations. Bacteria would be killed and the necessity for chlorination eliminated.

MR. T. D. WHITTET (London) said that at University College Hospital, deionised water was used for rinsing bottles and for the preparation of some culture media and biochemical reagents. He agreed that the plants at present available were not suitable for preparing water for injection. He had found that the two column process was better for removing pyrogens from water than the mixed bed process, but it gave water of lower chemical purity. Little work seemed to have been carried out in this country on the pyrogenicity of tap water. It had been reported that Cardiff tap water was pyrogenic and Manchester tap water was not; but no information had been given about whether the samples were examined before or after sterilisation. His own work suggested that London tap water was pyrogenic when unsterilised, but autoclaving removed the pyrogenicity.

MR. G. R. WILKINSON (London) asked if some information could be given about the possible radioactivity of potable water. Had the authors any information on the factors responsible for the corrosion of aluminium collapsible tubes? In the second paper the non-volatile residue after storage in polythene containers was mentioned. Was it not possible that volatile materials, included during fabrication, might be taken up from the plastic and give trouble? Considering the source of purified water, low pressure steam, partially condensed, was used in some factories, and he wondered whether the authors had examined such water.

DR. G. E. FOSTER (Dartford) emphasised the importance of the proper maintenance of storage tanks, and said that for pharmaceutical purposes tap water should be drawn directly from the mains. He had experienced difficulties in preparing a standard solution containing 1 p.p.m. of chlorine for checking *o*-tolidine tablets. The chlorine in a stronger solution was estimated, and then the solution diluted to give the required concentration, but some impurity in the water used for dilution reacted with the residual

chlorine. Could the authors suggest how the difficulty could be surmounted?

It had been stated that potable water could be used for some pharmaceutical purposes. He recalled rejecting some barium sulphate because it did not comply with the official test for the absence of soluble barium compounds. It was found that tap water had been used in the preparation of the barium sulphate and the reaction given was due to the presence of calcium salts.

Some time ago silver-lined tanks had been used for the crystallisation of sodium chloride required for intravenous purposes. Due to the presence of some free acid, traces of silver were present in the sodium chloride and affected the blood cells. Was any information available about the silver content of water stored in tanks lined with silver?

MR. J. W. HADGRAFT (London) referred to an example of the contamination of distilled water with traces of nickel. The water was used for the dilution of a strong solution of sodium hypochlorite and immediately produced a brown colour which did not occur when water from another still was used. It was found that traces of nickel in the water were coming from the Monel metal condenser tubes of the still. The nickel was present in the nickelous state and was not easily detected by the B.P. test for heavy metals. A haze developed with sodium sulphide solution after prolonged standing. The amount of nickel present was insufficient to produce a detectable colour with dimethylglyoxime but the reaction with sodium hypochlorite solution was immediately apparent and was capable of demonstrating the presence of nickel below concentrations of 0·5 p.p.m. A test was devised giving a quantitative reaction, the method was to add 5 ml. of strong sodium hypochlorite solution containing about 12 per cent. of available chlorine to 50 ml. of water in a Nessler cylinder. The test was far more sensitive than the B.P. method for the detection of heavy metals using sodium sulphide.

The ability of certain organisms to exist in water was of importance not only in relation to injections, but also in preparations for oral administration. He had recently seen a sample of barium meal smelling strongly of hydrogen sulphide, and chemical tests established that the preparation contained barium sulphide. On bacteriological examination, it was found that a sulphate-splitting organism was present which had attacked the barium sulphate and produce barium sulphide. This organism attacked the barium sulphate not only in a dilute solution of alcohol and saccharin, but in a simple suspension in distilled water.

MR. J. L. LIVINGSTONE (London) said that some rivers might contain water which had passed through power stations for cooling purposes and had been deoxygenated, and also water which might have been used for chemical processes and returned in anything but its original state. In areas relying on deep wells for part of the supply, the levels of the wells were dropping inches every year due to excessive demands. Was it likely that a serious shortage of water would occur, especially in lowland areas, in another 5 or 10 years time?

He had seen some examples of very bad pitting of aluminium vessels which had been used to heat water which had passed through copper pipes. Polythene tubing used for cold water supplies was becoming increasingly common, but that material was permeable to gas and there was the hazard that a leak of coal gas might cause the water to be contaminated.

DR. J. G. DARE (Leeds) referred to published work showing that comparatively small departures from neutrality could reduce the resistance of pyrogens to autoclaving. It would be interesting to know the pH of the London tap water which Mr. Whittet had used and what sort of buffering capacity it had. If the water were comparatively neutral, it might be that the pyrogens to which Mr. Whittet referred were relatively unstable.

MR. E. W. RICHARD (Upminster) said there were some areas in which the water, as it reached the consumer, was very hard. Did any of the water authorities consider that the installation of softening plants would be of advantage? If so, would it be an economic proposition from the point of view of the supplier as well as of the consumer? There was, he believed, a water softening plant at Leatherhead, but he did not know of any others.

PROFESSOR J. P. TODD (Glasgow) said that in his view pyrogens were being confused with pyrogenic reactions. Reactions similar to those resulting from the injection of pyrogenic solutions could be obtained in a number of ways, for example by the transfusing of incorrectly matched blood.

Dr. Shotton and Mr. Whittet were flirting with the idea of using ion exchange resins for the preparation of water for injection. Very much more work was required before it would be wise even to consider replacing distillation by such methods. Examination candidates frequently explained the presence of pyrogens by the mysterious process of entrainment. Either Dr. Shotton was wrong in his figure of 1 in 10,000 or he (Professor Todd) did not understand it. It had been shown that if distilled water was to be made pyrogenic by entrainment the water must contain 10,000 times the minimum dose when one started to distil it. The figures were probably right, and it would seem that over the years the word "entrainment" had been used when really what was meant was dirty condensers or containers.

It would be interesting to know whether Dr. Burman was at all worried about the fall-out of Strontium 90.

MR. J. H. OAKLEY (London) said that he had found ammonia contamination of distilled water sometimes occurred in cold weather, and he would be grateful to have Dr. Burman's comments.

The sterilisation of ion exchange resins by formaldehyde could cause complications, particularly if the demineralised water was used in an alcoholic preparation which was to be exported. For exporting alcoholic preparations one claimed a drawback on the residual spirit duty, and it was necessary to guarantee that the alcohol was free from methyl compounds. The test was based on the formaldehyde colour reaction, and if

any trace of formaldehyde was present in the deionised water the Government chemist would immediately interpret that as implying the use of industrial methylated spirit.

If the resins were in two separate towers, debris was removed almost completely from the potable water in the first tower—the Zeocarb cation exchanger—and it was a good practice to give it a daily back-wash to remove dirt from the surface.

MR. J. C. HANBURY (Ware) said that some years ago he had heard a radio talk on the serious position—thinking in terms of 50 or 100 years—of the water supply in South-East England where there was a maximum concentration of demand and the worst climatic conditions to meet it. One had always understood that afforestation had a profound long-term effect on water precipitation and storage and the subterranean availability of water. He understood that afforestation was a favourable factor in both attracting moisture and storing it. It would be interesting if Dr. Burman would enlarge on the question of afforestation and possibly on the effects on the water supply of deforestation and the large built-up areas in South-East England.

On a more specific point, the sewage effluent from the new town of Stevenage was now being added to the sewage deposited on the Rye Meads gravel bed, and water from deep wells nearby was being used by a water authority. Was any danger anticipated of long term bacterial contamination from the Rye Meads beds reaching the water in the nearby wells?

DR. F. WOKES (King's Langley) referred to the problem of trace elements in water. They were present in very small quantities—much less than 1 p.p.m.—and therefore the intake from drinking water might not be considered serious. But some elements were stored in the bones so that over the course of years they could accumulate in toxic amounts and on liberation might be responsible to some degree for the development of diseases. Toxic elements had been suggested as the possible causative factor of disseminated sclerosis. A paper was published by Campbell in 1950 in which he found that in areas where the disease occurred there was a much higher concentration of lead in the water. Further, the teeth of those who had the disease contained up to ten times as much lead as the teeth of healthy persons of the same age.

On use of water in pharmaceutical processes, he commented that very large quantities were used in the preparation of malt extract. Work had been published showing that the rate of extraction from the malt varied with the type of water used, factors responsible being the pH and the salts present.

DR. W. ANDERSON (Liverpool) suggested that pyrogens were likely to be present in deionised water until a system could be constructed which would remove all colloidal matter.

MR. M. B. BROPHY (Dublin) said that activated charcoal had been used for removing pyrogens. Had the authors any information on distilling water in the presence of depyrogenising charcoal for that purpose?

Would it be worth while combining ion exchange resins and depyrogenising charcoal?

PROFESSOR H. BRINDLE (Manchester) said that some eight years ago when he had required some natural pyrogens, he had experienced the greatest difficulty in obtaining any public water supply which was contaminated with pyrogens. He would be interested to learn whether the authors had any information about the presence or absence of pyrogens in London water at that time.

MR. R. L. STEPHENS (Brighton) asked whether the authors could say anything about the presence of synthetic detergents in potable water. The problem of detergents to sewage disposal authorities was well known, and it had been shown that a proportion was returned to the rivers. Were any steps taken to remove the detergents from the public supply? Synthetic detergents were incompatible with cationic antiseptics.

Tin was a traditional material for lining laboratory apparatus, and on one occasion he had found his supply of distilled water heavily contaminated with stannous salts. After cleaning out the apparatus the salts ceased to be present.

On the possibility of plasticisers being present in polythene he said there was only one plasticiser used with polythene and that was completely insoluble in water.

DR. F. HARTLEY (London) asked if appreciable amounts of sodium fluoride were contained in water, and that water were exposed to radioactive waste, would the hydrofluoric acid or fluorides present affect the behaviour of the ion exchange resins with which the water might subsequently be treated?

MR. EDWARDS (Harrow) said that Dr. Shotton had implied that electrode boilers were a new development. This was not so—they had been in use for many years. No mention had been made of the steam compression still. By compressing steam it was possible to obtain the equivalent of triple distillation with something like 2 per cent. of the heat required for single distillation. It was possible to obtain 50 gallons per hour of pure pyrogen-free water for the equivalent of about 10 kW of energy. Entrainment was prevented by the use of a cyclonic separator.

MR. W. P. HUTCHINSON (Oxford) stated that sterilisation by gamma radiation did not induce radioactivity.

DR. N. P. BURMAN, in reply, said that his only knowledge of the pyrogen content of London water came from Mr. Whittet. When the bacteriologist referred to the presence of bacteria in water he was referring solely to viable bacteria, and there might also be millions of dead ones present.

He had no knowledge of sterilisation by gamma rays, fission products, etc. He was not aware of any research going on within the water industry on those methods.

Contamination of water by radioactivity was a matter that was being closely watched in the waterworks world, both from the point of view of discharges as a result of the development of nuclear energy and from

radioactive fall-out. He could do no better than advise those interested in the effects of fall-out to read the appropriate section of the recent publication of the Medical Research Council on "The Hazards to Man of Nuclear and Allied Radiations".

The type of pitting corrosion of aluminium he had mentioned referred to ordinary grades of the metal. He had no experience of the highly purified grade used in collapsible tubes. Pitting corrosion was considered to be due to minute traces of metals setting up electrolytic cells. There was another type of corrosion which occurred frequently in aluminium kettles, due to traces of copper in the water. Precipitation of the copper and solution of the aluminium was the result.

Storage tanks with faulty covers presented a problem. The water authority had no jurisdiction over storage tanks, and it was the owner's concern if something went wrong with them. A far better standard could be devised for storage tanks than the very indifferent individually made wooden covers which were placed on them. Tanks could be designed which would eliminate all possibility of the access of small animals and birds. The same problem occurred on a large scale in the distribution system, such as service reservoirs, water towers or elevated water tanks. Very great care was taken to exclude animals and small birds from such places, and regular inspection of ventilators and covers was necessary.

On the subject of obtaining a standard colour with o-tolidine reagent he commented that if one started with a known quantity of available chlorine in a solution and diluted with water it was necessary to exercise care in selecting the water with which dilution was carried out. It must be high quality distilled water, free from organic matter, because organic matter would deviate the chlorine. The deviation of chlorine in a river water was quite considerable, and gradually increased with time. It was now the general practice of the Metropolitan Water Board in the case of their river-derived filtered waters, to insert contact tanks between the chlorination plant and the point at which the water was pumped into supply. Chlorine was added to the water in the contact tank, which was large enough to contain up to two hours' supply; there were baffle plates in the tank so that water could not flow directly from the inlet to the outlet, and during that two hours the chlorine was completely deviated. Up to 1 p.p.m. of chlorine may be added at the beginning while very much less than 0·1 p.p.m. would be found at the outlet. With deep chalk well water, if the same procedure were adopted, 1 p.p.m. would be found at the outlet as the quality of the water had a considerable effect on the deviation of chlorine. Excess chlorine was removed by sulphur dioxide.

There were certain filters on the market operating with what was known as a catadyn sand. There were also available types of kieselguhr filters impregnated with catadyn silver which was reputed to render the water completely sterile. If any silver found its way into the water, it was in such minute quantities that it was not detectable by normal means. They seemed to last almost indefinitely with no reduction in the amount of silver on the filter itself.

As to sulphate-reducing organisms in water, the Metropolitan Water

Board were more concerned with sulphate reducers in clay soils, which under the anaerobic conditions existing could reduce sulphate in the presence of iron from iron pipes and produce hydrogen sulphide, which would cause deterioration of the iron and the production of ferrous sulphide. That would produce severe and, in some circumstances, rapid corrosion of the pipe. In some soils this was a very serious problem.

The question of cooling water from power stations had been very carefully considered in connection with the new power station being built up on the Lea. The temperature of the river water was raised but not sufficiently to cause trouble; the temperature of the discharge from the power station was the subject of control. Chemical effluents could often be far more serious than bacterial pollution, and if there were both together, the chemicals left in the water might have a sterilising action, so that a false picture was presented. The pollution of rivers had, since the war, become the responsibility of the River Boards which now possessed much greater powers of control.

In London alone there were hundreds of private wells in addition to those possessed by the Board. In some cases the level and quality of the water had deteriorated so much that the wells had fallen into disuse, but an interesting experiment had been conducted in the past two years to re-charge the underground waters. In the winter, water was allowed to flow down certain wells instead of being pumped up. Filtered, chlorinated river water was used, and in the summer, if it were required, the water was pumped into the supply. However, the quality of the water might be quite different from that obtained from the wells previously.

Polythene tubing could absorb coal gas quite readily. One serious instance had been encountered where a local gas main leaked, and the gas was absorbed by the polythene tubing which was buried in the ground nearby. An objectionable odour and taste was produced in water which passed through the tubing and the gas absorbed was continuously given off for some time afterwards. Before approving the use of polythene tubing in the Board's area, a number of experiments were carried out on water after passage through the tubing, and the only difference found was that sometimes there was an increase in the bacteria capable of growing at room temperatures. That might have some effect on subsequent pyrogenicity but none on potability.

Potable water as supplied in some areas was very hard and he had been asked about the economics of water authority softening. The softening of the whole of London's water supply would be a costly procedure and it had been estimated that it would put up the cost of treatment by about 100 per cent. The number of people who would benefit by that increase in cost was limited, and the demand for soft water had considerably declined due to the increased use of detergents.

The question of the ammonia content of water in cold weather was very interesting. A polluted water did contain ammonia and ammonium salts, and in works where rapid sand filtration was used before slow sand filtration for clarification, *Nitrosomonas* (which convert ammonia to nitrite) and *Nitrobacter* (which convert nitrite to nitrate) develop around

the grains of sand. However, they only function at temperatures above about 4° C. and in cold weather they die. When the temperature rises there is a time lag before they function again properly.

On the long term effect of afforestation, it was rather surprising to learn of a report to the British Association opposing afforestation in upland catchment areas because of the greater amount of evaporation which occurred. There would be a greater amount of evaporation initially, but the advantages far outweighed that disadvantage.

Small quantities of crude sewage had been deposited on the gravel beds at Rye Meads for many years. It was hoped now that larger quantities of good quality sewage effluent could be disposed of in a similar manner with equal success. This plan will considerably reduce the degree of pollution of the River Lea and it is not anticipated that it will affect the wells in the vicinity because they already carry some degree of pollution and are pumped into the adjoining New River and treated as for a river water.

He was not aware of any routine observation of the content of trace elements in water, in the very low concentrations mentioned.

It was known that a trace of detergent residue was left in some domestic water supplies but this amount was considerably less than that consumed as a result of surface-active material from household detergents left on unrinsed china and cutlery after washing. Enquirers were referred to the "Report of the Committee on Synthetic Detergents" recently published by H.M.S.O. and a paper by C. Hammerton, Senior Chemist of the Metropolitan Water Board, on "Synthetic Detergents and Water Supplies", to be published in the Proceedings of the Society for Water Treatment and Examination.

DR. E. SHOTTON, in reply, suggested that low pressure steam referred to might more aptly be described as waste steam. He had not heard of it being used to any great extent in pharmaceutical preparations. Some waste steams could be very dirty indeed, and he would not normally recommend its use as a source of distilled water. He was not advocating the use of silver-lined plant, but it was worth reporting that it had been used presumably for the oligodynamic effect.

He had never found that tin caused troublesome contamination of water and he had no knowledge of nickel causing contamination of distilled water, but he had had experience of nickel contaminating acid solutions, and the better quality stainless steels were much more resistant than Monel metal. Stainless steel was probably the most suitable metal for a condenser if glass could not be used. He had experience of sulphate reducing organisms in an aluminium phosphate suspension. The source of the aluminium had been aluminium sulphate and traces of sulphate present had been reduced to sulphide.

He was not advocating the use of ion exchange resins to produce water for injection. That would be very hazardous at the present stage. It might be, however, that in the future a technique would be evolved whereby such water could be obtained. He agreed that if formaldehyde were

used as a sterilising agent for the resins, it must be completely removed before the water could be used.

With reference to the suggestion of charcoal for the removal of pyrogens, he would stress that columns could be very dangerous, whether containing charcoal or ion exchange resin, in that bacteria might grow in them. It was worth while emphasising that charcoals were very variable. Many charcoals contained high quantities of lead, arsenic, copper, zinc and other metals, and should be treated before being used for pharmaceutical purposes.

He was aware that immersion electrodes had been used, and he knew of some buildings in which the steam supply was maintained by the installation of those heaters; but it was new in that recently in the literature the still had been advocated for pharmaceutical purposes. The economics would depend upon the scale of production. For small scale production the cost would probably be higher than when ion exchange resins were employed.

He was not aware that steam compression stills were in use for the production of distilled water, although they were employed for evaporation.

DR. L. SAUNDERS, in reply, said that the problem of the sterilisation of ion exchange columns had not yet been solved. Formaldehyde seemed unsatisfactory and a more suitable material had to be found.

As to polythene containers and plasticisers, although it was stated that no plasticiser was used in polythene, some fabricators occasionally included a plasticiser.

The possibility of nickel being present in water raised the question of the B.P. test for heavy metals in water. At the moment there was one not very sensitive overall test for a number of metals. There were many sensitive reagents available for individual heavy metals, and some modification of the test might be considered. He suggested that cationic exchange columns might be useful in estimating the content of trace metals in water.

Although he had no personal experience of the behaviour of fluorides with ion exchange resins, he did not think that their presence would have any harmful effect on the resin.