OZONE: SCIENCE AND ENGINEERING
Vol. 5, pp. 95-101, 1983
Pergamon Press Ltd.
Printed in the USA.

0191-9512/83 $3.00 + .00
International Ozone Association

USE OF OZONE IN THE TECHNOLOGY OF BOTTLED WATER

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Abstract

A review is given on the EC requirements for mineral water and on the analytical examinations necessary for proving its natural purity.

It is shown that an ozone treatment in combination with filtration can remove several undesirable substances without any major alteration of the chemical composition. Such substances would otherwise impede the marketability of a water.

Sulphur, iron and manganese are easily oxidized by ozone and the iron and manganese hydroxides are removed by filtration. Arsenic is eliminated by coprecipitation with iron. Fluoride can be largely removed by filtration through alumina. Any off-taste, occasionally caused by natural organic substances, is prevented by the ozone treatment. Additionally, the possibility of sterilizing wine bottles with ozone-containing water, is shortly dealt with.

A report on the "ozonization of bottled water" has already been given in chapter 59 of the Ozonization Manual for Water and Waste Water Treatment edited by W. J. Masschelein (1).

In the meantime, new directives for mineral water, spring water and bottled drinking water have been issued by the European Community (2). There are transfered at present into national legislation by the individual member states.

EC-Requirements for Mineral Water

According to these directives, a mineral water must originate from subterranean resources, protected against any influences from the surface, and must be of so-called original purity as proved by comprehensive microbiological and chemical examinations.

The microbiological quality at the spring outlet must be so perfect that any secondary treatment for disinfection of the water can be excluded. Natural mineral waters must be free of pathogenic germs. This equirement is not met, if Escherichia coli, coliforms, faecal streptococci or Pseudomonas aeruginosa are contained in 250 ml or sulphite reducing, spore forming anaerobes in 50 ml of the water (limiting value).

The colony count at the spring outlet should not exceed a recommended value of 20/ml at an incubation temperature of $20 \pm 2\,^{o}C$ and of 5 ml at an incubation temperature of $37 \pm 1\,^{o}C$ (incubation time: 2 days).

Water samples, which are taken and examined within 12 hours after bottling, must not exceed a limiting value of 100 colonies/ml at an incubation temperature of $20 \pm 2\,^{o}C$ and of 20/ml at $37 \pm 1\,^{o}C$ (incubation time: 2 days). A mineral water, which is intended for bottling, must therefore meet these microbiological requirements.

Analytical Examinations for Proving the Original Purity of a Mineral Water

The Institut Fresenius carries out extensive physico-chemical and chemical analysis, besides the microbiological tests, in order to prove the original purity of a water. These examinations comprise the following groups:

Physical and physico-chemical tests, general measurements, analysis of gases, measurement of alpha-radioactivity, tritium analysis, possibly analysis of carbon and oxygen isotopes, qualitative spectral, X-ray fluorescence and fluorimetric analysis, quantitative determination of the so-called main components, quantitative determination of the detected trace substances or of their limiting concentrations, analysis for organic substances by group parameters as DOC, total cyanide, anion-active tensides, phenolic compounds, substances extractable with petroleum ether or carbon tetrachloride and their IR-spectrometric determination, determination of polycyclic aromatic hydrocarbons, gas-chromatographic examinations for so-called haloforms and chlorinated organic solvents, for phenols and phenol-like substances, for organochlorine pesticides, organophosphorus pesticides, phenylurea herbicides, triazine herbicides, herbicidal carbamates and herbicidal phenoxyalkanecarboxylic acids.

If the original purity has been proved by these comprehensive examinations, i.e. no environmental contaminants have been found, the water is regarded as originally pure, but possibly not yet as marketable. In order to attain the marketability a separation of instable compounds is permitted, e.g. of iron and sulphur compounds. Removal and re-addition of carbon dioxide is also permitted.

Treatment of Natural Mineral Water with Ozone-containig Air

A naturally pure mineral water, which is free of environmental contaminants, cannot directly be bottled in the presence of hydrogen sulphide because of its odour and taste. Neither can it be bottled in the presence of dissolved bivalent iron in concentrations of more than 0.05 - 0.1 mg/l as excess of air then couses the appearance of fine brown flocks. Furthermore, a naturally pure mineral water may contain manganese, arsenic and fluoride in concentrations above the limiting values for drinking water, which can exclude its marketability.

Further natural components, e.g. other heavy metals, which are originally present in the water but may impede its marketability in certain concentrations, do usually not occur according to our extensive investigations.

Such an originally pure water which contains naturally excessive concentrations of iron, manganese, arsenic or sulphur, may be treated by permissible oxidation and filtration. Ozonization has in particular found wide-spread use for that purpose. Fe^{2+}, Mn^{2+} and S^{2-} are easily oxidized by an addition of ozone.

The desulphurization of hydrogen sulphide containing waters can be performed with ozone-containing air without any problems and the oxidation usually is carried through to sulphate.

The possible reactions are e.g.

$$H_2S + O_3 \longrightarrow S + H_2O + O_2$$

$$3\,H_2S + 4\,O_3 \longrightarrow 3\,SO_4^{2-} + 6\,H^+.$$

So-called sulphur waters contain hydrogen sulphide in concentrations between 0.1 and 20 mg/l. Desulphurization does not only lead to a taste- and odourless water for bottling, but additionally the desulphovibrio bacteria are destroyed, which can reduce sulphate to sulphide. Such secondary reactions in the bottles are thus prevented.

If the dissolved bivalent iron is oxidized by ozone-containing air, a considerably more rapid flocculation of the iron(III)hydroxide is observed and the filtration is easier than in the case of oxidizing by air alone. This applies particularly to chloride-containing waters.

$$2\,Fe^{2+} + O_3 + H_2O \longrightarrow 2\,Fe^{3+} + O_2 + 2\,OH^-$$

Possibly also present arsenic, in concentrations above the limiting value of 0.05 mg/l is largely eliminated by adsorptive coprecipitation with the iron(III)hydroxide after the oxidation. We have employed the ozonization technique for the removal of iron from waters containing several mg/l of Fe^{2+}, at the same time saftely reducing the arsenic content from several tenths of mg/l to values below 0.05 mg of As/ml.

In exceptional cases the iron content might not be sufficient for diminishing the arsenic content by coprecipitation to values below 0.05 mg/l In such cases a safe elimination of the residual arsenic can be achieved together with the demanganization by means of ozone. Manganese is oxidized from the bivalent to the heptavalent stage and is subsequently reduced to the tetravalent from by filtration through activated carbon. During this process almost all residual arsenic is eliminated together with MnO_2.

$$2\,Mn^{2+} + 5\,O_3 + 3\,H_2O \longrightarrow 2\,MnO_4^- + 5\,O_2 + 6\,H^+$$

$$MnO_4^- + 2\,C + 3\,H_2O \longrightarrow MnO(OH)_2 + 2\,CO_2 + 4\,H^+$$

In this way, iron, manganese and arsenic can be removed from a mineral water of interesting natural composition. Phosphates are also eliminated, without any decisive alteration of the other components and trace substances. Any co-precipitation of trace substances in the concentration ranges occurring in mineral waters (under 0.01 mg/l) has scarcely been observed in these processes. Bromide and iodide are oxidized to bromine and iodine, ore bromate and iodate, respectively, and the reaction products are removed by activated carbon. An occurrance of haloforms, as e.g. CHB_3 or CHI_3, was not observed after ozone oxidation and filtration through activated carbon. Fig. 1 shows the scheme of such a mineral water treatment.

The ozone treatment of natural mineral water was however a further important aspect, i.e. it prevents an often inexplicable secondary impairment of the taste of the bottled water. A plant using ozonization completely dispenses with chlorine. Bottle cleaning is also done with ozonized water.

Originally pure mineral waters occasionally contain natural organic substances, e.g. humic acids, which can cause an off-taste of the bottled water under conditions not completely known. Investigations are going on in the Institut Fresenius by means of GC - MS coupling in order to clarify the mechanisms involved and the type of substances affecting odour and taste.

We have, however, observed that there are no complaints about such an off-taste in all mineral water bottling plants employing oxidation with activated (O_3-containing) air for removing iron, manganese or sulphur. This concerns waters which are practically free of manganese and do not require on activated carbon filter, as also those containing Mn and requiring such a filter.

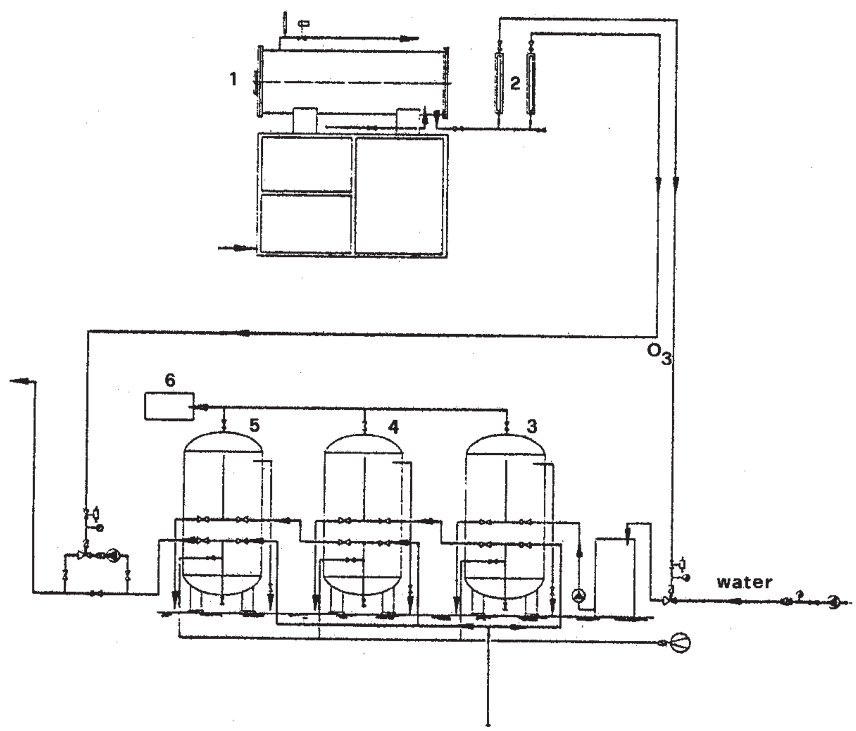

Fig. 1 Scheme of a mineral water treatment
1 = ozone generator, 2 = dryers, 3 + 4 = gravel filters
5 = activated coal filter, 6 = exhaust treatment

Subsequent to the ozonization, gravel and activated carbon filtration, the water is filtered through a small safety filter, impregnated with carbon dioxide and bottled. Such waters are absolutely neutral in odour and taste, pure, and retain their unobjectionable microbiological and chemical quality for many years, as had been shown by the results of examinations carried out by Institut Fresenius.

If a thus treated mineral water is to be bottled without or with only slight carbonation, a so-called after-ozonization has proved suitable, i.e. a fresh addition of very low ozone concentrations after the activated carbon filter. The water is then bottled with this low ozone excess in the concentration range of 0.1 to 0.2 mg/l. The ozone decomposes in the closed bottle with a half-life of about 1 hour (depending on the HCO_3^- content and pH-value) to molecular oxygen. Such waters also retain their perfect quality for many years, if the closures are tight and glass bottles are used preferably.

In all the above mentioned cases ozone is not used for the purpose of disinfection, but for the purpose of permitted oxidation and for the removal of substances which are originally contained in the mineral water, which however impede its marketability in too high concentrations.

Removal of Fluoride

A naturally too high fluoride content of a mineral water can be decreased by filtration through aluminia in the acidic pH-range (3). This process can be carried out subsequent to a preceding ozone treatment. For example, a natural fluoride content of about 10 mg/l was reduced to 4 mg/l ba means of this aluminia filtration technique. When considering the fact that about half the fluoride taken in with a mineral water is excreted with the urine on the same day (as has been reported by (4), approx 2 mg/l remain for use in the body, e.g. for caries prophylaxis. That means that a 0.7 l bottle of such a water covers the daily fluoride demand for caries prophylaxis.

It can be stated in conclusion that several undesirable substances can be eliminated from a naturally pure mineral water without any major effect on its chemical composition by means of an oxidizing treatment with ozonized air in combination with filtration.

Sterilisation of Bottles, in particular Wine Bottles, with Ozone-containing Water

An investigation was carried out on the effect of ozone-containing rinsing solutions, as employed in bottle cleaning machines, on wine yeasts. For the tests the bottles were inoculated with germs. 1 ml of germ suspension was added to each bottle. The blank values of the suspensions were as follows (see Table 1).

Table 1: Blank values of the germ suspensions

1. Yeasts	11 000 / bottle
2. Yeasts	61 000 / bottle
3. Yeasts	87 000 / bottle
4. Bacteria	1 200 / bottle
5. Bacteria	39 000 / bottle

Bacteria suspension:

E. coli, Pseudomonas aeruginosa, Staphylococcus aureus, Bac. subtilis

The inoculated bottles were treated with ozone-containing rinsing solution. The ozone concentration was between 2.5 and 3.0 mg/l, the pH-value was 7.9. The bottles were then examined in the laboratory. Blank samples were treated in the same way. In all cases a complete elimination of the germs was observed. For examination, the bottles were rinsed with 10 ml of sterile NaCl solution which was tested by the plate technique according to Koch. Additional tests were made with bottles inoculated with bacteria in order also to find out the effect of ozone solutions for the elimination of bacterial germs. A complete elimination was observed in thise case, too. The results of the tests are compiled in Table 2.

Table 2: Results of the ozone treatment of bottles

	Incubation 2 and 4 days at 28°C and 37°C, respectively							
	Sabouraud agar				Wort agar			
	2 days		4 days		2 days		4 days	
	1. bottle	2. bottle	1. bottle	2. bottle	1. bottle	2. bottle	1. bottle	2. bottle
1. Blank value	5900	-	8400	-	4900	-	7900	-
Yeasts after treatment	0	0	0	0	0	0	0	0
2. Blank value	36000	-	36000	-	33000	-	34000	-
Yeasts after treatment	0	0	0	0	0	0	0	0
3. Blank value	58000	-	64000	-	60000	-	62000	-
Yeasts after treatment	0	0	0	0	0	0	0	0

	Incubation 2 and 4 days at 37°C							
	Nutrient agar				Casein-Soya-peptone agar			
	2 days		4 days		2 days		4 days	
	1. bottle	2. bottle	1. bottle	2. bottle	1. bottle	2. bottle	1. bottle	2. bottle
4. Blank value	15000	-	17000	-	15000	-	18000	-
Bacteria after treatment	0	0	0	0	0	0	0	0
5. Blank value	46000	-	52000	-	50000	-	58000	-
Bacteria after treatment	0	0	0	0	0	0	0	0

Examination of the influence of the pH-value. Tests were carried out with a neutral solution of pH about 7.8, an acid solution of pH 1.9 - 2.0 and an alkaline solution of pH about 11.1. The most effective elimination of yeasts and bacterial germs in the presence of high concentrations of organic substances (sugars, wine residues) was observed in acid medium. An original yeast content of 10 000 - 30 000 per bottle was reduced to 10 - 30. In neutral medium (pH about 7.8) it was reduced under comparable conditions to about 100 per bottle. In alkaline medium (pH about 11.1) the remaining content was between 1000 and 20 000. With the same quantity of ozone passed in, about 7 mg/l were measured in the acid solution, about 3 mg/l in the neutral and about 0.5 mg/l in the alkaline solution. This is caused by the differently rapid ozone decomposition in these solutions. pH-values in the acid or weakly acid range with a residual ozone content of several mg/l therefore appear to be most favourable for eliminating yeasts and bacterial germs. Fig. 2 gives an impression of the time-dependant decrease of ozone in such bottles.

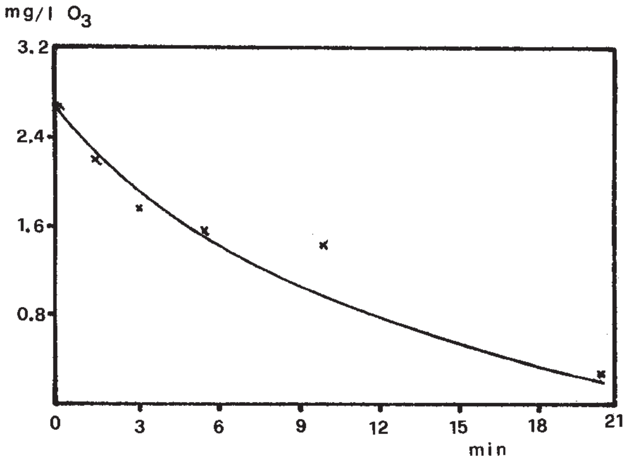

Fig. 2: Decrease of ozone concentration in inoculated bottles dependant on time

Key words

Bottled water, ozonation, germ treatment, bottle sterilization

References

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Résumé

Les regulations de l'eau potable données par la Communauté Européenne sont discutées et aussi les possibilitées de traiter ces eaux par ozone. La diminuition des germs pendant le lavage de bouteilles avec de l'eau ozonisée est montrée.

Auszug

Die von der EG-Richtlinie für Trinkwasser ausgehenden Probleme werden erörtert, wobei die Behandlung des Wassers mit Ozon in vielen Fällen Vorteile bringt. So können Schwefelverbindungen, Eisen-II oder organische Substanzen, die zu Geruchs- und Geschmacksbeeinträchtigungen führen, bei Einsatz geeigneter Anlagen eliminiert werden. Auch Probleme mit Verkeimungen in Flaschen können statt durch Verwendung von Chlor durch Ozoneinsatz gelöst werden.