

## SEAWATER OZONIZATION AND SHELLFISH DEPURATION

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### Abstract

French coastal water pollution has necessitated construction of shellfish depuration stations. Physical and chemical studies indicated that while ozone and bromates are absent from ozonized seawater, there is an increase in dissolved oxygen and residual oxidants. Water quality, temperature, and variations in shellfish filtration capacities appear to govern oxidant longevity.

The increasing pollution of French coastal waters resulted in the contamination of shellfish which were formerly eaten at will by consumers. Although it was fairly easy to forbid fishing in certain contaminated areas, it was more difficult to order the closing of the shellfarms where shellfish are grown by professionals. Consequently, in order to utilize shellfish which may be contaminated, it was decided to build purification plants in some badly affected regions.

There are differences from one depuration plant to the next, but the basic principle remains the same: seawater is first disinfected and then used for filling the troughs where the shellfish remain for certain periods of time (Fig. 1). Shellfish purification, therefore, can be divided into two stages:

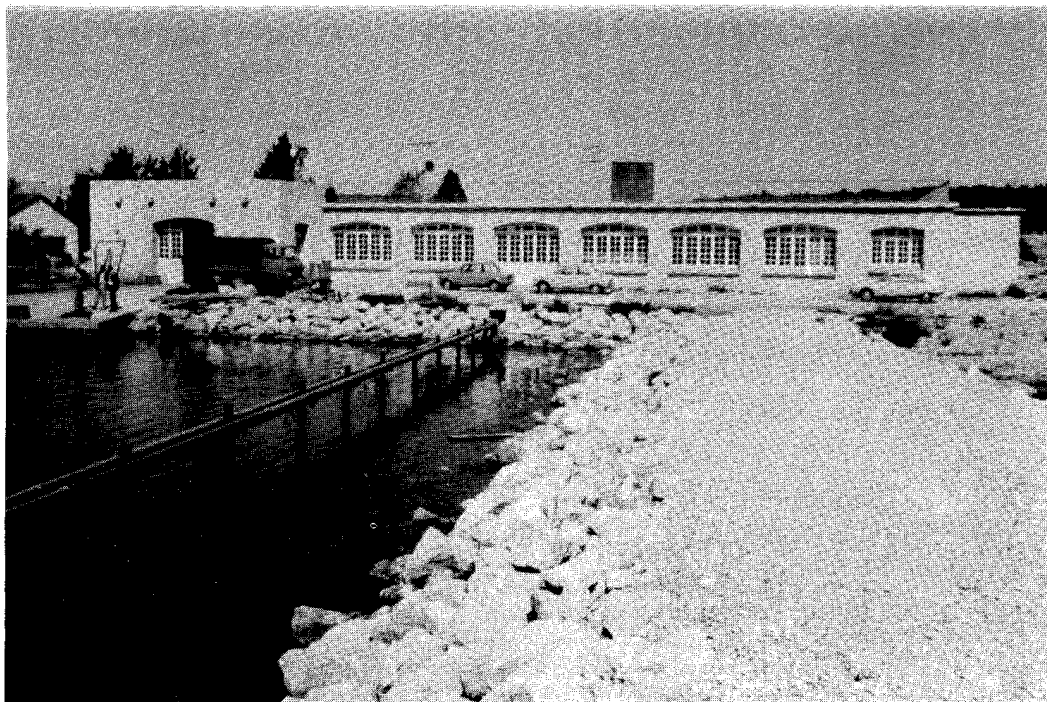
- 1) Disinfection of the seawater to eliminate the pathogenic microbes which may be present.
- 2) Keeping the shellfish in a trough where they will gradually release the unwanted microorganisms through their characteristic pumping action.

One of the various available techniques, ozonization, is now being increasingly applied as it gives excellent results, especially when it is used in conjunction with an especially developed retention trough. Such a system is in use at the "Cote Bleue" shellfish purification plant located at Bouzigues in the south of France.

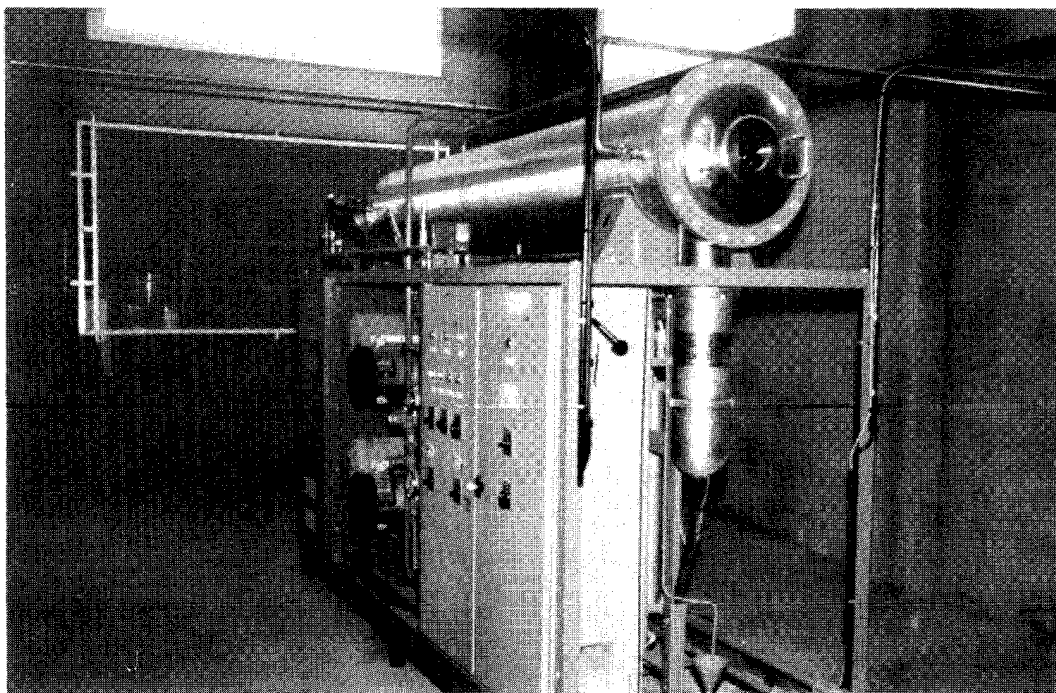
The purpose of the present paper is to describe the plant and to comment on the physical and chemical results obtained in mussel and oyster purification.

### The "Cote Bleue" Shellfish Purification Plant

Located within the shellfarming area by Thau Lake, the Cote Bleue plant primarily purifies mussels, oysters, and clams liable to contamination. Taken from the lake at some fifty meters away from the bank, the seawater is pumped at a maximum rate of 150 cubic meters per hour and is ozonized for disinfection. Ozone is supplied by a Monobloc 18 tube generator, able to produce 270 grams of ozone per hour from air.



General view of the "Cote Bleue" Shellfish Purification Plant



Ozone generator used for seawater disinfection

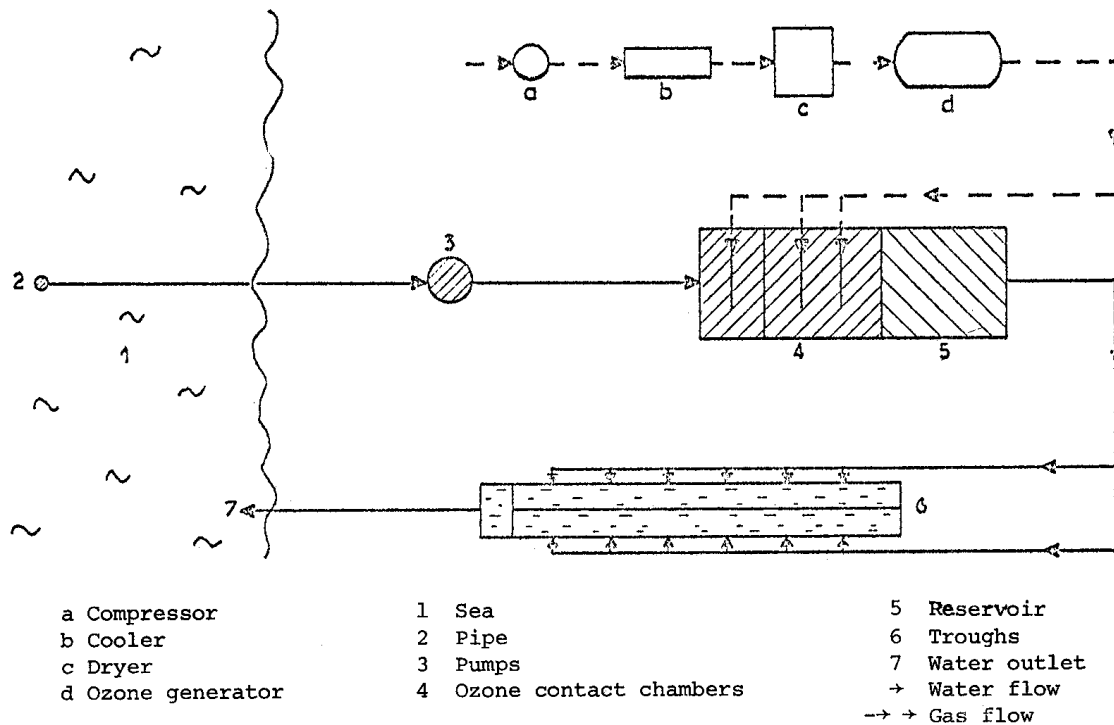


FIG. I  
General diagram for seawater treatment

Contact between ozone and seawater is accomplished by porous diffusers in a two compartment chamber. The total retention time varies from 6 to 10 minutes, the treatment ratio from 1 to 1.5 ppm and the water depth is about 3.5 meters.

After ozonization, the water cascades into a tank of 25 m<sup>3</sup>/h maximum capacity. It includes a min/max level indicator whereby, depending on the water depth in the tank, pumping and ozonation will be started or stopped automatically.

The treated seawater is then supplied to the eight shellfish purification troughs of 20 m<sup>3</sup> each which are divided lengthwise into two compartments (Fig. 2). Their measurements are about 10m in length, 1 meter in height on the average, and their bottom slopes down by 2%. The baskets containing the shellfish are elevated above the bottom of the troughs by means of supports built on the longitudinal walls. The ozonized seawater is added through ports which are located in the upper part of the trough and are equally spaced on one of the longitudinal walls. Drainage of the water is accomplished by a removable plug at the deepest end of the trough. A baffle plate has been provided at the optimum point to dispose not only of the surface water but also of the water at the bottom of the compartments.

The water is discharged into the lake after use. Its renewal varies in the troughs from 2 to 5 m<sup>3</sup>/h when the treatment is applied continuously. The shellfish are always distributed evenly in the baskets up to 35 kg/m<sup>2</sup>.

#### Analysis of the seawater after Ozonation

The laboratory analyses involved the ozonation of various solutions and several

seawater mixes under conditions as similar to depuration plants as possible. The species that were present, and more particularly total oxidants, were then identified and measured.

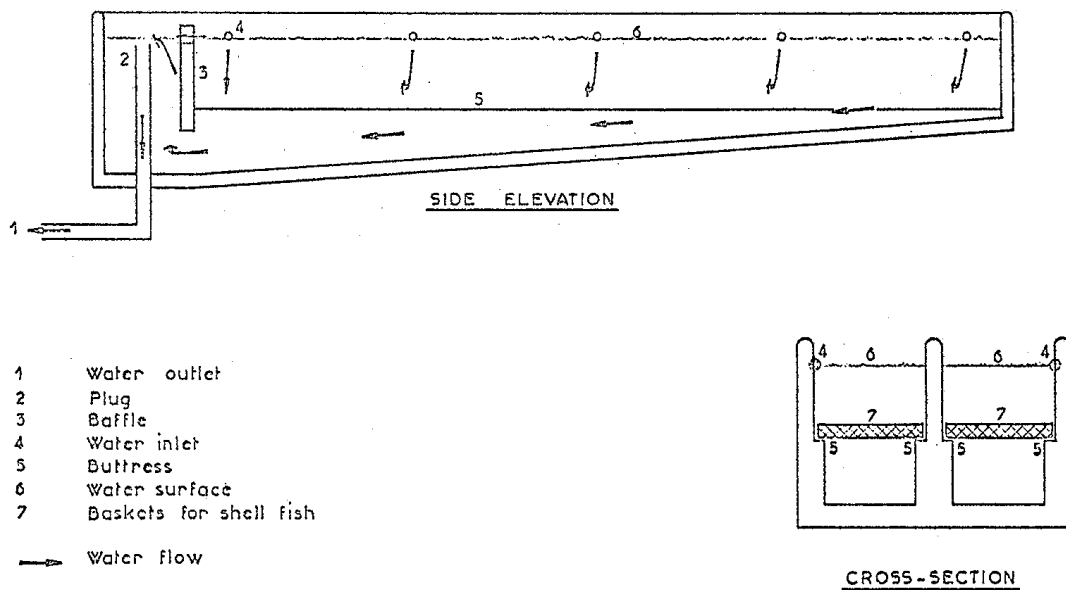


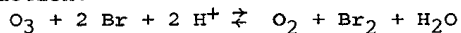
FIG. II  
Details of a Trough

The following analyses were carried out during the study:

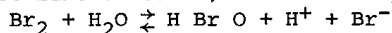
- dissolved oxygen (Beckman Monitor Model 123305)
- salinity (Electronic Switch Gear Apparatus Model MC5/2)
- pH (Tacussel instrument Type PT)
- oxidation-reduction potential (Tacussel Minisis 5000)
- bromates (Pulse-type polarography with Tacussel PRG5)
- residual dissolved ozone (qualitative method by absorption at 254 nm; spectrophotometer Philips Pye Unicam)
- total oxidants (iodometric method with measurement of absorption at 350 nm)
- residual oxidants other than ozone (same method as above after adding 2g/l of glycine)
- residual amount of dissolved ozone (quantitative evaluation obtained by differentiating the above two methods).

During the laboratory experiments, ozonation took place in ozone demand bottles. Ozone was produced from air by means of a laboratory generator type LABO 70.

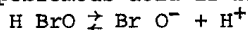
Referring to the theory of oxidation-reduction potentials, it can be said that ozone, the most powerful oxidant after fluorine, can normally release chlorine and chlorides and mainly bromine and bromides as per the following equation reaction:

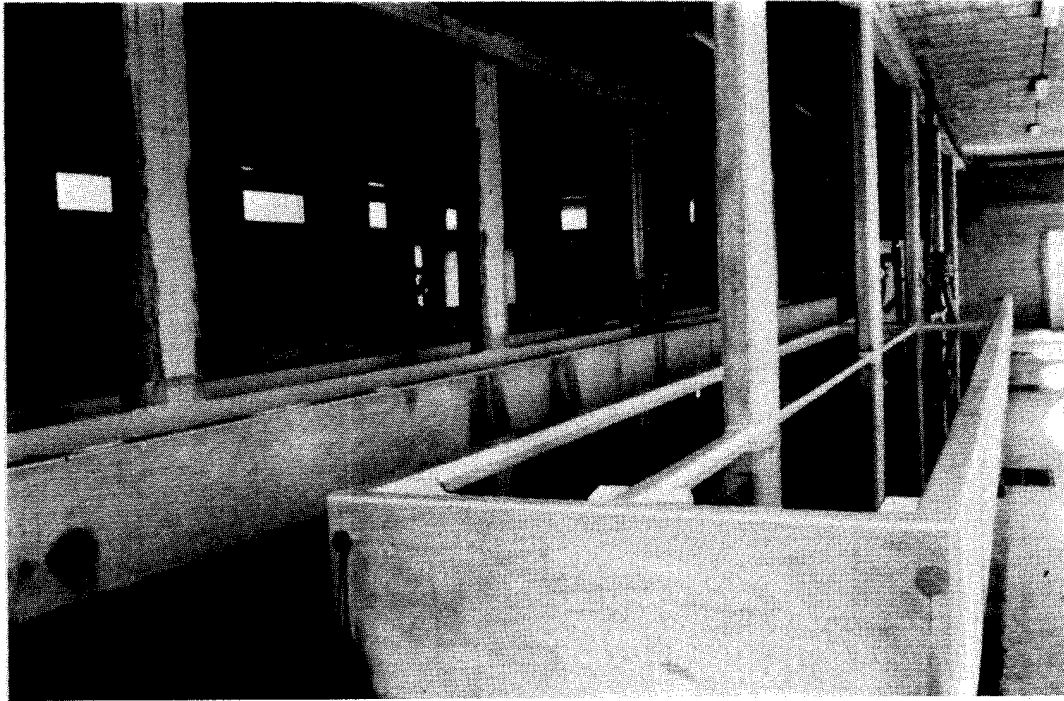


Just like chlorine, bromine is hydrolyzed in water:

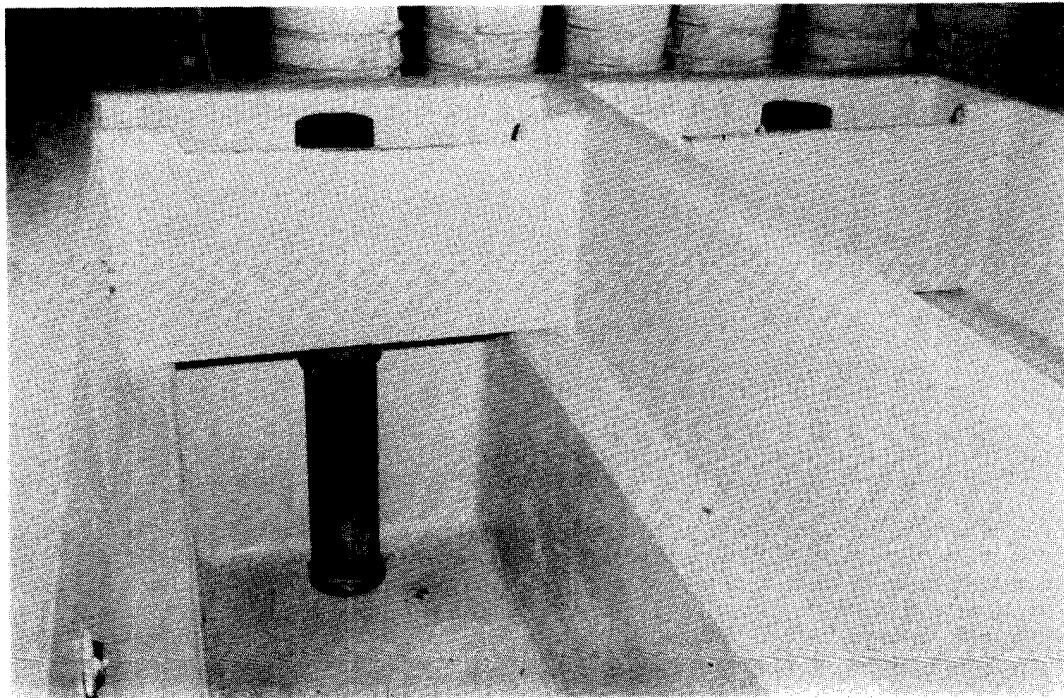


Hypobromous acid is broken down in its turn:



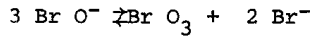
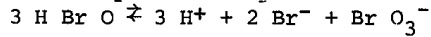


Inside view of the plant showing the troughs



Detail of a trough

Bromates may also be formed:



Due to the low iodide content in seawater (about 0.06 mg/l) the amount of iodide liberated after ozonation is considered negligible. In return, ozone can, in theory, generate hypobromous acid plus ions of hypobromite and bromates from the 65 mg/l of bromides, and also hypochlorous acid plus ions of hypochlorite and chlorates from the 19 g/l of chlorides.

Synthetic solutions of halides were ozonized in order to identify those species (Fig. 3).

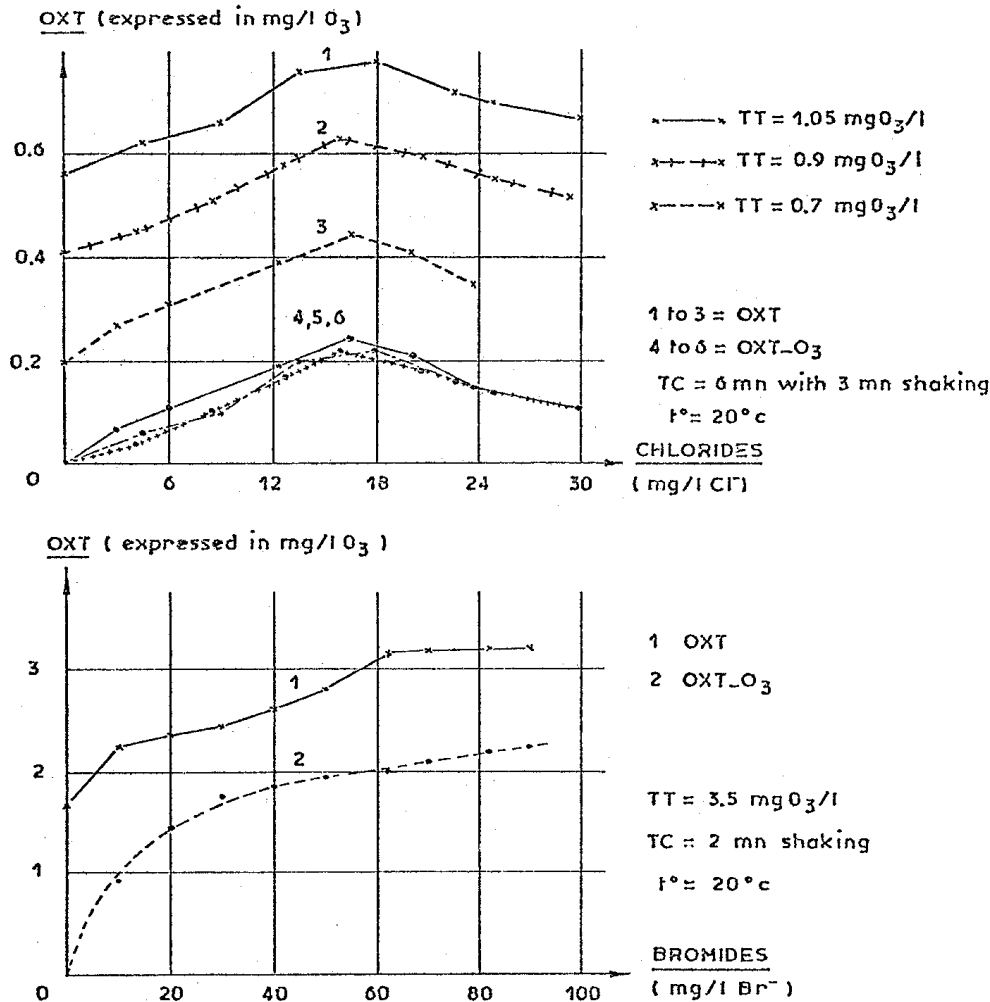


FIG. III

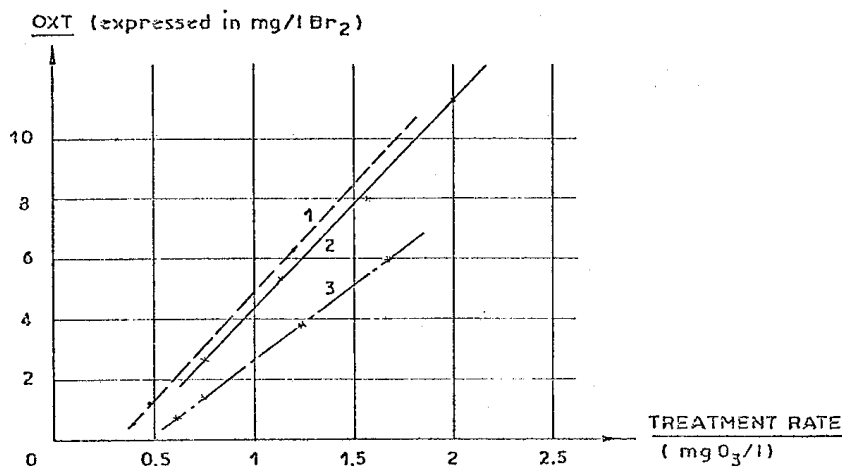
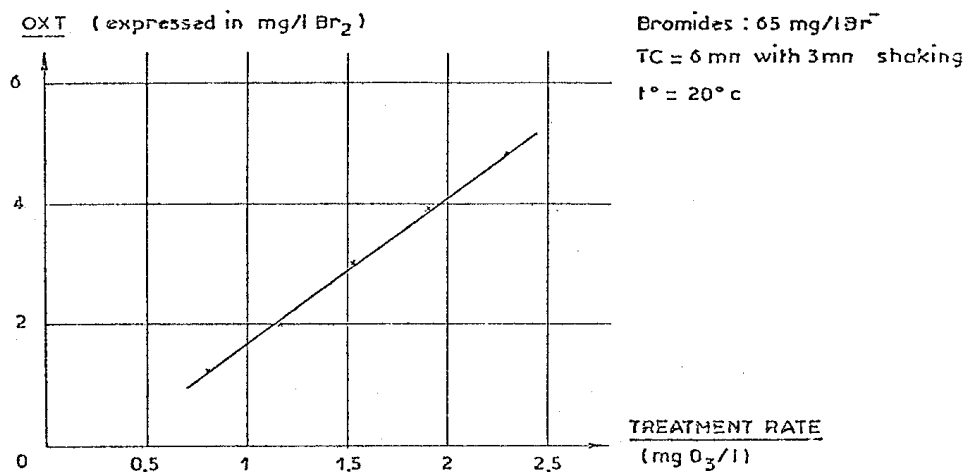
Total oxidizers (OXT) induced by ozonizing solutions of chlorides and bromides

When solutions of increasing chloride content in distilled water are ozonized, the total amount of residual oxidant reaches a maximum which corresponds to a chloride concentration comprised between 16 and 17 mg/l, whatever the treatment ratio (the latter ranging from 0.7 to 1.05 mg ozone per liter). Such residual oxidants include both chlorine and ozone, but no presence of chlorate could be evidenced. Residual ozone is proportional to the treatment ratio and seems independent of the chloride content.

A very different phenomenon occurs when bromide solutions are subjected to ozonation. In effect, Fig. 3 shows that residual ozone can be measured immediately

after the gas has been dissolved and, most importantly, residual bromine is formed and increases with the bromine content.

It can be seen in Fig. 4 that after 3 minutes, there is no dissolved ozone and that a residual oxidant is present. The oxidant increases with treatment as a linear function of the treatment ratio. For the same amount of injected ozone, the residual quantity varies with temperature and also with the geographical location where the sample of seawater under study has been taken.



- 1 sea water from S<sup>t</sup> Suliac (France) .  $t^\circ = 10.5^\circ \text{c}$
- 2 sea water from Trouville (France) .  $t^\circ = 9^\circ \text{c}$  "
- 3 sea water from S<sup>t</sup> Suliac (France) .  $t^\circ = 21^\circ \text{c}$

TC = 6 mn with 2 mn shaking.

FIG. IV  
 Total oxidizers (OXT) induced by ozonizing  
 solutions of bromide and samples of seawater

The various polarographic measurements made have not enabled the determination of bromates in ozonated seawater under conditions similar to depuration plant conditions (Fig. 5). The total oxidant residual measured included hypobromous acid and ions of hypobromites (78% and 22% respectively for seawater at  $25^\circ \text{C}$  with a pH of 8.2). If the water contains ammonia however, then bromamines are formed. The small residual amount of chlorine obtained after ozonation, will

release bromine from bromides and will, therefore, disappear.

But what is going to happen to residual bromine which will be called "total oxidants" in the rest of this paper? Obviously the half-life is governed by temperature and also by season and the location where the water has been sampled.

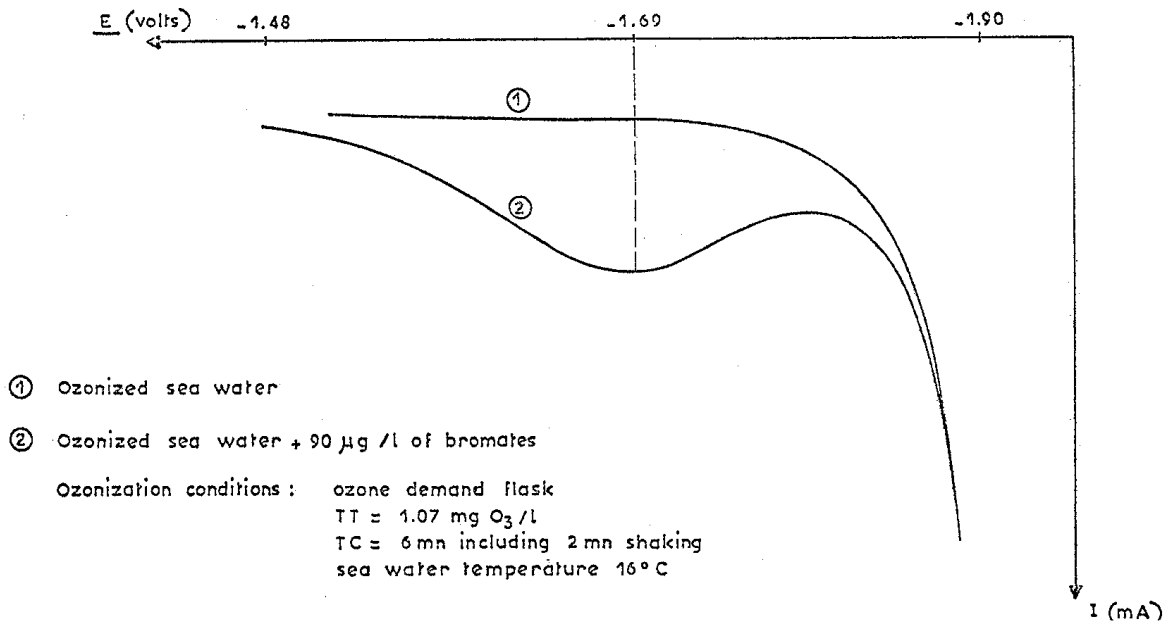


FIG. V  
Anodic bromate waves

Figure 6 shows that whatever the conditions of ozonation, total oxidants will be phased out in accordance with the following law during the first hours:

$$\frac{1}{\text{Total Oxidants}} = aT + b$$

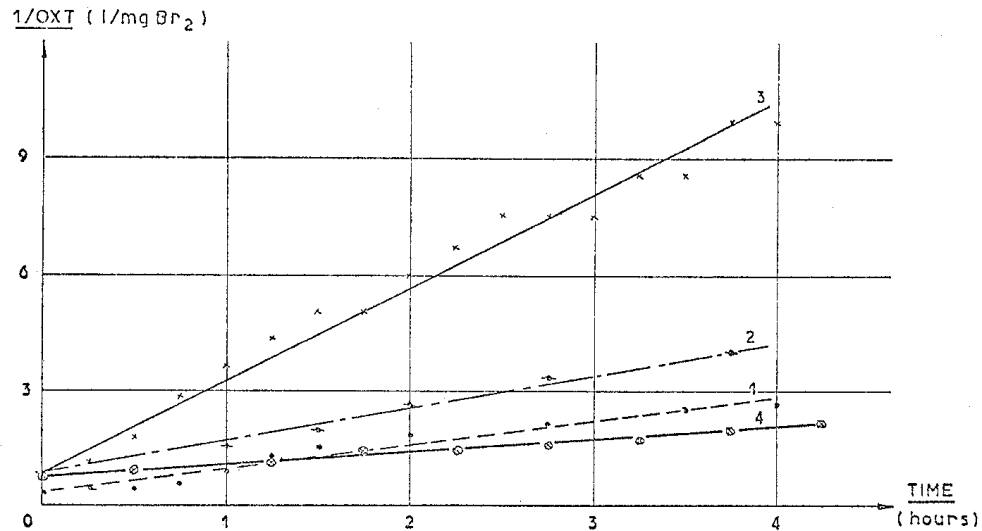
where a and b are parameters governed by such factors as temperature, pH, oxidable materials, and conditions of ozonation. Total oxidants will, therefore disappear more quickly in the summer than during the winter. In addition, the higher the treatment ratio, the greater the amount of residual bromine and the slower it disappears, just as if ozonation lowers the bromine demand in the ozone-treated seawater.

The same dynamics for the phasing out of total oxidants will be found in the purification troughs. In effect, if those are filled with previously ozonated seawater and if the water is not renewed as is the case with discontinuous purification, residual bromine decreases quickly at first and then more slowly as time goes by.

Figure 7 shows the persistence of seasons on total oxidants. A 50% reduction is obtained in a maximum period of one hour in the summer whereas the same decrease is attained in two hours during the winter. This is due to temperature and mainly to the percentage of oxidable material in seawater. In the summer, that percentage is higher, so the bromine demand increases and the residual amount of product is reduced faster.

When the shellfish purification troughs are supplied continuously with ozonated

seawater, the total oxidants decrease less markedly and stabilization is attained gradually with time and according to where the analyses are made. This can be explained by the continuous input of renewal water which tends to limit the decrease of residual bromine in the trough.



- 1: Atlantic sea water - Spring - Laboratory test -  $t^{\circ} = 16^{\circ}\text{c}$  - Treatment rate =  $1.77 \text{ mg O}_3/\text{l}$
- 2: Mediterranean sea water - Summer -  $t^{\circ} = 23^{\circ}\text{c}$
- 3: Atlantic sea water - Spring - Laboratory test -  $t^{\circ} = 16^{\circ}\text{c}$  - Treatment =  $1.07 \text{ mg O}_3/\text{l}$
- 4: Mediterranean sea water - Winter -  $t^{\circ} = 13^{\circ}\text{c}$

FIG. VI  
Evolution of total oxidizers (OXT) according to time  
(No shellfish and no feeding)

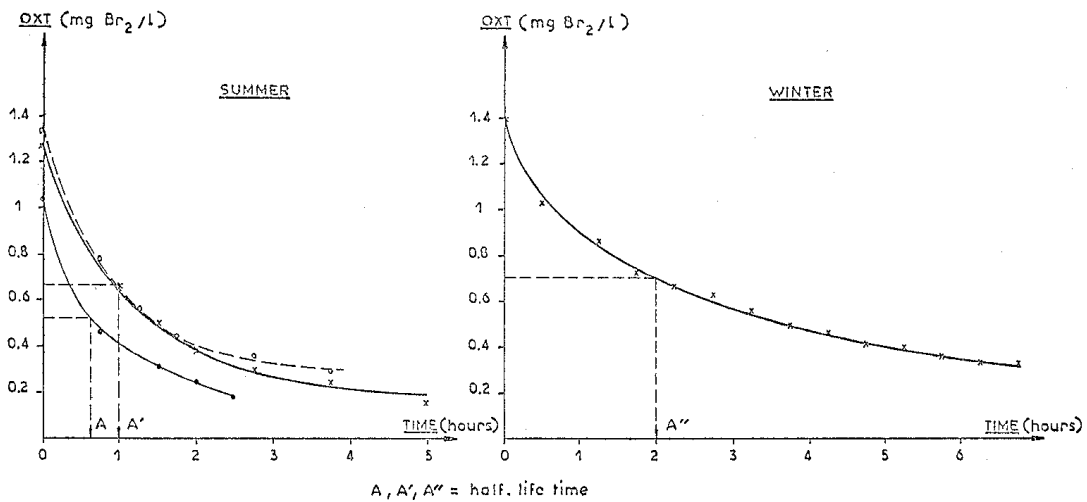
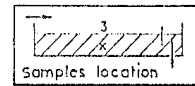


FIG. VII  
Evolution of total oxidizers (OXT) in a trough filled  
with ozonized seawater (no shellfish)

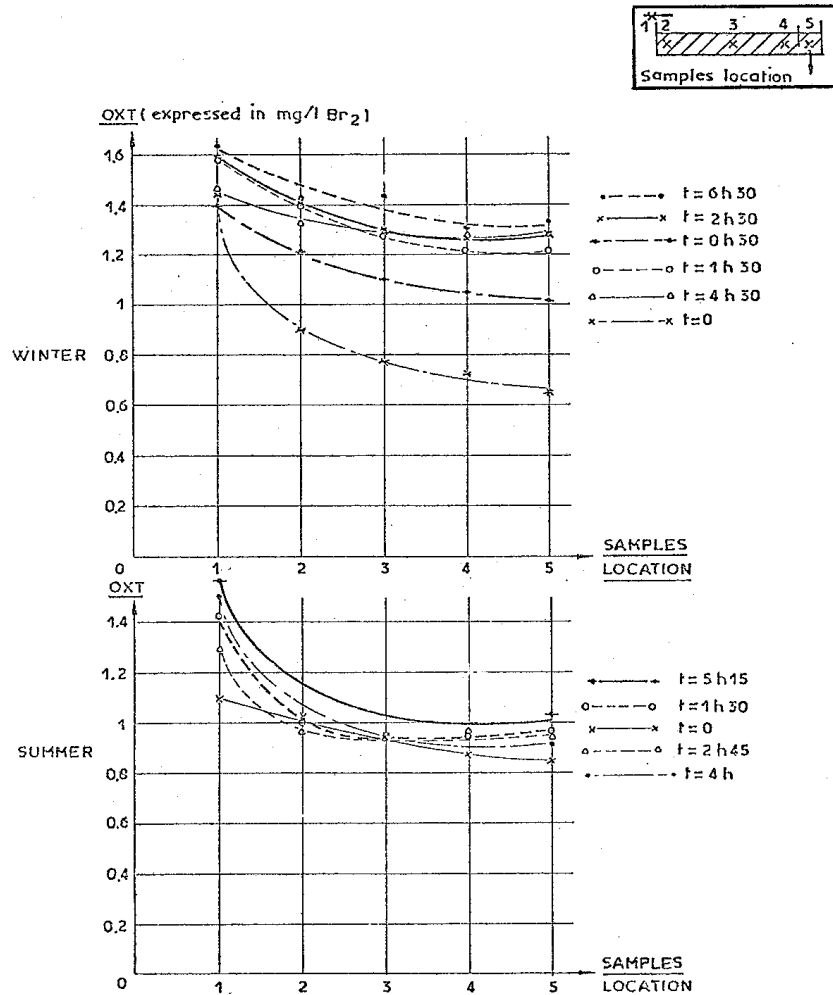


FIG. VIII  
Evolution of the total oxidizers (OXT) in a  
trough fed continuously with ozonized seawater

Figure 8 indicates the changes that can be observed through the seasons. The drop in total oxidant in inlet water reaches 37.5% in the summer but does not go beyond 18% during the winter. Residual bromine increases from 1ppm to 1.35 ppm between summer and winter. The measurements were made in the center and at the medium height of the trough 90 minutes after filling. It is confirmed (Fig.9) that total oxidants decrease by 45% in winter and 62% during the summer when the water is not renewed as opposed to 16% (winter) and 34% (summer) when it is replaced.

The conclusion is that residual bromine decreases in purification troughs, even in the absence of shellfish, and that its concentration is greater in the winter than in the summer, especially when the seawater is renewed.

#### Changes in the water during shellfish purification

After studying the persistence of total oxidants in seawater after ozonization, the specific case of shellfish purification was surveyed as follows:

The response of mussels (*Mytilus galloprovincialis*) and oysters (*Crassostrea gigas*), to two depuration techniques (continuous and discontinuous) was examined.

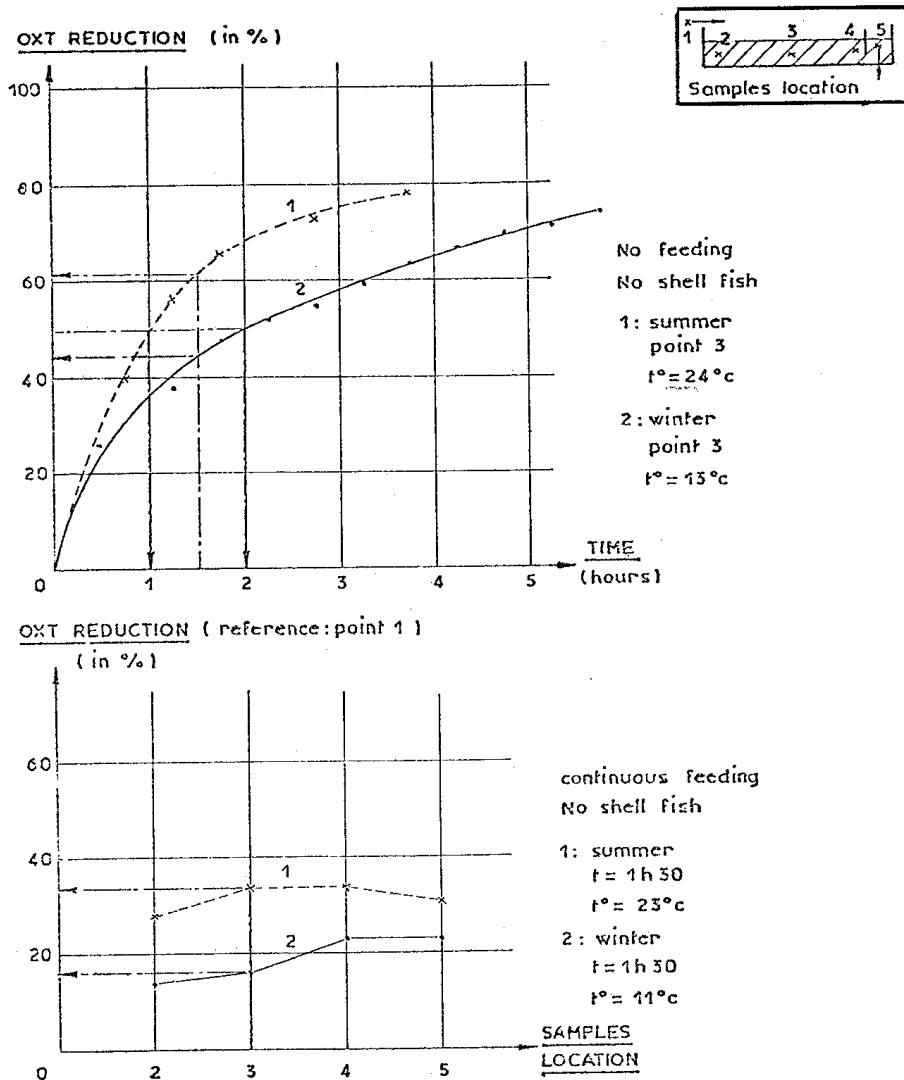


FIG. IX .  
Total oxidizers reduction (OXT reduction)  
in a trough according to the seasons  
(No shellfish)

In the first case, after filling the trough, the water is renewed with ozonized seawater, the amount used corresponding to some 10 to 20% of the trough volume per hour. If purification is discontinuous, the trough is filled with previously ozonized water but the latter is discharged after a certain period of time to be replaced again by treated water, the frequency of refilling being variable. In practice, the frequency depends on the season and on the type of shellfish to purify, but it generally ranges from 2 to 3 times a day. Prior to filling, the shells are cleaned with a jet of water under pressure.

Whatever the purification mode, the water is never recirculated after staying in the troughs but is discharged. The retention time for shellfish is governed by several parameters such as their nature, their degree of pollution, and the season, but in any case they remain in the troughs for at least 48 hours.

The purpose of purification is to eliminate pollution from shellfish. To this purpose, the molluscs, by absorbing seawater free of pathogenic microbes, gradually get rid of any unwanted matter which may be present in them in their tissues. A good purification system, therefore, must include a good hydraulic circuit in the case of continuous treatment, as it is necessary to eliminate the contaminated water in order to avoid any reinfection of the shellfish.

The following section will be concerned with the discontinuous purification process.

### Discontinuous purification

It is well-known that ozonization oxygenates the liquid medium to a non-negligible extent. Figure 10 illustrates a high amount of dissolved oxygen, this amount being greater in the winter than in the summer. During cold periods, the values and the dynamics for the disappearance of dissolved oxygen appear increased during the first hours for both mussels and oysters, after the second or third exposure to ozonized water.

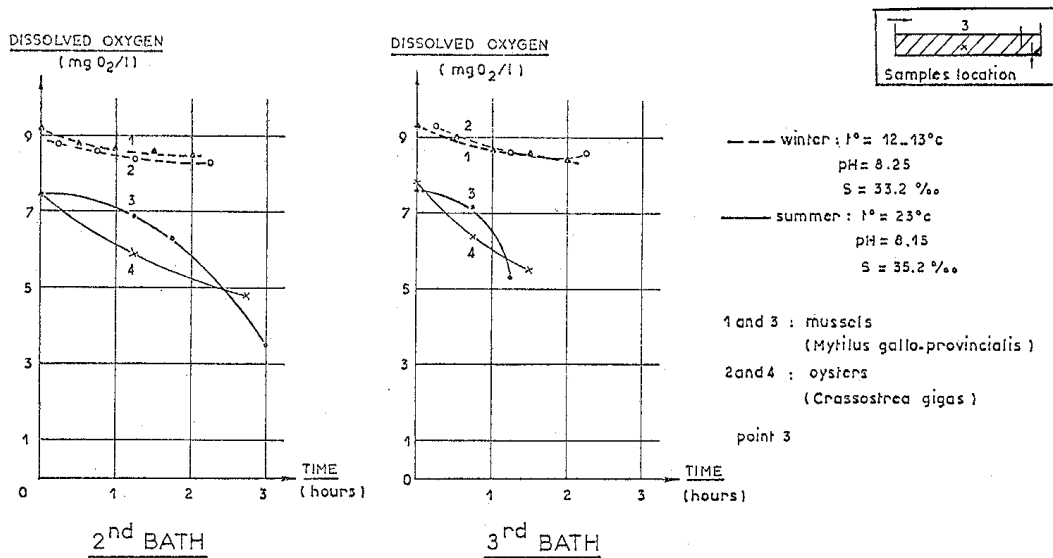


FIG. X

Dissolved oxygen evolution in a trough filled with ozonized seawater

The findings can be extremely different in the summertime. In the case of oysters, the amount of dissolved oxygen decreases quickly and then more slowly, both in the second and third baths.

With mussels, however, oxygen decreases slowly at first and then more quickly. This is very striking at the third bath, where the decrease amounts to 30% after one hour against 8% for the second bath.

Supplementary experiments would be necessary to have confirmation of the trend, but in any case, the disappearance of dissolved oxygen is faster in the summer than in the winter.

Figure 11 gives a visual representation of how total oxidants change during the discontinuous purification of oysters in the summer. In this specific case, the retention time in the purification trough was two days and the oysters were subjected to five baths in succession. The results obtained call for the following comments:

- The discrepancies between the value measurements on the water at the head and tail of the trough tend to decrease as the number of baths increase.
- Whatever the bath, the reduction of total oxidants is much greater in the presence of oysters than in their absence which seems to imply some consumption by the oysters themselves.
- The amount of the residual bromine varies with the bath in seawater. This is due to the variable retention time in the tank

after ozonization.

- During the first day, the decrease in total oxidants occurs quickly at the beginning of each bath and then slows down gradually. On the contrary, the amount of residual bromine seems to decrease in a linear manner during the second day (baths #4 and #5). This may be due to some incipient mortality of the shellfish as observed during the second day, thus inducing a greater bromine demand stemming from the oxidation of moribund tissue.

This assumption seems substantiated by Fig. 12 which shows the reduction in total oxidants for each bath as time goes by. In effect, during the winter, when no mortality is observed, the time necessary for 90% of the residual amount of bromine to disappear increases with the number of successive baths: 1 H 24, 1 H 30, 2H, 2H 18, and 2 H 30 respectively.

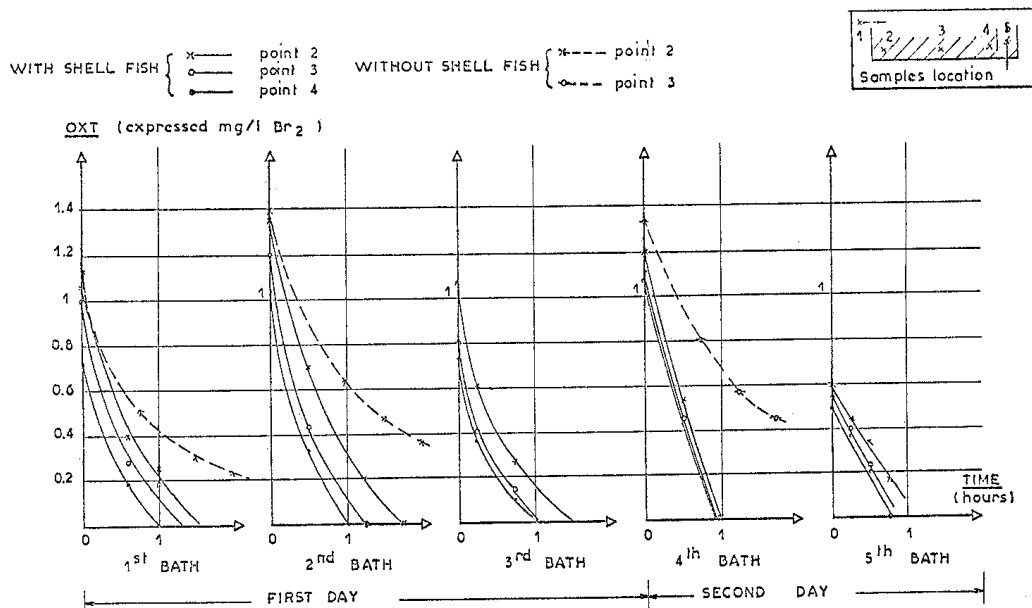


FIG. XI

Total oxidizers (OXT) evolution in a trough filled with ozonized seawater (Summer period. Oysters *Crassostrea gigas*)

This phenomenon is even more striking in the case of mussels (Fig. 13). In the winter it takes 2 H 6 for the first bath to diminish an amount of total oxidants by 90%. Interestingly, the shorter time for the second and third baths corresponds to the period when the mussels spawned in the water, which led to temporarily increased consumption. In the summer, it takes much less time for the disappearance of 90% of residual bromine (54 min., 1 H 18, 1 H 6, 54 min., and 42 min. successively). Here again, incipient mortality is observed from the third bath, which coincides with an increased consumption of total oxidants.

All these results are summarized in Fig. 14 where curve 4 corresponds to the purification of oysters in the winter. It shows that residual bromine disappears more slowly from bath to bath. This leads to the gradual oxidation of the organic compounds by bromine, due to the dirt on the outside of the shells. No threshold or plateau has been attained in the curve, thus evidencing that the very specific consumption by oysters has not been reached. As to curve 2, it shows a greater decrease in total oxidants from the third bath, thus indicating the influence of mortality on the dynamics of disappearance.

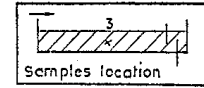
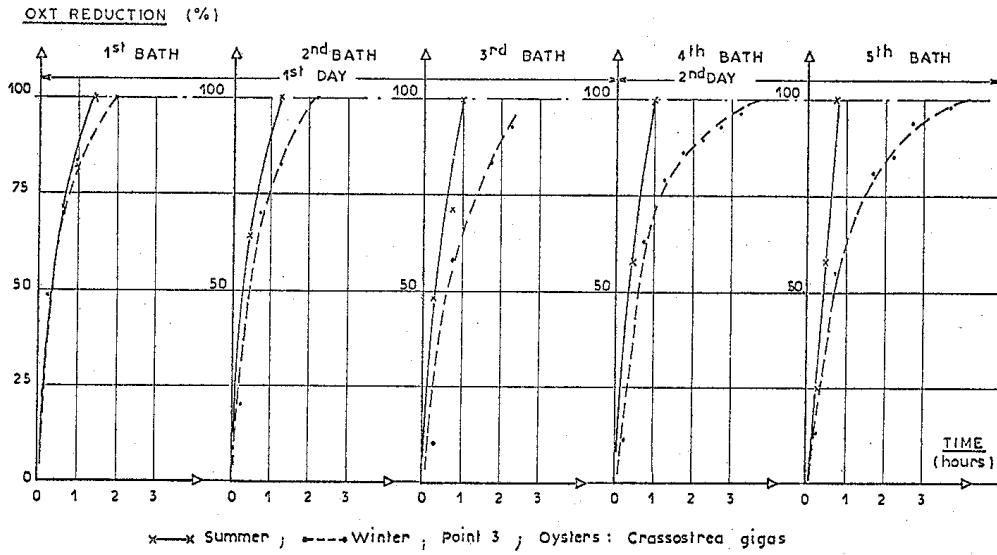


FIG. XII  
Total oxidizers (OXT) reduction in a trough filled with ozonized seawater in the presence of oysters

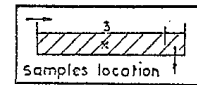
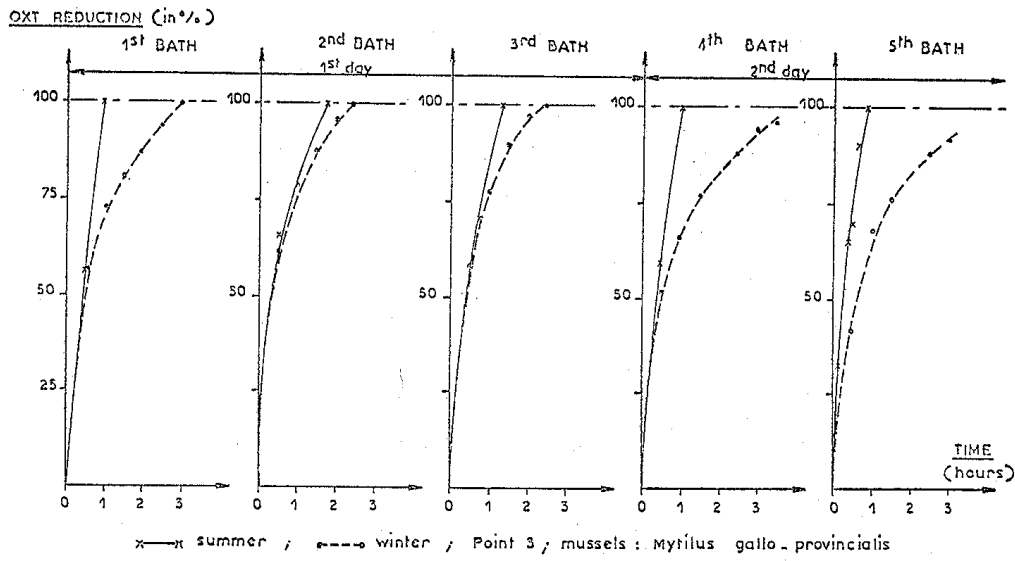
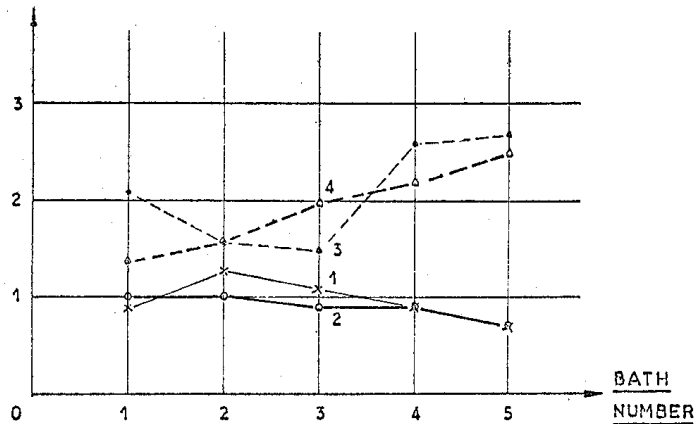


FIG. XIII  
Total oxidizers (OXT) reduction in a trough filled with ozonized seawater in the presence of mussels

TIME NECESSARY FOR A  
90% OXT REDUCTION ( hours )



1 and 3 : mussels : *Mytilus gallo provincialis*

2 and 4 : oysters : *Crassostrea gigas*

1 and 2 : summer period

3 and 4 : winter period

point 3

FIG. XIV

Bath influence on OXT reduction in a trough filled with ozonized seawater

The same applies to the purification of mussels in the summer, and the previous two cases are summarized in Fig. 1: firstly, the time necessary for 90% reduction in total oxidants increases, this being due to the gradual oxidation of organic matters because the shells are dirty; furthermore, the appearance of incipient mortality causes the bromine content in the trough water to decrease.

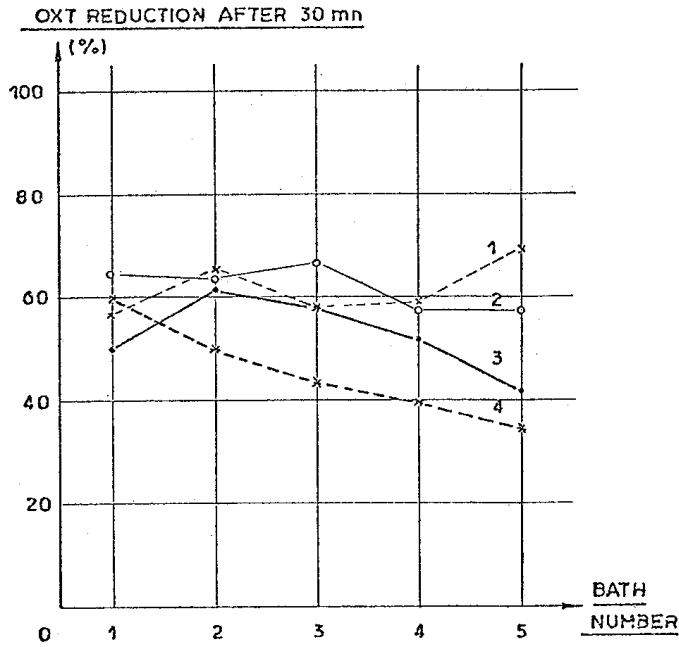
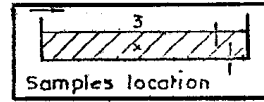
Lastly, Fig. 3, which corresponds to the purification of mussels in the winter, shows that total oxidants are sensitive to the organic matter present in the medium as residual bromine decreases while mussels are spawning.

In short, it appears that total oxidants are more largely reduced in the summer than in the winter and mainly that the reduction is governed by the oxidable product content (Fig. 15). When the organic matter content does not increase, the amount of total oxidants decreases less strongly with the number of baths, thus showing that oxidable products get more and more oxidized because of the external dirt on the shells. However, it was not possible to determine the consumption specific to each type of shellfish after a purification period of two days, including five successive baths. This may be explained by the slow reaction of the residual bromine and also by the important quantity of organic compounds liable to be oxidized.

#### Continuous purification

When the seawater is renewed constantly, as is the case with constant purification then a totally different evolution can be expected from total oxidants.

Figure 16 shows how residual bromine is reduced as a function of the time which



1 and 3 : mussels : *Mytilus gallo-provincialis*  
 2 and 4 : oysters : *Crassostrea gigas*  
 1 and 2 : summer period  
 3 and 4 : winter period

Point 3  
 contact time : 30 mn

FIG. XV

Total oxidizers (OXT) reduction in a trough filled with ozonized seawater

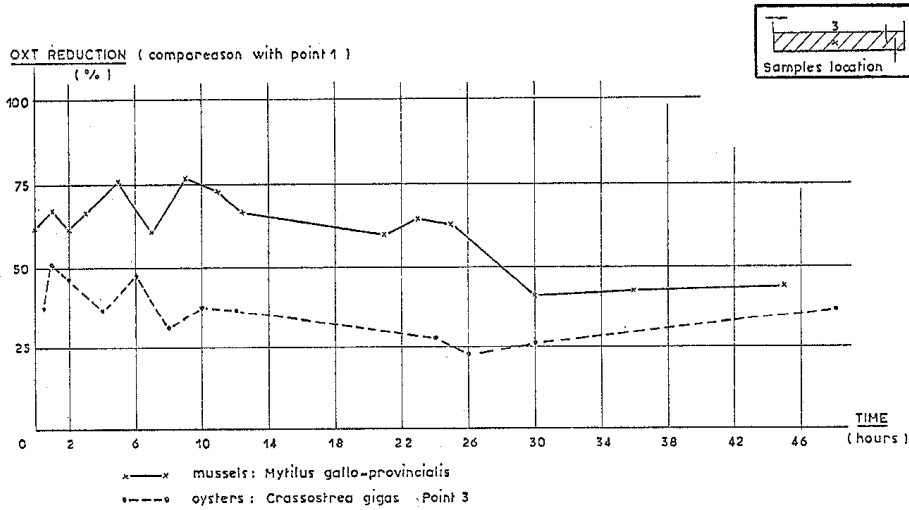


FIG. XVI

Total oxidizers (OXT) reduction (OXT) in a trough fed continuously with ozonized seawater (winter period)

the shellfish are retained in the troughs during the winter. For both mussels and oysters, total oxidants decrease more and more until they reach relatively stable values after a certain period of time: about 30 hours for mussels and 23 hours for oysters although the latter is dirtier on the outside.

The specific consumption by mussels and oysters was difficult to determine because of the variations in total oxidants in the treated water supplied to the trough and also because a representative indicator is not easy to set up. It appears, however, that mussels cause a greater decrease in residual bromine than oysters, even during the summer (Fig. 17).

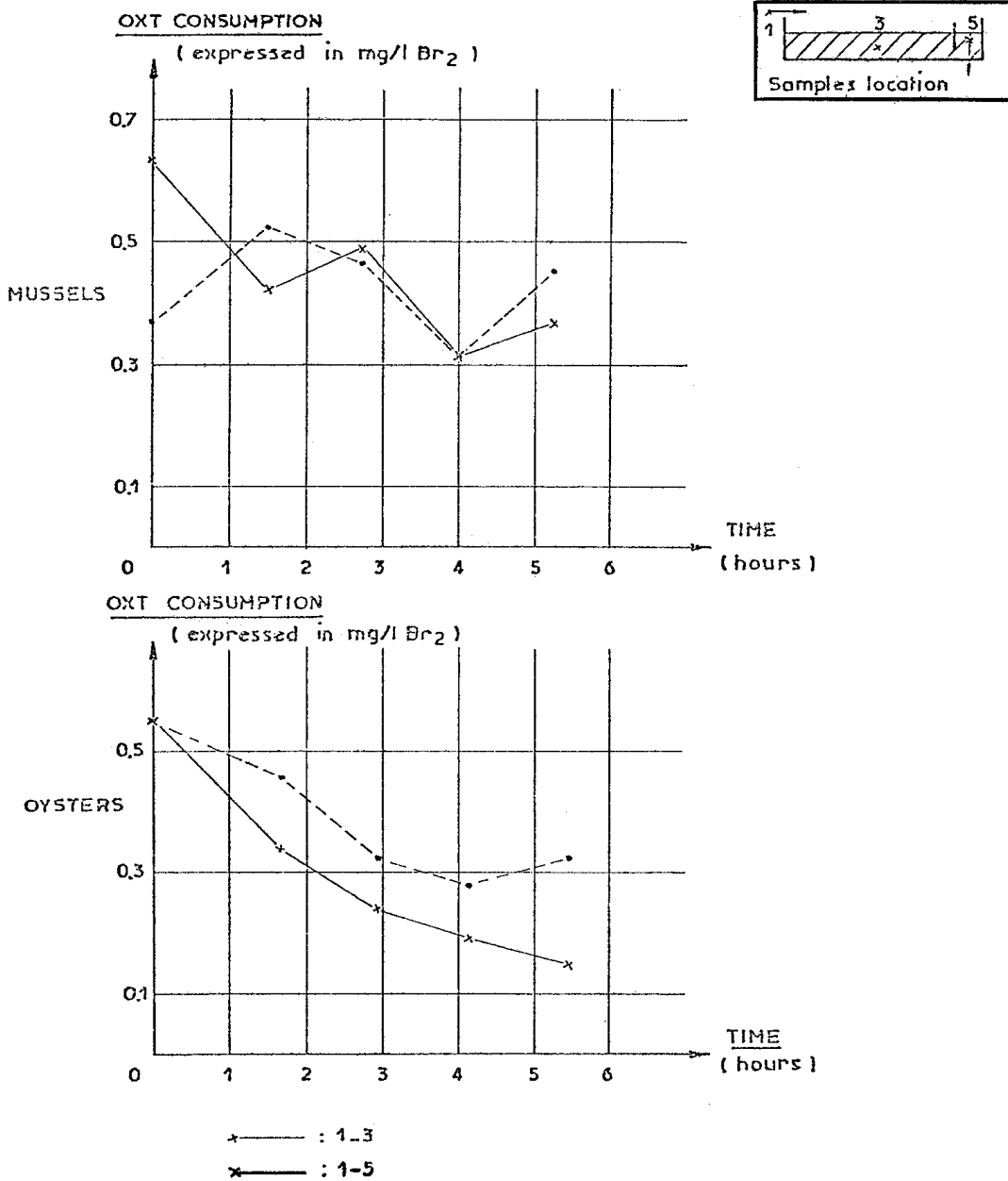


FIG. XVII  
 Total oxidizers (OXT) consumption by shellfish  
 in a trough fed continuously with ozonized seawater (Summer period)

Consumption by shellfish, which is calculated by taking into account the natural disappearance of total oxidants, tends to decrease slowly during the first hours in the case with mussels and faster when oysters are considered. After four hours and for the first half of the trough, it reached 1.9 mg/l of bromine for oysters and 3.2 mg/l for mussels, whose high consumption can be explained by some incipient mortality (about 5%). That loss of mussels is normal because of the long trip which they made from Spain in the summer and of the three re-dippings in troughs during the journey.

The calculation of total oxidant consumption by the shellfish contained in the troughs gives the following mean values:

- For mussels: 29.6% Winter  
                  29.2% Summer
- For oysters: 22.0% Winter  
                  29.3% Summer

This calls for several comments:

#### Importance of dirt on the shells

In the summer, both mussels and oysters were fairly clean and oxidant consumption was equal, but during the winter, the mussels were dirty and oxidant consumption was elevated accordingly for this species.

#### Increased oxidant consumption in the summer

This is a very striking phenomenon in the case of oysters. Although they are about as clean in the summer as they are in the winter, they consume approximately 25% more total oxidants during the summer period. One of the reasons for this may be that their filtering capacity increases with temperature (optimum level 18°C). The conclusion, therefore, is that the species - oysters or mussels - is not a governing factor in the decrease of total oxidants. In summary, what determines oxidant consumption is the filtering capacity of the species and the external dirt on the shells. These two parameters seem to have the most decisive influence on the amount of total oxidants present in the water.

#### Summary

Two different shellfish purification techniques have been described briefly: with or without continuous renewal of the ozonized seawater.

The use of ozone turns out to be a technique extremely well suited to shellfish purification. In effect, ozone destroys the pathogenic microbes in the water and adds an important quantity of dissolved oxygen which is beneficial to the shellfish. Furthermore, the technique imparts no taste or smell liable to be perceived by consumers. The survey has shown that under effective conditions of use, there is no residual amount of free dissolved ozone and there are no bromates in the water of the troughs. In return, residual oxidants can be measured; they include mainly hypobromous acid and ions of hypobromites. The life of such residual bromine varies with the purification mode and its disappearance is fostered by the high presence of oxidable material and by a rise of the water temperature. The shellfish themselves participate in the consumption and no noxious effect seems to be induced. It would be interesting in further research to study the shellfish tissues in order to determine whether specific consumption is due to the oxidation of dischargeable organic matter or whether it stems from fixation of tissues. Additional surveys would also enable one to clarify the influence of filtration by studying other species of shellfish such as clams, cockles, etc., having filtration yields other than those of mussels and oysters.

Lastly, failing any statistical survey concerning the matter, the continuous process seems to be the one giving best results in terms of shellfish purification. In effect, after being polluted, the water is drained continuously and replaced by water of acceptable quality. One thing that should be recommended is

the installation of a retention trough between ozonation and the purification trough in order to keep total oxidants at a sufficiently low level. In this respect, 0.1 mg/l seems to be a reasonable value in the case of continuous purification. If purification is discontinuous, a higher value is acceptable as the renewal water is not introduced constantly. Having such residual bromine is a characteristic of a disinfecting medium.

The development of shellfish farming concurrent with the increased consumption of mollusks and the increased degree of pollution (organic, bacterial, and viral), indicates a need for reliable purification systems for this vital protein resource. The satisfactory performance of ozone depuration plants in France should help to insure that products of reliable quality are available to consumers under conditions of maximum public health safety.

#### Key Words

Seawater ozonization, shellfish depuration

#### Auszug

Die Verunreinigung der französischen Küstengewässer machte den Bau einer Schalfischbereinigungsstation notwendig. Physikalische und chemische Studien zeigten, dass während Ozon und bromsauerer Salz vom ozonisierten Seewasser fehlte, erhöhte sich die Menge des gelösten Sauerstoffes und des Residuums der Sauerstoffträger. Die Wasserqualität, die Temperatur und die Abweichungen der Schalfischfiltrierungskapazität scheinen die Dauer der Sauerstoffträger zu bestimmen.

#### Abrégé

La pollution dans les eaux côtières de la France a nécessité la construction de postes d'épuration de mollusques. Des études physiques et chimiques indiquent que, même si l'ozone et les bromates sont absents de l'eau de mer traitée à l'ozone, il y a une augmentation d'oxygène dissous et d'oxydants résiduels.