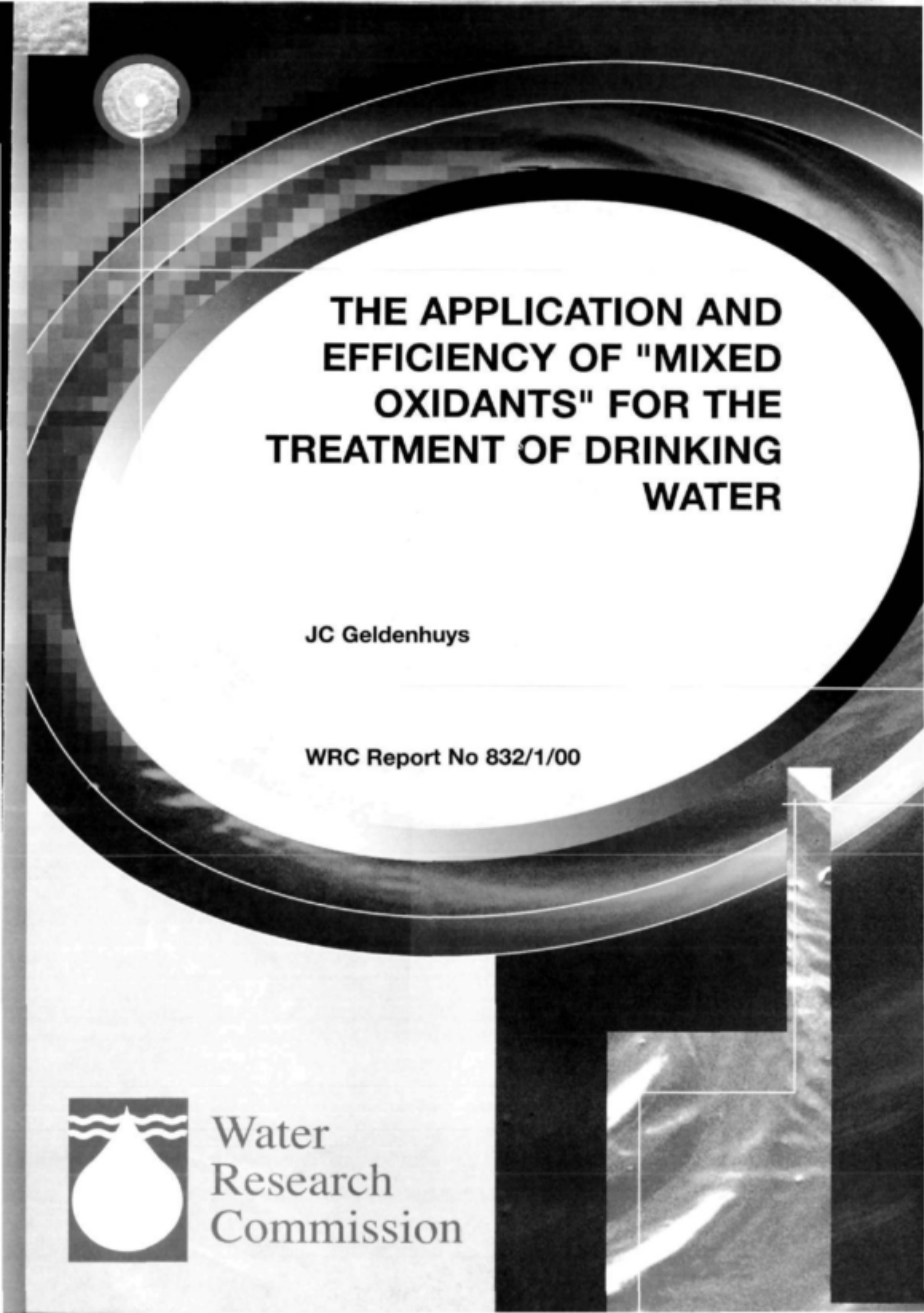

THE APPLICATION AND EFFICIENCY OF "MIXED OXIDANTS" FOR THE TREATMENT OF DRINKING WATER

JC Geldenhuys

WRC Report No 832/1/00

Water
Research
Commission

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Final report to the
WATER RESEARCH COMMISSION

by
J.C. Geldenhuys

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Executive Summary

Ongoing research into new technologies is required to develop less expensive water treatment processes without sacrificing water quality.

The process of disinfection is one of the areas that needs to be examined continuously to find more efficient disinfectants against presently known micro-organisms and the potentially harmful ones that are discovered.

In addition, growing concerns about the use of chlorine with its potentially harmful by-products place greater emphasis on the need for water utilities to investigate water disinfection alternatives to chlorination. A seemingly advanced technology, new to Western practice but utilised for some time now in many of the Eastern bloc states, has received much acclaim of late. The general concept is that of an electrolytic cell and electrolyte used to generate amounts of anolyte and catholyte, said to contain a variety of oxidants, the mixture of which is referred to as **"mixed oxidants".** The oxidants include amongst others, chlorine, chlorine dioxide, hydrogen peroxide, ozone and hydroxyl radicals. This technology is purported to present the following advantages over present disinfection methods:

- The efficiency of the oxidants produced is, by mass, higher than that of chlorine;
- Oxidant mixtures can be produced on-site using only electricity and sodium chloride;
- Oxidant concentration and composition may be adjusted according to specific needs, and
- A residual may be maintained in product water.

Although there is no record of the large-scale application of this technique in water disinfection, it could be considered as a means of primary disinfection on small water treatment plants and to augment depleted disinfectant concentrations in distribution systems. Chlorination in various forms is regarded as a reliable, cost-effective method for disinfecting water for drinking purposes. It is used on small, remote plants and on large-scale sophisticated drinking water treatment plants. However in

remote areas the application of chlorine presents problems where difficulties such as the following, may exist. These and other reasons may give impetus into investigating other disinfectants.

- Distance from the place of chlorine manufacture
- Transport and delivery schedules are unreliable or non-existent;
- Lack of sufficient expertise on the proper dosing of chlorine (especially of gaseous chlorine);
- The quality of chlorine gas obtained causes problems at the point of dosing.

Definitive research is required into the evaluation of the application of mixed oxidant technology for the treatment of drinking water, especially for use in remote areas as a primary disinfectant.

The objectives of this research project were as follows:

- To evaluate a relatively new concept that could be used for disinfection of water supplied to small and rural communities; and
- To make recommendations on the application of mixed oxidants and the possible benefits and shortcomings of such a system.

Conclusions

The results obtained in this study confirm that there are aspects of the production of mixed oxidants that are not well understood and therefore not well defined either. There also seems to be an overlap between the new emerging science of electrochemical activation of water (ECA) and the electrochemical formation of mixed oxidant solutions by electrolytic means. The results and affects claimed to be achieved by the application of ECA technology sometimes borders on the meta-physical and not enough conclusive evidence is available to either support or discard the claims made. Since only two different Electrochemical Activation (ECA) devices were examined, and both posed or developed operational problems during the tests, it would unfair to make comments on any other ECA devices that may be available commercially or on the functioning of improved models as those

that were tested. Results obtained however indicate that despite the operational problems experienced that it is possible, based on the redox potential of the solution, to produce an anolyte of consistent quality. Reproducibility of the results was good and it can be expected that this aspect of the performance of the mixed oxidant generators could be equaled or improved in devices which are of better design and construction. This aspect was not only important for the execution of the tests which were done, but would also be of significant importance if commercial use of a mixed oxidant generator had to be considered. Redox potential of the anolyte taken over a period of time showed that the decay in the oxidative power was slow and in the tests it could be kept constant long enough to expose the bacteria to solution with a known redox value.

The possible application of mixed oxidants as a disinfectant, was investigated. Although care was taken in the experiments to preserve the mixed oxidant (anolyte) solution to harvest the total potential oxidative power, and the possible synergistic effects of all the oxidants present, its effect did not significantly exceed that of chlorine. This was in spite of the fact that the anolyte vapours, and presumably the anolyte solution as well, contained other strong oxidants such as ozone and hydrogen peroxide. It was also confirmed that the catholyte solution did not contain chlorine at concentrations that would have significant microbiocidal properties. This fact is also supported by the low or negative redox potential measured in the catholyte.

Results from batch experiments show that the greatest reduction in the bacterial numbers took place within the first minute. In most cases both the anolyte and chlorine killed more than 99% of the bacteria present during the first minute of exposure. Increased contact time did not significantly reduce the numbers of the bacteria any further. In all the batch tests the average percentage reduction in bacterial numbers were 99,55 and 97,84 for the anolyte and chlorine solution respectively after five minutes contact time. The overall percentage reduction in the continuous flow tests were 99,85 for the anolyte and 99,61 for the chlorine.

It can therefore be concluded that under the test conditions that prevailed that the mixed oxidant generators examined did not produce anolyte solutions with all the properties as claimed in literature. The units tested did not produce a product that behaved significantly differently from chlorine either.

Although it seems as though mixed oxidant solutions of consistent quality can be produced from Electrochemical Activation (ECA) devices, and improvements in the functioning of the equipment can be expected in future, the use of such disinfectant generators in the rural areas would probably not be practical. As with other electrolytic chlorine generators a reliable electricity source is essential whilst, in most rural areas this cannot be guaranteed. The availability of high purity sodium chloride to use in the mixed oxidant generator may also present a problem. A further problem could be the disposal of the alkaline catholyte solution of which a volume equal to about one sixth of the volume of the anolyte, is produced.

Recommendations for future research

The following aspects of the generation and application of mixed oxidants warrant further investigation:

- Examine and understand the principle of operation of the mixed oxidant generator.
- Develop methods to analyse for the different oxidative compounds present in the anolyte.
- Develop methods to analyse for the different compounds present in the catholyte.
- Design of a system in which the mixed oxidant solution can be applied such that full oxidative potential of all the compounds present in the fluid as well as the vapours can be utilised.
- Examine potential non-conventional applications and benefits of mixed oxidants.

A member of a previously disadvantaged population group participated in the research for this project.

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THE APPLICATION AND EFFICCIENCY OF " MIXED OXIDANTS" FOR THE TREATMENT OF DRINKING WATER

The Steering Committee responsible for this project, consisted of the following persons:

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GLOSSARY

CT	Product of oxidant concentration and contact time.(mg/*l* *minutes)
DPD	N,N- di-diethyl-p-phenylenediamine
ECA	Electrochemical Activation
E_h	Hydrogen electrode potential
FAS	Ferrous ammonium sulphate
HOCl	Hypochlorous acid
ORP	Oxidation Reduction Potential
Redox	Oxidation Reduction potential
THM	Trihalomethane

1. INTRODUCTION

Statisticians estimate that more than 12 million South Africans have no access to potable water (*i.e.* water which has been treated to a quality acceptable for drinking purposes). Rural communities lack both the infrastructure and the finance required to ensure potable water, but local authorities are now obliged to provide all sectors of the community with access thereto. Research into new technologies is therefore being sought, to develop less expensive water treatment processes without sacrificing water quality.

Producing readily available potable water is a challenge as water utility companies are unable to guarantee the quality of the treated water put into supply once it leaves the purification plant and enters a distribution network. Water quality deteriorates with time, and chlorine levels which should prevent recontamination by micro-organisms are often so low that the desired effect is not achieved. As a result the water at the end of a distribution network is often not of the quality expected by the consumer or specified by quality standards.

In addition, growing concerns about the use of chlorine with its potentially harmful by-products place greater emphasis on the need for water utilities to investigate alternative water disinfection to chlorine. The production and application of solutions containing various strong oxidants, collectively called "Mixed Oxidants" is one of these alternatives. Mixed oxidants generally refer to a mixture of hydroxyl radicals, ozone, chlorine dioxide, hydrogen peroxide, chlorine and other strong oxidising species. This mixture is produced electrochemically on site as required from a sodium chloride solution in a unit comprised of anodes and cathodes of specially selected alloys. Research conducted at the Russian Scientists' Centre for Electrochemical Activation Techniques (RSCEAT), suggests that the efficiency of the oxidants are by mass higher than that of chlorine, and produce residuals that can be maintained in treated water. Although there is no record of the large scale application of this technique in water disinfection, instances have been recorded where the mixed oxidants have apparently been used successfully for disinfecting water in refugee camps. It is at this stage not suggested that mixed oxidants should be used as the sole means of water disinfection. However because of the purported ease and efficiency of generation and application it could be considered as a means to augment depleted disinfectant concentrations in a distribution system.

Motivation

Chlorination in various forms is regarded as a reliable, cost-effective method for disinfecting water for drinking purposes. It is used on small, remote plants and on large-scale sophisticated drinking water treatment plants, however in remote areas the application of chlorine presents problems where difficulties such as the following, may exist. These and other reasons may give impetus into investigating other disinfectants.

- Distance from the place of chlorine manufacture
- Transport and delivery schedules are unreliable or non-existent;
- Users lack sufficient expertise on the proper dosing of chlorine (especially gaseous chlorine);
- The quality of chlorine gas obtained causes problems at the point of dosing.

The presence of chlorine disinfection by-products like trihalomethanes, organic halogens, and mutagenic substances, is still a cause for concern. The only way in which the formation of potentially dangerous compounds may be avoided is to remove the precursors of these compounds, or use a means of disinfection alternate to chlorine. Disinfection by electrochemically-produced oxidants may be an option, but this method also has its limitations: oxidants that do not produce harmful by-products, in general, do not produce a residual either.

A seemingly advanced technology, new to Western practice but utilised for some time now by many of the Eastern block states, has received much acclaim of late. The general concept is that of an electrolytic cell and electrolyte used to generate amounts of anolyte and catholyte, said to contain a variety of oxidants, the mixture of which is referred to as **"mixed oxidants"** (MIOX). The oxidants include amongst others, chlorine, chlorine dioxide, hydrogen peroxide, ozone and hydroxyl radicals. This technology is purported to present the following advantages over present disinfection methods:

- The efficiency of the oxidants produced is, by mass, higher than that of chlorine;
- Oxidant mixtures can be produced on-site using only electricity and sodium chloride;
- Oxidant concentration and composition may be adjusted according to specific needs; and
- A residual may be maintained in product water.

Definitive research is required into the evaluation of the application of mixed oxidant technology for the treatment of drinking water, especially for use in remote areas as a primary disinfectant or to augment disinfectant residuals at outlying areas of water distribution networks, where chlorine residual may be low or lacking.

The objectives of this research project were as follows:

- To evaluate a relatively new concept that could be used for disinfection of water supplied to small and rural communities; and
- To make recommendations on the application of mixed oxidants and the possible benefits and shortcomings of such a system.

2. LITERATURE REVIEW

2.1 Disinfectants produced by electrolysis

Disinfection with chlorine and chlorine products is an established process in the provision of safe drinking water, but in developing countries a regular supply of chemicals is a serious problem. With special attention being focussed on rural programmes, on-site production of disinfectants could fill a need, provided operation and maintenance could be simplified. Electrolytic production of gaseous chlorine is a well-known process in the chemical industry, although small production cells have still to prove their reliability and low maintenance requirements (Wabner and Fleischmann, 1986). Small electrolytic sodium hypochlorite production units using sodium chloride as a feed stock have been marketed successfully for some time. These units are typically used to chlorinate small drinking water supplies or swimming pools.

Strong oxidants have among the effective disinfectants, a prominent position. Oxidants like chlorine, hypochlorite and ozone are today the most important chemicals for drinking-water disinfection. To produce these chemicals (which possess high positive redox potentials), electrochemical methods are preferred as they provide in a simple elegant manner, the strong oxidation conditions required. The technology of mixed oxidant production claims simple process control, separated oxidation and reduction zones and no need for storage of oxidising chemicals (Wabner and Fleischman, 1986).

2.1.1 Chlorine

Chlorine, the most widely used disinfectant in water purification, has been produced electrochemically in great quantities for more than 100 years. The products of brine electrolysis are chlorine, sodium hydroxide and hydrogen according to the following reaction :

$2NaCl + 2H_2O \rightarrow Cl_2 + 2\,NaOH + H_2$ ……… (1)

With an anodic reversible discharge potential of +1.247V for the reaction

$2Cl^- \rightarrow Cl_2 + 2e^-$, ……… (2)

Possible side-reactions at the anode are:

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

$6\,ClO^- + 3\,H_2O \rightarrow 2ClO_3^- + 4\,Cl^- + 6H^+ + 1{,}5\,O_2 + 6e^-$ ……… (3)

The quantitatively more important reaction is the oxygen generation according to reaction 3. For direct drinking water disinfection the chlorate formation should be closely monitored because of it's high toxicity. Other side reactions reducing chlorine yield also occur in chlorine solutions, *viz*:

$2OH^- + 2Cl_2 \rightarrow ClO^- + Cl^- + H_20$

$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$

$2HOCl + NaClO \rightarrow NaClO_3 + 2\,HCl$

The products are hypochlorite and chlorate; the latter can thus be formed at the anode as well as in solution (Wabner and Fleichman, 1986).

2.1.2 Hypochlorites

Hypochlorites are of the most important disinfectants. They too are produced electrochemically as a by-product of chlorine production. Therefore this method is well investigated and documented. The generated hypochlorite can decompose on both the cathode and the anode:

Anode: $12\ ClO^- + 6\ H_2O \rightarrow 4\ ClO_3^- + 8\ Cl^- + 12H^+ + 3\ O_2 + 12\ e^-$

Cathode: $ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$

The rate of chlorate generation is proportional to the concentration of $HOCl + ClO^-$ in the solution and can be minimized by reduced retention times of the electrolyte in the cell. The chemical chlorate generation from hypochlorite is negligible if the electrolyte is kept at temperatures under 30°C and pH values outside the range 4 to 6. The reaction,

$ClO^- \rightarrow Cl^- + 0.5\ O_2$

is slower than the chlorate reaction, but is catalyzed by impurities like cobalt, nickel and copper. Hypochlorite solutions decompose according to these two reactions and cannot be stored for extended periods. Both the sodium and calcium hypochlorites are produced and used for disinfection purposes.

2.1.3 Ozone

Ozone is one of the strongest oxidants known (redox potential of 2.07 V). It has become increasingly important for water-disinfection, for which it was first used in 1893 in the Netherlands, on Rhine River water. Though ozone was discovered in the electrolysis of water in 1839, the most important and economic method to produce ozone is still by silent corona discharge from dried air or oxygen in generators of different designs. In recent years the electrochemical generation of ozone has been reinvestigated intensively using new materials as anodes. This has increased the efficiency of the generators and ozone yields of up to 18% by volume of the anodically-generated gas are said to be obtainable.

Ozone production is in proportion to the energy applied to the ozone generator as demonstrated in the following reactions. The oxone- generation reaction is initiated when free electrons in the corona dissociate oxygen molecules:

$e^- + O_2 \rightarrow 2O + e^-$

This is followed by ozone formation from a three-body collision reaction:

$O + O_2 + M \rightarrow O_3 + M$

Where M is any other molecule in the gas. (White, 1992)

2.1.4 Percompounds

Inorganic peroxocompounds like peroxides, perborates, perphoshates, and percarbonates are strong oxidants and have been used for disinfection, for instance in oral hygiene, cosmetics and the food industry. They play a significant role in water purification as well; hydrogen peroxide has to date been used for that purpose in the United States of America and the former United Soviet Socialist Republic. Solid peroxides are commercially available for swimming pool-disinfection. In this application they are combined with metal salt activators to increase the reaction rate. All these compounds can be electrochemically prepared (Wabner and Fleischman, 1986).

2.1.5 Mixed Oxidants

Research into various aspects of a phenomena referred to as "Electrochemical Activation" or ECA which is defined as: "decomposing water with electricity is a physical-chemical modification of water composition with ions H^+, OH^-, metal oxide hydrates, acids, peroxide compounds and radicals, free chlorine, ozone, hydrogen peroxide, hypochlorite anion, etc. appearing in it;" led to the development of two related designs for generators, employing the same principles, but used for different purposes. Both designs are commercially available for producing anolytes and catholytes from either purified slightly mineralised water containing about 100-200 mg/*l* of dissolved salts or sodium chloride brine solutions (5 -7 g/*l*). ECA units are sold under the trade names such as Emerald, Sapphire and Crystal. These devices utilise the same basic Flow Electrolytic Module (FEM) but the options exist to mix or recirculate the anolyte and catholyte streams to obtain specific effects. The anolyte produced has a lower pH and positive redox potential. The catholyte displays a high pH and a negative redox potential. The FEM unit is comprised of titanium-ruthenium oxide anodes and cathodes that operate under a potential of "several million volt/cm^2 The electrodes are separated by a ceramic diaphragm. Any number of FEM units can be incorporated into a single unit called a Flow Electrochemical Reactor (FER) to increase the capacity of the production unit. See Figure 1.1 for a schematic diagram of the FEM unit.

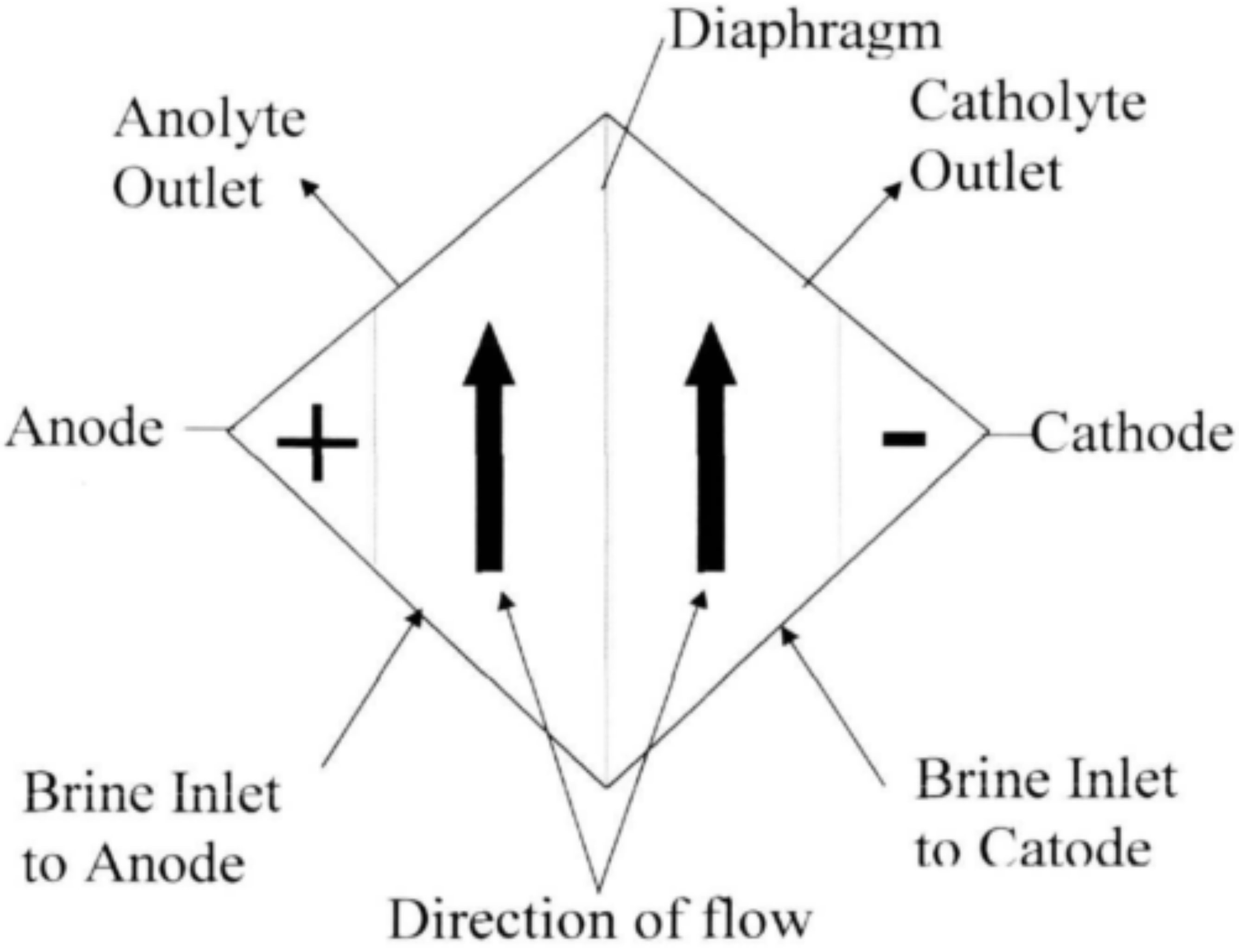


Figure 1.1 Diagram of Flow Electrolytic Module

According to the literature sited and information supplied by manufacturers, when using slightly mineralised water as the electrolyte the two product streams produced have many economic applications in the medical, agricultural and general health and biology fields. Some of the observations made and results achieved when applying the products from the ECA, border on the metaphysical and are difficult to explain. Some of the observations include:

- Apparent changes in the wetting properties of water.
- Softening of rock that improves the milling efficiency.

- Improved germination of seed that had been watered with the catholyte.
- More rapid mass gain in pullets that received catholyte in their drinking water.
- Reduction of salmonella infection in eggs and an improved percentage of chick hatchlings after receiving intermitted doses of anolyte.

The devices used to produce anolyte and catholyte streams from sodium chloride brine is commercially available as the "STEL" and "REDO" units. The redox potential and pH values of the anolyte and catholyte streams produced from brine span a much wider range as those produced from slightly mineralized water.

Simplified, the main processes that take place in an electrolyser can be expressed in the following way:

1. Oxidation of the water at the anode: $2H_2O - 4e^- \rightarrow 4H^+ + O_2$
2. Reduction of water at the cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
3. Formation of gaseous chlorine in chloride solutions at the anode: $2Cl^- - 2e^- \rightarrow Cl_2$
4. Formation of highly active oxidants in the anodic chamber: *i.e.*
   Cl_2O, ClO_2, ClO^-, $HOCl$, $Cl^\bullet$, $O_2^\bullet$, O_3, HO_2, $OH^\bullet$, H_2O_2
5. Formation of highly active reductants in the cathodic chamber:
   OH^-, H_3^-, O_2^-, H_2, $HO_2^\bullet$, $HO_2^\bullet$, $O_2^\bullet$

Presence of enough strong oxidants and free radicals in the anolyte turns it into a solution with marked biocidal properties. Catholyte solutions saturated with reductants exhibit improved adsorption and chemical ability as well as good cleaning properties. The level of pH and ORP (Oxidation Reduction Potential) in the anolyte and catholyte produced from solutions with different salinity are characterized by changes that are related to the initial values: in the anolyte the pH value is reduced and the ORP elevated to the extreme positive (oxidant) value; in the catholyte the pH is increased and the ORP reduced to the extreme negative (reductant) value.

Table 1.

Properties of anolyte and catholyte solutions produced by the STEL apparatus using a 3000 mg/*l* sodium chloride solution as electrolyte

Anolyte

pH	ORP (mV)	Active ingredients	Concentration of active ingredients, mg/*l*
≤ 4.5	1100 to 1200	ClO_2, ClO_2^-, Cl, HOCl, O_2, O^-	If concentration of active chlorines ≤ 200 mg/*l*, O_2 and O^- concentration is 1 to 3 mg/*l*
6 ± 1	800 to 950	HOCl, ClO^-, ClO_2^-, O_3, O_2, H_2O_2, HO_2^-	If concentration of active chlorine ≤ 200 mg/*l*, O_3, O_2 and H_2O_2 concentration is 1 to 3 mg/*l*.
7.5 ... 8.5	650 to 800	HOCl, ClO^-, O_3, O_2, H_2O_2, HO_2^-	If concentration of active chlorine ≤ 200 mg/*l*, O_3, O_2 and H_2O_2 concentration is up to 10 mg/*l*

Catholyte

pH	ORP (mV)	Active ingredients
11.5 ± 0.5	-800 to –900	Na^+, OH^-, $OH\cdot$, H_2O_2, HO_2^-, O_2^-, H_2

ORP = Oxidation Reduction Potential
(Table from Strand,1994)

The STEL unit is used to produce anolyte streams with potentially high disinfecting power that could be attributed to the high positive redox potential.

Examples of such applications are:

- Sterilisation of surgical instruments used in hospitals. In cases the internal structure of *Pseudomonas aeruginosa*, as observed by electron microscope was found to be irreversibly damaged by applying an anolyte solution with a pH of 3,7 and an ORP of 950 mV.
- Decontamination of pipelines and equipment in food processing plant.
- Decontamination of slaughtered animal carcasses in abattoirs.
- Control of microbiological contamination of fruit in cold storage.
- Production of emulsions for pest control on plants.
- Disinfection of swimming pool water.
- Water treatment.

The Centre for Applied Microbiology and Research in Salisbury, United Kingdom (1995) reported on the preliminary evaluation of the Enigma Electrochemical System. This equipment is comparable to the STEL and REDO apparatus. The anode is made of titanium coated with ruthenium oxide, iridium and platinum, while the cathode is titanium polished or coated with pyrocarbon and glass carbon. The membrane separating the anolyte and catholyte consists of ultrafiltration electrocatalytic ceramics on a bed of zirconium, yttrium, aluminum and niobiurn oxides. Depending on the chemical and mineral composition of the original electrolyte used the pH and redox potential of the anolyte and catholyte produced are within the limits of ·2 to 8, 400 to 200 mV and 7 to 12, -80 to -900 mV, respectively. It is claimed that water flowing through the Enigma system is altered by the electric field of several million volts per square centimeter causing an imbalance in the water structure enriching it with electrochemical products which may be: Cl_2, $HOCl$, $ClO^\bullet$, $Cl^\bullet$, HO_2, $HO_2^\bullet$, O_2, $HO^\bullet$, O_3, O_2, $O^\bullet$, H_3O^+, $H^\bullet$, H_2O_2, Cl_2O, ClO_2^-, HCl, Cl_2O_7, $S_2O_8^{8-}$, $C_2O_6^{2-}$, H_2SO_4, HSO_3Cl in the anolyte and HO^-, $H_3O_2^-$, O_2^-, HO_2^- H_2O_2, H_2, HO, H_2^-, $NaOH$, KOH, $Ca(OH)_2$, $Mg(OH)_2$ in the catholyte. A weak anolyte solution was prepared using electrochemical activation at 32 volts and a current of 2 amps from water, while a strong anolyte solution required 16 volt and a current of 10-13 amp in an electrolyte containing 7500 mg/*l* of sodium chloride. The strong anolyte had a pH 5,9 and a redox potential of 978 mV.

Pathogens like *Vibrio cholera, Shigella dysenteriae, Salmonella enteritidis, Legionella pneumophila* and *Escherichia coli* were exposed to the undiluted anolyte to determine how efficient the solution would be in killing the micro-organisms. For comparative purposes these organisms were also exposed to 50 mg/*l* of chlorine. Fresh undiluted anolyte killed all the micro-organisms in 30 seconds. Concentrations of 50 mg/*l* chlorine gave similar results.

Dilutions of 1:800 of the anolyte proved to be ineffective and unreliable to achieve the killing of the bacteria in 30 seconds and the contact time had to be increased to 10 minutes. Similar results were obtained when diluting the 50 mg/*l* chlorine solution. A 1:300 dilution of the chlorine solution, which is equivalent to about 0,16 mg/*l* of chlorine, was more effective in killing the bacteria than similar applications of the diluted anolyte. (Strand, 1994)

2.2 Aspects of Oxidation Reduction Potential

2.2.1 Oxidation-reduction potential

Oxidation and reduction (redox) reactions mediate the behavior of many chemical constituents in drinking-, process-, and waste water as well as most aquatic compartments of the environment. The reactivities and mobilities of important elements in biological systems (e.g. Fe, S, N and C), as well as those of a number of metallic elements, depend strongly on redox conditions. Reactions involving both electrons and protons are pH- and E_h-dependent; (Hydrogen Electrode Potential) therefore, chemical reactions in aqueous media often can be characterized by pH and E_h together with the activity of dissolved chemical species. Like pH, E_h represents an intensity factor. It does not characterize the capacity of the system for oxidation or reduction.

The potential difference measured in a solution between an inert indicator electrode and the standard hydrogen electrode should not be equated to E_h, a thermodynamic property, of the solution. The assumption of a reversible chemical equilibrium, fast electrode kinetics, and the lack of interfering reactions at the electrode surface are essential for such an interpretation. These conditions are rarely (if ever), met in natural water.

Thus, although measurement of E_h in water is relatively straightforward, many factors limit the interpretation of these values. These factors include irreversible reactions, electrode poisoning, the presence of multiple redox couples, very small

exchange currents, and inert redox couples. The measurement of redox potential, when properly performed and interpreted, is useful in developing a more complete understanding of water chemistry.

2.2.2 Oxidant Demand/Requirement

Oxidants are added to water supplies and wastewater primarily for disinfection, although their beneficial uses include slime removal, oxidation of undesirable inorganic species (e.g. ferrous ion, reduced manganese, ammonia), and oxidation of organic constituents (e.g. taste- and odour-producing compounds). Oxidant demand refers to the difference between the added oxidant dose and the residual oxidant concentration measured after a prescribed contact time at a given pH and temperature.

The fate of oxidants in water and wastewater is complex. For example, chlorine reacts with sample constituents along three general pathways: oxidation, addition and substitution. First, chlorine can oxidize reduced species, such as Fe^{2+}, Mn^{2+}, and sulfide. In these reactions, chlorine is reduced to inorganic chloride (Cl^-). Second, chlorine can add to olefins and other double-bond-containing organic compounds to produce chlorinated organic compounds. Third, chlorine can substitute onto chemical substrates. The addition and substitution reactions produce organochlorine species (e.g. chlorination of phenol to chlorophenols), or active chlorine species (e.g. chlorination of ammonia to produce monochloramine). Chlorine reacts with naturally occurring organic compounds via a combination of these mechanisms to generate such products as trihalomethanes (THMs).

Oxidant demand and oxidant requirements are significantly affected by the chemical and physical characteristics of the sample and the manner in which the oxidant consumption is measured. In particular, oxidant reactivity is influenced by temperature, pH, contact time, and oxidant dose. Sample temperature strongly affects reaction kinetics, and thus affects also the demand exerted in a given contact time. Sample pH affects reaction kinetics and thus the nature and extent of the demand. For example, ozone is unstable at high pH values and ozone demand is especially sensitive to sample pH. Oxidant demand increases with time and therefore the demand must be defined for a given contact time. Oxidant demand also is very dependent on oxidant dose. Increasing oxidant dose usually will increase demand, but it is incorrect to assume that doubling the oxidant dose will double the oxidant demand. For these reasons, it is difficult to extrapolate oxidant demand data from one set of conditions to another.

2.2.3 Redox Control for Pathogen Management

The control of pathogenic bacteria and viruses in potable water has evolved into a complicated set of checks and procedures. It is no longer sufficient to simply add chlorine to a specified level and leave it at that. The greatest concern these days is the level of disinfection byproducts, the possible dissolution of metals like copper and lead, the potential loss of disinfectant along the distribution lines and a host of other consequences.

It is becoming very clear that the less chlorine is added and still ensure the disinfection required, the better. This however, is made difficult by the chemical characteristics of chlorine; a portion of the added chemical will almost certainly combine with constituents in the water to form less germicidal compounds. In addition, changes in water conditions such as pH impact strongly on chlorine's ability to disinfect.

The CT value, which is the product of the disinfectant concentration (in mg/*l*) and contact time (in minutes), gives an indication of the total oxidative power available to kill micro-organisms in a specific configuration. The CT values for different oxidants and micro-organisms vary. Stronger oxidants like ozone would require a lower concentration and shorter contact time, and therefore a smaller CT value, to achieve the same result as a weaker oxidant such as monochloramine. CT values could be used to control disinfection but there are legitimate concerns about whether the approach accomplishes effective disinfection. For one thing it fails to recognize the failing of residual measurement to indicate disinfecting power or work value.

Redox is an analytical technique that measures the potential for oxidation to take place in a treatment system. Since disinfection by oxidants like chlorine, chlorine dioxide, bromine or ozone result from the oxidation of micro-organisms, it stands to reason that measuring the potential for oxidation to occur should give a clear picture of the disinfection power of a treatment system. Several studies would indicate that redox potential accurately predicts disinfection rate. Indeed, oxidative effects are known to be responsible for the disinfection phenomenon.

In the 1960s, Ebba Lund was studying virus inactivation rates resulting from the addition of various oxidants to test samples. Her studies revealed a direct correlation between redox potential and inactivation rate. Her studies found too, that the correlation between chlorine concentration (residual) and inactivation rate, was poor. It was discovered that in addition to pH and temperature, the quality of water had a direct impact on chlorine's ability to disinfect. Any material in water that has the ability to lower the redox potential reduces the ability of a given residual of chlorine to kill micro-organisms.

Oxidation is the loss of electrons from some species. The species may be organic or inorganic, living or dead. The species which gains electrons, is the oxidizer and is said to have been reduced. When a species is oxidized or reduced it changes chemical characteristics due to the electron transfer. For instance, the conversion of metallic iron to iron oxide (rust) is caused by oxidation. Even though the substance still exists after oxidation took place, its chemical structure had been altered. Experiments demonstrated that a given redox potential maintained for a period of time would produce a repeatable inactivation curve for micro-organisms. Residual oxidant concentration was tracked in the same experiments and produced very different results. Holding a constant residual showed no consistent relationship to inactivation rate.

Harriette Chick was the first researcher to apply the principals of reaction kinetics to the disinfection process. Her studies led to the establishment of what became known as Chick's Law, which states:

$$-\frac{dN}{dt} = kN$$

Where:

N = quantity of reactant,

k = reaction constant,

t = time.

Lund's work led to the development of a third and more practical equation. Lund's Law states that:

$$\frac{dN}{dt} = k'(E - E_c)N$$

E-E_c represents the redox potential maintained in excess of a minimum threshold. Using calculus to rearrange the equation the simplified final form results:

$$-\ln\frac{N}{N_o} = k'(E - E_c)^n t$$

n = Calculated constant

Lund's Law states that *the log decrease in micro-organism activity is proportional to the product of the redox maintained and the contact time.* The purpose of Lund's Law is to provide a practical equation that can be reliably used in actual water treatment situations to predict inactivation time, based on a parameter that is easily measured and controlled. Unlike the current CT rules, E_h values are independent of chlorine species, pH, temperature and water quality. (Stand,1994)

The formation of disinfection by-products is now a major concern in potable water treatment, especially as their regulated limits are continuously being lowered. THMs take three days or more to fully develop and the lower the chlorine dosage, the lower the ultimate THM level. Redox technology can help minimize levels in both of these areas, by reducing the over dosage of chlorine.

Chlorine residual has always served as basis of control but displays several shortcomings. Redox monitoring however, shows promise in overcoming these. By continuously reporting the actual disinfecting power of the chlorinated process, redox-based control schemes can regulate chlorine feed rate to exactly match the requirement. This chlorine minimization will in turn reduce the exposure to THM formation (Strand, 1994).

3. METHODS AND EQUIPMENT USED

3.1 Methods used for chemical and physical determinations

3.1.1 Redox Potential

A redox potential electrode from Swiss Laboratories with platinum titrode part no. 6.0431.100 was used throughout the test program and was calibrated every day of use in the recommended solution.

3.1.2 pH

A sleeve diaphragm Metrohm pH electrode was used and the calibrations done every day of use at pH 4 and 7. The accuracy of the electrode was tested by measuring the pH of a buffer at pH 10.

3.1.3 Chlorine and oxidant concentration

N, N- di-diethyl-p-phenylenediamine (DPD) was used as indicator in the titrimetic procedure with ferrous ammonium sulphate (FAS) as titrant to measure the concentration of chlorine and other oxidants in the solutions. Where applicable distinction was made between the various chlorine species, i.e. monochloramine and di-chloramine that could be present by the addition of small amounts of iodine to the solution. The same reagents and methods were used to determine the concentration of the mixed oxidants, specifically the anolyte, and the results expressed as mg/ℓ chlorine. The minimum detection limit with these methods is 0.018 mg/ℓ of chlorine. Method #45566 American Public Health Association (APHA), American Water Works Association (AWWA) and Water Pollution Control Federation (WPCF), *"Standard Methods for the Examination of Water and Wastewater"*.

3.1.4 Ozone, chlorine and hydrogen peroxide concentrations in the gas phase.

Dräger reaction tubes were used to measure the concentration of ozone, chlorine and hydrogen peroxide where it could not be done be conventional means in the anolyte and catholyte vapours. The following tubes were used:

	Tube number	Measuring range
Ozone (O_3)	CH21001	20 to 300 parts per million (ppm) (1 ppm = 2 mg O_3 /m^3)
Chlorine (Cl_2)	CH 20 701	50 to 500 parts per million (ppm) (1ppm Cl_2 = 2,95mg Cl_2 /m^3)
Hydrogen peroxide (H_2O_2)	CH 30 301	0,1 to 3 parts per million (ppm) (1ppm H_2O_2 = 1,4 mg H_2O_2 /m^3)

(Drägerwerk Aktiengesellschaft Lübeck, 1997)

3.2 Methods used for microbiological determinations

Standard Plate Count

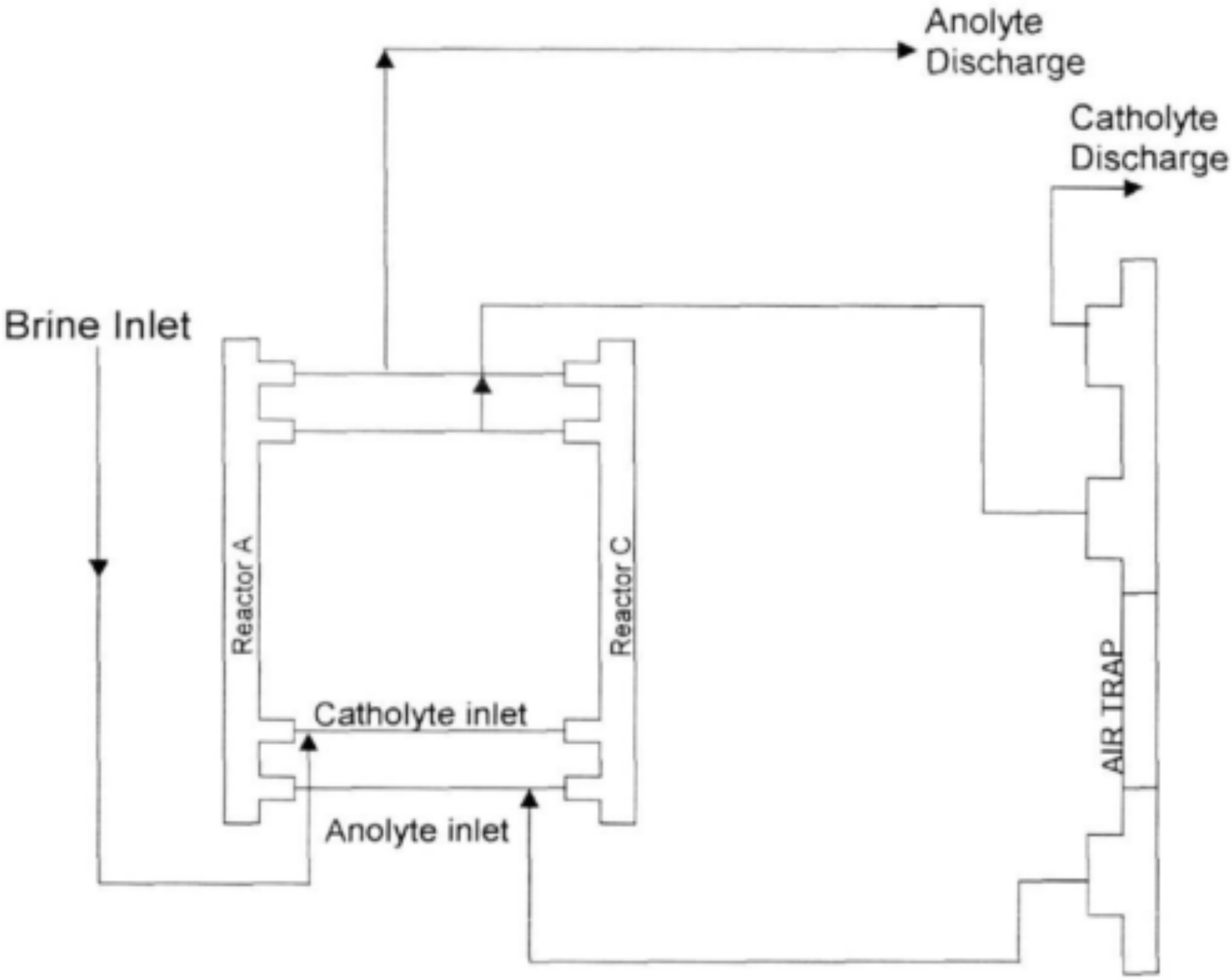
Escherichia coli was used in the bacterial suspension exposed to the oxidants. The original culture was isolated from water with the membrane filter technique on M-FC agar incubated at 44,5°C for 18 hours according to accredited method No 1.2.2.03.1 of Rand Water.

Standard plate counts at 37°C for 48 hours were performed to determine the efficiency of the mixed oxidants or chlorine against *E coli* as an example of typical heterotrophic bacteria. Pour plates with dilutions as required were made with yeast extract agar according to the accredited laboratory method No 1.2.2.01.1 of Rand Water. Results were expressed as the number of colony forming units per m*l*. (cfu/m*l*).

3.3 Description of equipment used.

3.3.1 Mixed oxidant generator.

The number of different mixed oxidant generators available on the local market is limited with the result that only two different mixed oxidant generators could be tested. Flow through the devices were more than significantly influenced by the level of the salt in the reservoir and the height of the anolyte and catholyte discharge tubes in relation to the mixed oxidant generator. The flow resistance in these tubes also had a significant affect. A locally assembled unit, using Russian made components, proved to be particularly difficult to operate as the flow through the unit fluctuated and precise control was not possible. The fully imported Electrochemical Activation (ECA) unit, REDO Diaphragmalyser produced by the Russian firm NPO Perspektiva based in Dubna, Russia proved to be more reliable. However it was found that the quality of the product also was very sensitive to adjustments to either the electrical current applied or restricted discharge of the products. To avoid this problem calibrated peristaltic pumps were used to dispense the anolyte and catholyte solutions in the correct proportions as required. A calibrated peristaltic pump was used to dispense the volumes of bacterial suspensions when required. See Figure 3.1 for a schematic diagram of the ECA equipment, REDO Diaphramalyser, as used in the experiments.



Reactor A: Reactor in which anolyte is produced.

Reactor C: Reactor in which catholyte is produced

Figure 3.1 **Diagram of Electrochemical Activation Equipment (ECA)**

Of the emphasized and promoted attractions of the mixed oxidant generators are the economical running costs based on the low electrical consumption and the use of cheap freely available table salt. It was found that the brine produced with this salt tended to clog the tubes and damage the membranes very quickly, requiring frequent descaling of the systems. Iodinated salt was not used to avoid the possibility of forming undesirable iodine based by-products during the electrolytic process. To circumvent these problems, laboratory grade sodium chloride was used.

Changes in the ambient temperature also affected the performance of the generators and the quality of the anolyte and catholyte negatively. Throughout the experiments tap water was used for the brine preparation. Manuals supplied with the generators advised that the salt concentrations used in the electrolyte could be between 3 and 10 percent. It was clear that this concentration had a strong influence on the current that could be applied and the quality of anolyte and the catholyte. On advice of the supplier of the equipment a 3% sodium chloride solution was used to feed the generator. At this concentration the frequency of cleaning the membranes is reduced as well as the possibility of damage as a result of build up of scale. This sodium chloride concentration was the lowest at which an electric current of suitable strength produced high concentrations of oxidants at low pH in the anolyte and the catholyte was strong alkali.

3.3.2 Apparatus used to expose bacterial cultures to mixed oxidants

During the course of the test programme it became clear that the way in which the anolyte, as the solution that contains the strong disinfectants is mixed with the bacterial suspension would be important. Since it is possible that the anolyte contains oxidants with a very short half-life, experiments were designed such that the oxidative power in the solution could be preserved until, and while the micro-organisms were exposed to anolyte. To dilute the anolyte to a concentration equivalent to that of a chlorine solution used for the disinfection of drinking water and apply it in small bench scale experiments, was difficult and did not produce the desired results. Experiments were then designed in which the bacterial suspensions were exposed to the anolyte of the desired concentration in either batch or flow- through mode.

In all the experiments where the oxidative or microbiocidal power of the anolyte was tested it was compared with an equivalent concentration of chlorine. The concentrations (activity) of both the anolyte and chlorine solutions were determined with DPD titrations using FAS as a titrant and the results expressed in terms of mg/*l* chlorine. The aim normally was to use chlorine concentrations similar to those used for disinfection of drinking water. This would be in the order of 2-4 mg/*l* of free available chlorine.

The batch experiments were done in a 200 litre plastic container with a stirrer. The bacteria were suspended in 100 litre of unchlorinated clarified water and the amount of oxidant (anolyte) added was equal to the chlorine concentration applied in a duplicate experiment. Anolyte was added through a submerged tube at the bottom of the drum to avoid any loss of the anolyte to the atmosphere and to ensure good mixing. Addition of the anolyte continued until the desired oxidant concentration in the water was obtained. Samples for bacteriological and chlorine determinations were taken after respectively 1,5,10 and 30 minutes contact time from the containers. See Figure 3.2 for a schematic diagram of the equipment used for the batch experiments.

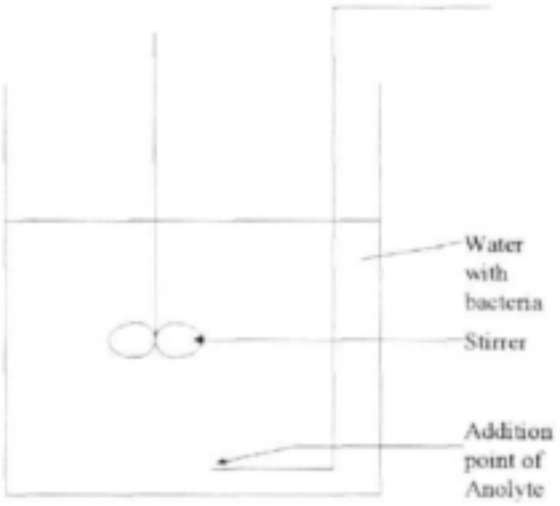


Figure 3.2 Diagram of equipment used for batch experiments to test bactericidal effects of the anolyte and hypochlorite

As the possibility existed that volatile and reactive oxidants present on the anolyte could escape from the solution or react with constituents other than the bacteria in the water a flow through system in closed vessels was designed.

The flow-through system comprised of five identical glass vessels of 50 cm^3 each connected in series. Anolyte and hypochlorite solutions and suspensions of the bacteria to be tested were metered with calibrated peristaltic pumps and mixed in the desired proportions in the glass vessels. Flows through the reaction vessels were adjusted to achieve the required contact time of one minute in each vessel. Samples could be taken at any stage in the system with a maximum contact time of five minutes. See Figure 3.3 for a schematic diagram of the flow-through system.

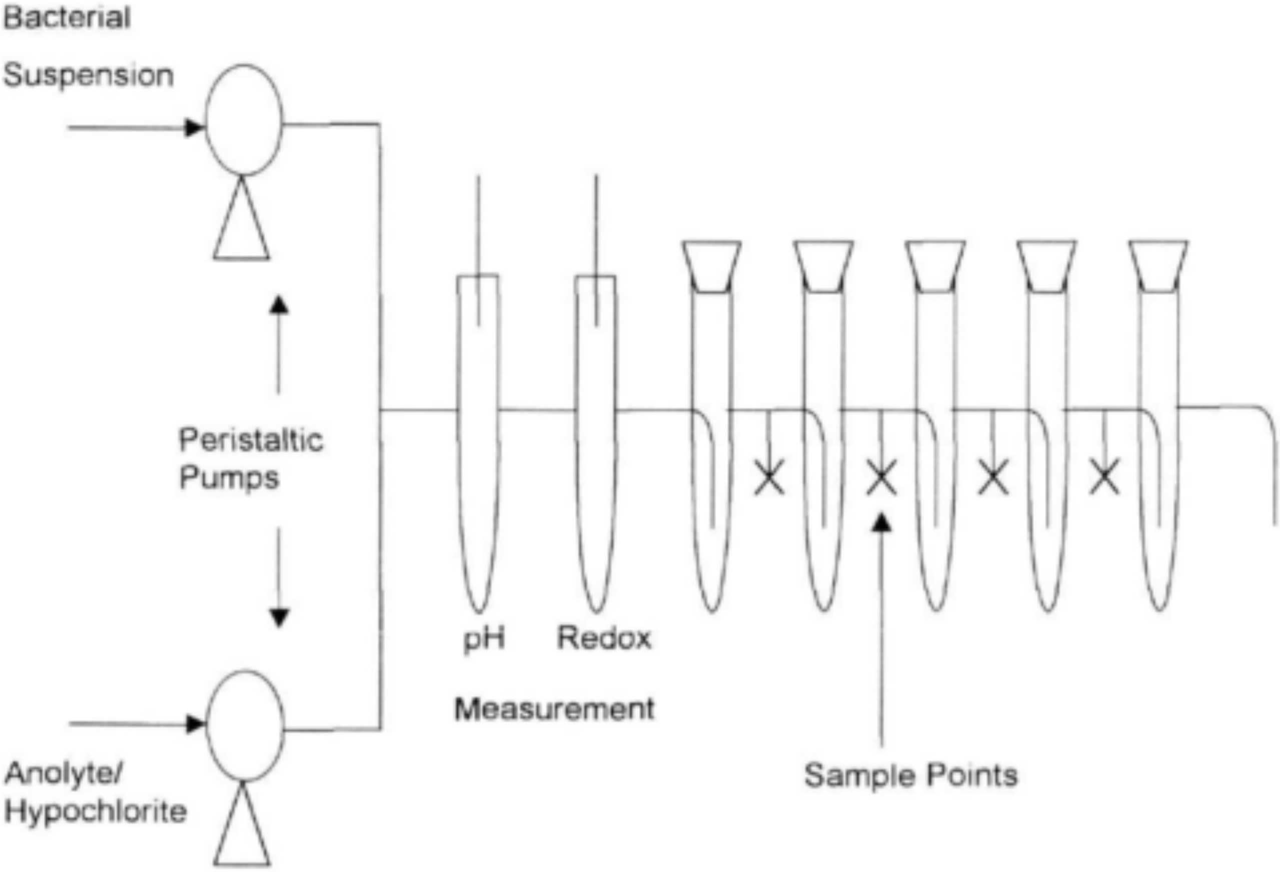


Figure 3.3 **Diagram of the flow-through system used to test the bactericidal effect of the anolyte and hypochlorite**

4. RESULTS AND DISCUSSION

4.1 Reliability of the equipment and consistency of the product

The two mixed oxidant generators available were tested for reliability, ease of operation, the consistency of the product produced and the repeatability of results under the same conditions. After selecting a brine concentration and the current setting the quality of the anolyte and catholyte solutions were measured over a period. The performance of both the mixed oxidant generators were influenced by operating factors like the level of the brine containing vessel and the product discharge tubes in relation to the generator and the electrical potential over the electrodes. Electrical controls on the generators were corroded by the anolyte and catholyte vapours resulting in failure, poor control and difficulty in setting the current that was applied accurately. Although similar operational problems were experienced with both the generators, the ECA (REDO Diaphragmalyser) unit was used predominantly as it was more reliable, was relatively easy to operate and the reproducibility of the products were high.

4.1.1 Relationship between redox potential and pH in the anolyte and catholyte

Figure 4.1 depicts the relationship between redox potential and pH. From this it is clear that higher redox potential were obtained at low pH in the anolyte while the inverse, producing a lower redox potential at high pH, was true for the catholyte. This is in keeping with the fact that the anolyte contained the strong oxidising compounds responsible for the biocidal effects. Redox potential values as high as + 1200mV were recorded.

The low pH can be attributed to the high chlorine concentration, up to 1500 mg/*l*, present in the anolyte while the hydroxide anion concentration present in the catholyte is responsible for the high pH.

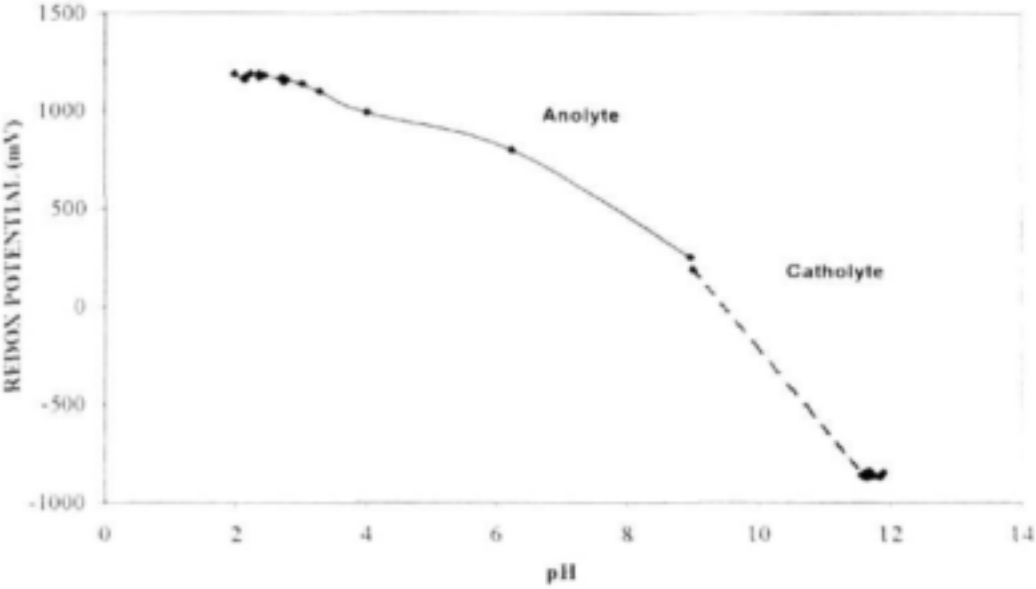


Figure 4.1 Relationship between redox potential and pH in anolyte and catholyte

4.1.2 Relationship between flow rate through the generator and redox potential

As can be seen from Figure 4.2 , flow rate through the generator influenced the redox potential of the anolyte. Higher redox potential values were recorded at lower flow rates with longer detention time in the reactor.

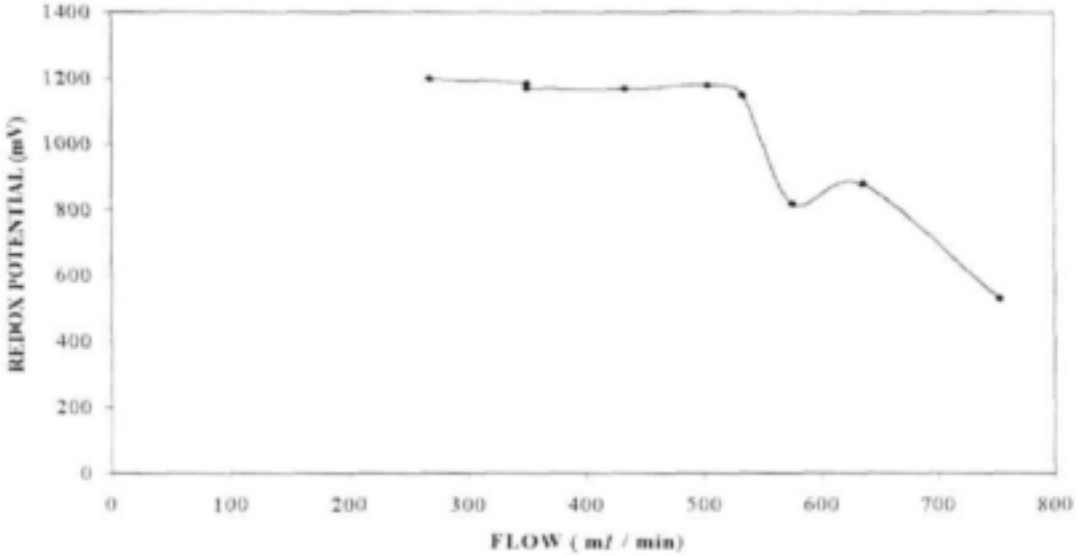


Figure 4.2 **Relationship between flow rate through the generator and redox potential in the anolyte.**

4.1.3 Reproducibility of results

The ability of the anolyte and cathloyte generator to repeatedly produce a product of consistent quality was tested by running the generator under the same operating conditions using the same instrument settings a number of times in succession. From Figure 4.3 it is clear that a product of consistent quality, as measured by the redox potential, could be produced under the same operating conditions if repeated in different test runs. The results of nine such tests are shown in Figure 4.3.

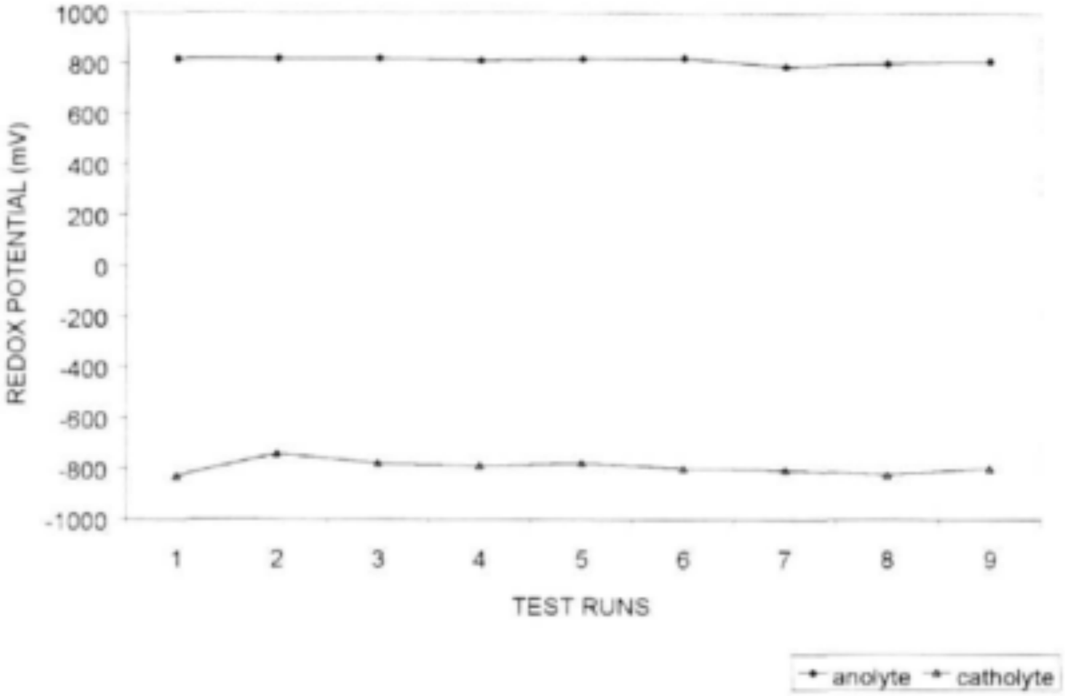


Figure 4.3 **Reproducibility of anolyte and catholyte quality in successive operations**

4.1.4 Consistency of the anolyte quality

The potential of the anolyte to achieve a specific redox potential value in water was compared to that of a sodium hypochlorite solution. Redox potential measurements for both oxidants were taken in stirred batch as well as continuously flowing solutions while the data was recorded electronically. The aim of the experiments was two fold: 1. To determine at what rate the redox potential of the respective solutions would change due to decay in the batch process. Based on the results it would then be possible to see if there is a cut off point before the bacteria had to be introduced without losing any of the oxidative power. 2. Whether the redox potential would remain constant in the continuously flow experiment Figures 4.4 and 4.5 show the results for respectively the anolyte and the sodium hypochlorite in the stirred batch experiments and Figures 4.6 and 4.7 in the continuously flowing experiments. From these graphs it can be seen that the quality of the oxidants remained consistent during the recording period. This gave the assurance that the redox potential in the solutions would remain constant for periods long enough to introduce and expose the bacteria to a known redox potential.

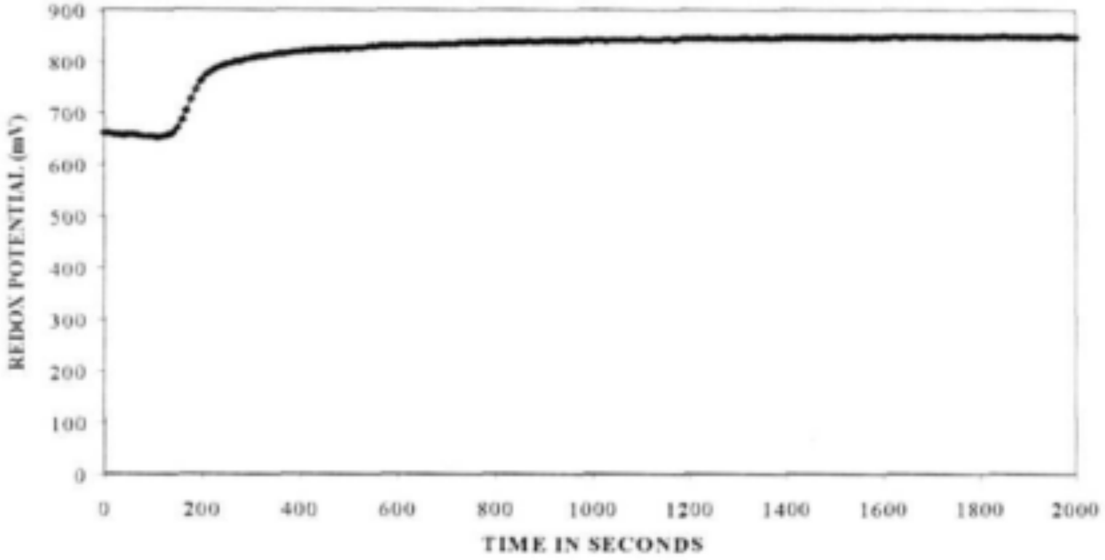


Figure 4.4 **Redox potential as measure of anolyte activity in a stirred batch volume against time.**

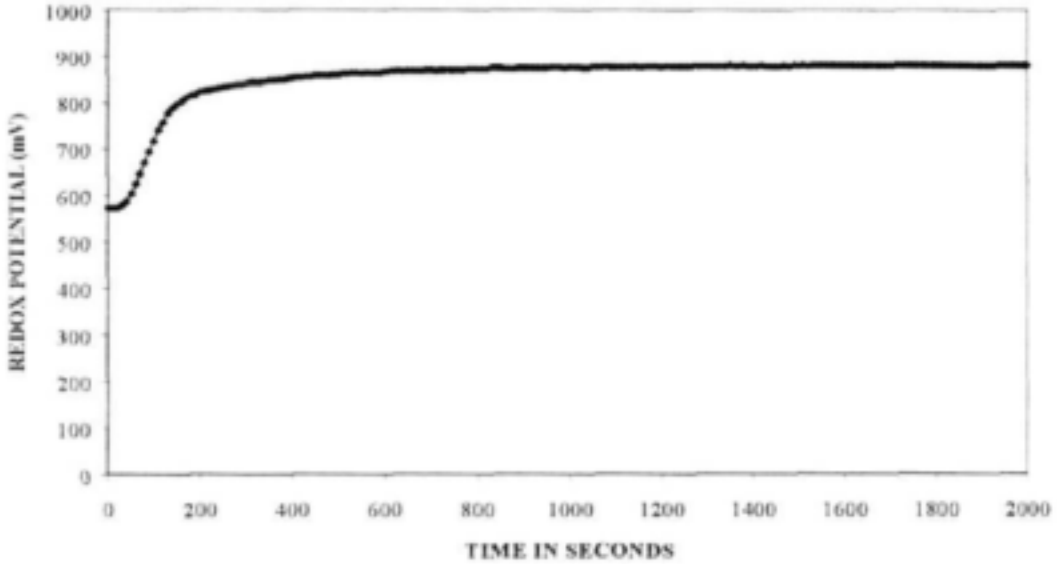


Figure 4.5 **Redox potential as measure of chlorine activity in a stirred batch volume against time.**

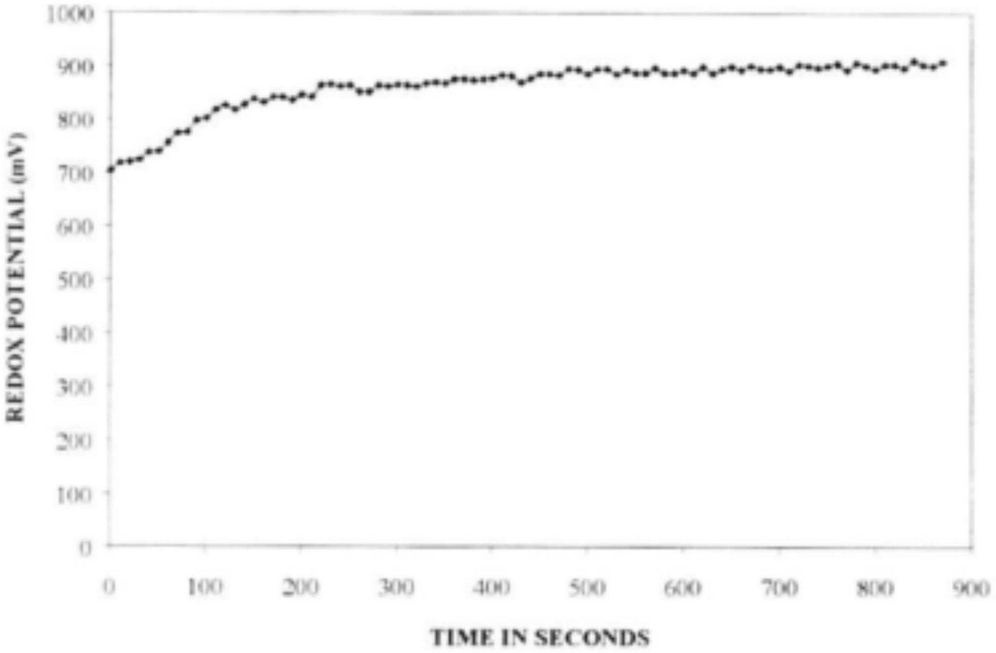


Figure 4.6 Redox potential as measure of anolyte activity in a continuously flowing steam against time.

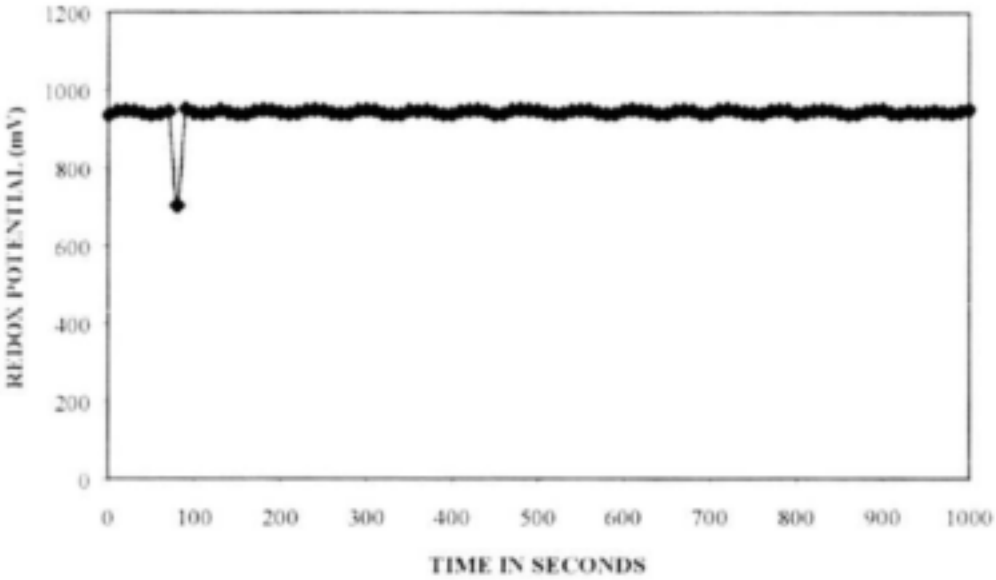


Figure 4.7 Redox potential as measure of chlorine activity in a continuously flowing steam against time.

4.2 Chemical composition of the anolyte

At all times during the operation of the mixed oxidant generator relatively large volumes of gas, in proportion with the volume of anolyte or catholyte, were produced. The anolyte contained about 15% by volume of gas and the catholyte some 30%. Analyses of the gas in the product streams confirmed that oxygen was present in the anolyte and hydrogen in the catholyte. The gas is most likely due to the electrolysis of water.

It was not possible to analyse the product streams for all the possible oxidants that, according to literature and the information on the generators, could be present. The following compounds that could be detected more easily in the fluid or the gas phase were analysed for: chlorine, monochloramine, di-chloramine, ozone and hydrogen peroxide.

Table 4.1 The concentration of the various determinants in the anolyte and catholyte fluid and vapours

		Concentration in the fluid (mg/*l*)	Concentration in the vapour (mg/m^3)
Anolyte fluid	Chlorine	1200	
	Mono-chloramine	< 1	
	Di-chloramine	< 1	
Anolyte vapour	Ozone		600
	Chlorine		1475
	Hydrogen peroxide		20
Catholyte fluid	Chlorine	1	
	Mono-chloramine	< 1	
	Di-chloramine	< 1	
Catholyte vapour	Ozone		200
	Chlorine		<1
	Hydrogen peroxide		80

The concentration of the oxidative species in the vapours were determined with the commercial Dräger Tube apparatus. Tubes sensitive for the various compounds that were suspected of being present in the vapours were used and the readings obtained, converted to express the concentration as mg /m^3 of vapour. Determination of oxidant concentrations other than that of chlorine in the anolyte and catholyte fluid presented many problems and no reliable results were obtained. This was possibly due to the combined effect of the various oxidative species present and the analytical methods that were used. The methods included the DPD and the potassium indigo trisulphonate colorimetric methods of determination for chlorine and ozone respectively. Disadvantages of these methods are that they are not specie or compound specific and false positive results can be obtained in mixtures of strong oxidants. The masking of possible interfering compounds present in the solutions was not attempted

No suitable method could be found to determine the presence or the concentration of free radical species that are purported to be present in the product streams.

4.3 Microbiocidal effects of the anolyte

The results of the microbiological tests are summarised in Tables 4.2 and 4.4 and the percentage reduction of the bacteria on exposure to the two oxidants in the batch and continuous flow experiments are given in Tables 4.3 and 4.5 respectively.

Table 4.2 Comparison between the bactericidal effect of anolyte and chlorine solutions in batch experiments.

Test	Oxidant Concentration	Standard Plate Count (cfu/m*l*) and [oxidant concentration] (mg/*l*)				
		Before exposure to oxidant	After exposure for:			
			1 Minute	5 Minutes	10 Minutes	30 Minutes
1	Anolyte	29000	71	40	34	37
	Eqv. Chlorine conc.	[4.6]	[4.4]	[4.0]	[3.8]	[3.5]
	HOCl	19800	62	100	1500	38
	Chlorine conc.	[3.2]	[2.7]	[2.0]	[1.8]	[1.5]
2	Anolyte	1900	30	20	24	11
	Eqv. Chlorine conc.	[4.4]	[4.0]	[3.9]	[3.7]	[3]
	HOCl	2800	300	40	12	16
	Chlorine conc.	[3]	[3]	[3]	[3]	[2]
3	Anolyte	89000	30	120	60	500
	Eqv. Chlorine conc.	[4.0]	[4.0]	[3.7]	[3.5]	[3.0]
	HOCl	97000	38	90	32	15
	Chlorine conc.	[4.0]	[3.8]	[3.3]	[3.1]	[2.5]
4	Anolyte	181000	No result	2100	520	15000
	Eqv. Chlorine conc.	[3.0]	[3.9]	[3.7]	[3.6]	[3.4]
	HOCl	103000	930	4700	460	3100
	Chlorine conc.	[4.0]	[2.8]	[2.5]	[2.2]	[1.9]
5	Anolyte	21600	47	60	40	10
	Eqv. Chlorine conc.	[2.0]	[1.8]	[1.9]	[1.7]	[1.2]
	HOCl	1600	5	70	40	80
	Chlorine conc.	[3.0]	[2.4]	[2.0]	[2.0]	[1.6]

HOCL = Hypochlorite solution

Eqv chlorine concentration = Equivalent oxidant activity measured as "chlorine" concentration in anloyte.

Chlorine conc = Chlorine concentration as measured in the hypochlorite solution.

CFU = Colony forming units

Test conditions: pH of water 7,9 Temperature of water: 15°C

Table 4.3 Comparison between the percentage reduction of bacterial numbers exposed to anolyte and chlorine solutions in batch experiments

Test	Oxidant	% Reduction in Standard Plate count after exposure for				Overall % reduction in test
		1 Minute	5 Minutes	10 Minutes	30 Minutes	
1	Anolyte	99,75	99,86	99,88	99,87	99,84
	Eqv. Chlorine conc.	[4,4]	[4,0]	[3,8]	[3,5]	
	HOCl	99,68	99,49	92,42	99,80	97,84
	Chlorine conc.	[3,2]	[2,7]	[2,0]	[1,8]	[1,5]
2	Anolyte	98,42	98,94	98,73	99,42	98,87
	Eqv. Chlorine conc.	[4,0]	[3,9]	[3,7]	[3]	
	HOCl	89,28	98,57	99,57	99,42	96,71
	Chlorine conc.	[3]	[3]	[3]	[3]	[2]
3	Anolyte	99,96	99,86	99,93	99,43	99,79
	Eqv. Chlorine conc.	[4,0]	[3,7]	[3,5]	[3,0]	
	HOCl	99,96	99,90	99,96	99,98	99,95
	Chlorine conc.	[3,8]	[3,3]	[3,1]	[2,5]	
4	Anolyte	No result	98,84	99,71	89,91	99,48
	Eqv. Chlorine conc.	[3,9]	[3,7]	[3,6]	3,4]	
	HOCl	99,09	95,43	99,55	96,99	97,76
	Chlorine conc.	[2,8]	[2,5]	[2,2]	[1,9]	
5	Anolyte	99,78	99,72	99,81	99,95	99,81
	Eqv. Chlorine conc.	[1,8]	[1,9]	[1,7]	[1,2]	
	HOCl	99,68	95,62	97,5	95,00	96,95
	Chlorine conc.	[2,4]	[2,0]	[2,0]	[1,6]	

HOCL = Hypochlorite solution

Eqv chlorine concentration = Equivalent oxidant activity measured as "chlorine" concentration in anloyte.

Chlorine conc = Chlorine concentration as measured in the hypochlorite solution.

Test conditions: pH of water 7,9   Temperature of water: 15°C

Overall % reduction in test: Results calculated from the percentage reduction obtained after respectively 1 to 5 minutes contact time.

Table 4.4 **Comparison between the bactericidal effect of anolyte and chlorine solutions in continuous flow experiments.**

Test	Effect of Anolyte (Oxidant)				Effect of Hypochlorite			
	Eqv. Chlorine conc. (mg/*l*)	Initial Standard Plate Count (cfu/m*l*)	Eqv. Chlorine conc. after 5 min. (mg/*l*)	Standard Plate Count after 5 min. (cfu/m*l*)	Chlorine Conc. (mg/*l*)	Initial Standard Plate Count (cfu/m*l*)	Chlorine conc. after 5 min. (mg/*l*)	Standard Plate Count after 5 min. (cf/m*l*)
1	3.3	13200	2.3	30	3.8	12500	3.3	7
2	4.2	54800	3.4	6	4.1	21100	0.2	230
3	6.2	89000	3.5	25	5.4	42000	4.1	180
4	5.4	8300	4.5	29	6.1	8300	5.1	26
5	7.2	42000	5.1	20	6.1	48000	5.1	11

Eqv chlorine concentration = Equivalent oxidant activity measured as "chlorine" concentration in anloyte.
Chlorine conc = Chlorine concentration as measured in the hypochlorite solution.
cfu = Colony forming units
Test conditions: pH of water 7,9 Temperature of water: 15°C

TABLE 4.5 **Comparison between percentage reduction in bacterial numbers exposed to anolyte and chlorine solutions in continuous flow experiments.**

Test	Effect of Anolyte (Oxidant)			Effect of Hypochlorite		
	Eqv. Chlorine Conc. (mg/*l*)	Eqv. Chlorine conc. After 5 min. (mg/*l*)	% Reduction after 5 min.	Chlorine Conc. (mg/*l*)	Chlorine conc. After 5 min. (mg/*l*)	% Reduction after 5 min.
1	3,3	2,3	99,72	3,8	3,3	99,94
2	4,2	3,4	99,98	4,1	0,2	98,91
3	6,2	3,5	99,97	5,4	4,1	99,57
4	5,4	4,5	99,65	6,1	5,1	99,68
5	7,2	5,1	99,95	6,1	5,1	99,97

Eqv. Chlorine concentration = Equivalent oxidant activity measured as "chlorine" concentration in anolyte.
Chlorine conc. = Chlorine concentration as measured in the hypochlorite solution.
Test conditions: pH of water 7,9 Temperature of water: 15°C

In the above experiments it was endeavoured to apply as close as possible similar oxidant concentrations measured as mg/*l* of chlorine in the form of anolyte and chlorine solution to the bacterial suspensions. From the results it can be seen that both the oxidants were efficient in reducing the number of bacteria present by a large margin. In case of the batch experiments it was clear that the largest reduction in the bacterial numbers took place within the first minute after the oxidant had been added for both the anolyte and the chlorine solution. The percentage reduction after five minutes contact time in this case varied between 99,87 and 99,89 for the anolyte and between 96,71 and 99,95 in case of the chlorine solution, while the overall average reduction was 99,56 and 97,84 for the anolyte and chlorine respectively after five minutes contact time. The apparent poorer results obtained with the chlorine may be due the experimental error in the Standard Plate Count determination where in some instances an increase in the counts were noticed after five minutes contact time. If these figures are excluded from the calculations the overall percentage reduction by the chlorine will be slightly higher at 98,92 percent. Similar results were obtained in the flow through experiments. Bacterial numbers exposed to the anolyte was reduced by between 99,65 and 99,98 percent and between 99,57 and 99,97 percent by the chlorine. In these cases the overall average reduction was 99,85 and 99,61 for the anolyte and the chlorine respectively.

From the above it can be seen that little difference could be detected between the effect of the anolyte and chlorine solutions on the number of bacterial present in either the batch or the continuous flow experiments at approximately the same oxidant concentration as expressed in terms of chlorine concentration. Although it seems as if the percentage reduction in bacterial numbers caused by the anolyte is higher than caused by chlorine, the difference is absolutely marginal.

5. CONCLUSION

The results obtained in this study confirm that there are aspects of the production of mixed oxidants that are not well understood and therefore not well defined either. There also seems to be an overlap between the new emerging science of electrochemical activation of water (ECA) and the electrochemical formation of mixed oxidant solutions by electrolytic means. The results and affects claimed to be achieved by the application of ECA technology sometimes borders on the metaphysical and not enough conclusive evidence is available to either support or discard the claims made. Since only two different Electrochemical Activation (ECA) devices were examined, and both posed or developed operational problems during the tests, it would unfair to make comments on any other ECA devices that may be available commercially or on the functioning of improved models as those that were tested. Results obtained however indicate that despite the operational problems experienced that it is possible, based on the redox potential of the solution, to produce an anolyte of consistent quality. Reproducibility of the results were good and it can be expected that this aspect of the performance of the mixed oxidant generators could be equaled or improved in devices which are of better design and construction. This aspect was not only important for the execution of the tests, which were done but would also be of significant importance if commercial use of a mixed oxidant generator had to be considered. Redox potential of the anolyte taken over a period of time showed that the decay in the oxidative power was slow and in the tests it could be kept constant long enough to expose the bacteria to solution with a known redox value.

The possible application of mixed oxidants as a disinfectant, was investigated. Although care was taken in the experiments to preserve the mixed oxidant (anolyte) solution to harvest the total potential oxidative power, and the possible synergistic effects of all the oxidants present, its effect did not significantly exceeded that of chlorine. This was in spite of the fact that the anolyte vapours, and presumably the anolyte solution as well, contained other strong oxidants such as ozone and hydrogen peroxide. It was also confirmed that the catholyte solution did not contain chlorine at concentrations that would have significant microbiocidal properties. This fact is also supported by the low or negative redox potential measured in the catholyte.

Results from batch experiments show that the greatest reduction in the bacterial numbers took place within the first minute. In most cases both the anolyte and chlorine killed more than 99% of the bacteria present during the first minute of exposure. Increased contact time did not significantly reduce the numbers of the bacteria any further. In all the batch tests the average percentage reduction in bacterial numbers were respectively 99,55 and 97,84 for the anolyte and chlorine solution after five minutes contact time. The over all percentage reduction in the continuous flow tests were 99,85 for the anolyte and 99,61 for the chlorine.

It can therefore be concluded that under the test conditions that prevailed that the mixed oxidant generators examined did not produce anolyte solutions with all the properties as claimed in literature. The units tested did not produce a product that behaved significantly differently from chlorine either. Although it seems as though mixed oxidant solutions of consistent quality can be produced from Electrochemical Activation (ECA) devices, and improvements in the functioning of the equipment can be expected in future, the use of such disinfectant generator in the rural areas would probably not be practical. As with other electrolytic chlorine generators a reliable electricity source is essential whilst, in most rural areas this cannot be guaranteed. The availability of high purity sodium chloride to use in the mixed oxidant generator may also present a problem. A further problem could be the disposal of the alkaline catholyte solution of which a volume equal to about one sixth of the volume the anolyte, is produced.

6. RECOMMENDATIONS FOR FUTURE RESEARCH

The following aspects of the generation and application of mixed oxidants warrant further investigation:

- Examine and understand the principle of operation of the mixed oxidant generator.
- Develop methods to analyse for the different oxidative compounds present in the anolyte.
- Develop methods to analyse for the different compounds present in the catholyte.
- Design of a system in which the mixed oxidant solution can be applied such that full oxidative potential of all the compounds present in the fluid as well as the vapours can utilised .
- Examine potential non-conventional applications and benefits of mixed oxidants.

7. REFERENCES

Adham, S.S., R.R. Trussell, P.F. Gagliardo, and A.W. Olivieri. 1997. Membranes: a barrier to micro-organisms. *Blackwell Science Ltd, World Congress 1997.* **SS1-24 - SS1-28.**

American Public Health Association (APHA), American Water Works Association (AWWA) and Water Pollution Control Federation (WPCF), *"Standard Methods for the Examination of Water and Wastewater"*, 18th ed., Washington, 1992, American Public Health Association, p 294 - 319

Bakhir, V.M. 1990. Electrochemical Activation: The Chemical Compound and Properties of Electrochemically Activated Solutions. *Moscow, Russia.* **pp. 1-11.**

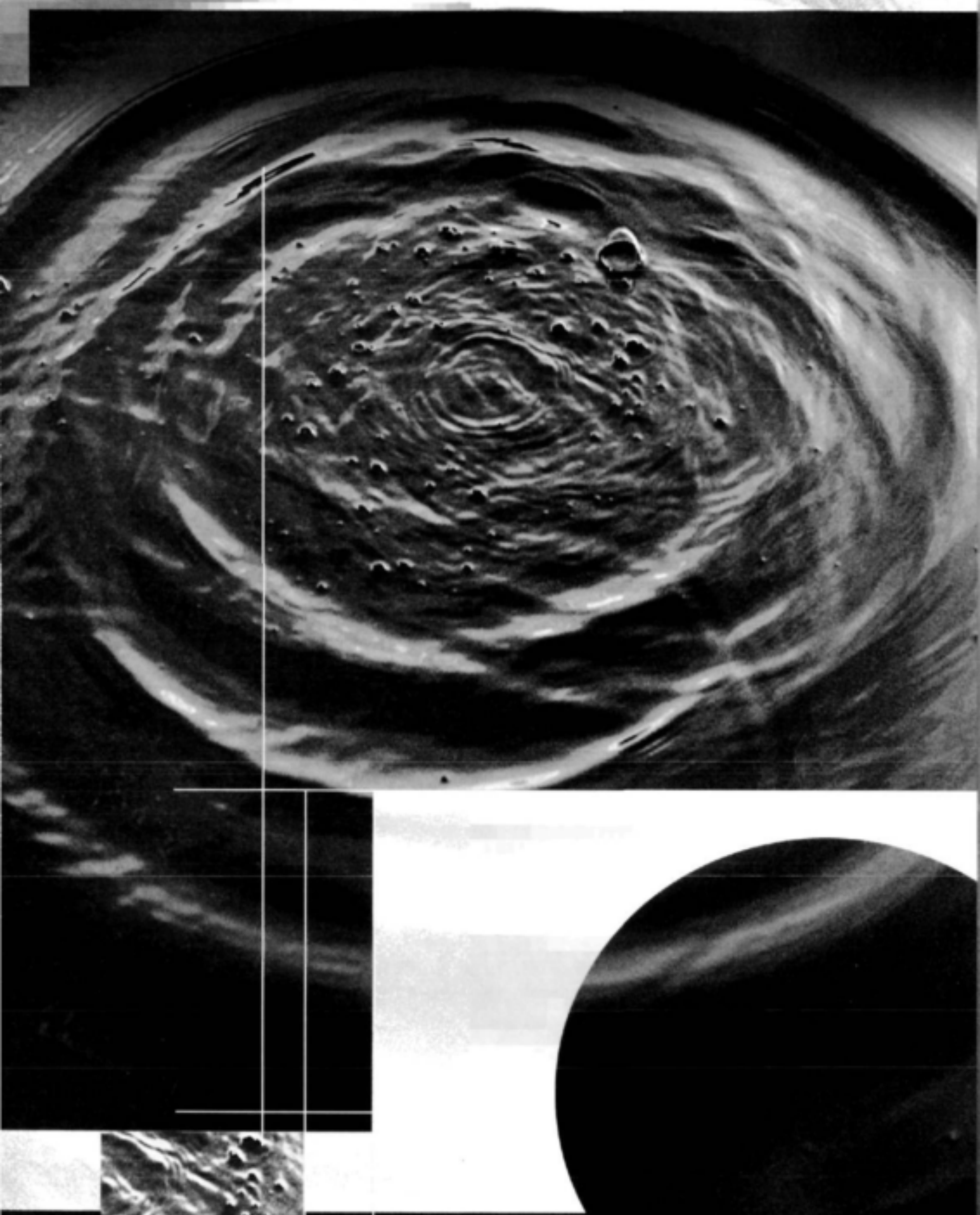
Drägerwerk Altiengesellschaft Lübeck, 1997. Dräger-Tube Handbook. Soil, water and air investigations as well as technical gas analysis. 11th Edition.

Los Alamos Technical Associates. 1993. MIOX Operations User's Guide. *Albuquerque, N.M.* **pp.i 22.**

Strand, R.L. 1994. Redox Automation for Pathogen Management. *Stranco Incorporated, Bradley, Illinois.* **pp. 1-7.**
Srand,R.L. 1994. Istumental Methods for Meeting Rechlorination Requirements.

Wabner, D.W., and W.D. Fleischmann. 1986. Electrolytic Disinfection Production for Small Water Supplies. *Munich, Germany.* **pp. 1-37**.

White, G.C. 1992. Handbook of Chlorination and Alternative Disinfectants. Van Norstrand Reinhold .New York.1308 p.



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