Urban Water Research Association of Australia

Effects of Chloramination of Potable Water on the Performance of Materials

Research Report No. 141

URBAN WATER RESEARCH ASSOCIATION OF AUSTRALIA (UWRAA)

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Effects of Chloramination of Potable Water on the Performance of Materials

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FOREWORD

This report is based on UWRAA Research Project No AM-13, "Effects of Chloramination of Potable Water on the Performance of Materials" which was undertaken during the period March 1991 - May 1997. This project was also an extension of some initial work carried out in UWRAA Project No 15, Chloramination of Water Supplies which was carried out over the period March 1987-June 1990. The Organisational responsibility for the current project was as follows:

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1. Introduction

The corrosion resistance and behaviour of materials in water reticulation systems can be markedly changed by the water chemistry. Total dissolved solids, in particular chlorides, sulphates, bicarbonates, and pH have the greatest influence from a corrosion aspect. But for any given water supply the addition of disinfection agents (which are usually strong oxidising agents) can also change the corrosivity of the water. Chlorination is a major disinfection process and its corrosive effects have been widely investigated (Dillon & Yeo [1], Dillon[2], Nicholas[3]) and it is known that this accelerates the corrosion of copper based alloys. Chloramination is less widely adopted as a method of disinfection but its use is increasing. The effects of chloramination on materials performance has similarly been less widely investigated particularly with respect to metallic materials. The original concerns with the chloramination process was related to the use of ammonia. Excessive levels of ammonia and/or ammonium ions are known to be very aggressive to copper and copper based alloys and it was considered that the presence of these compounds could accelerate the corrosion of these materials which are widely used in water reticulation systems.

As a result a testing program was devised to determine the effects of chloramination on materials commonly used in water reticulation systems. The project consisted of a combination of field and laboratory testing.

2. Chloramination in Australia

Chloramination is used as a method of disinfection of water in all mainland states of Australia. With the exception of Brisbane, the use of chloramination has been restricted to regional/country water supplies up until approximately 1990. Since then the growing acceptability of chloramination has seen the introduction into parts of South Australia, New South Wales and Victoria. The principal reason for the introduction has been to improve microbiological quality in long distance systems. An important secondary consideration is the desire to reduce or minimise taste and odour.

The earliest use of chloramination in Australia was in Brisbane where it was introduced in 1936. Chloramination systems for several other supplies were commissioned in 1960's and 1970's with a substantial increase in the mid to late 1980's[4]. Since this period there has been only a minor increase in its use but it is likely that the implementation of the most recent NHMRC guidelines for drinking water may result in an increasing use of chloramination[5]. The use of chloramines in open reservoir systems is not widely employed as the increased nutrient load can lead to wide spread algae problems.

3. Chemistry of Chloramination

The process of producing inorganic and organic chloramines is described as chloramination. When chlorine and ammonia are present together in aqueous solution, they react to form inorganic chloramines in a series of stepwise reactions[6].

$$HOCL + NH_3 \Rightarrow NH_2CL + H_20$$

(monochloramine)

$$HOCL + NH_2CL \Rightarrow NHCL_2 + H_20$$

(dichloramine)

$$HOCL + NHCL_2 \Rightarrow NCL_3 + H_20$$

(trichloramine or nitrogen trichloride)

Chlorine can also react with nitrogen containing organic compounds such as amino acids and proteinaceos material to form organic chloramines. A general expression is

$$R-NH_2 + HOCL \Rightarrow R-NHCL + H_20$$

Together the inorganic and organic chloramines are collectively known as combined chlorine or combined available chlorine.

4. Materials and Methods.

4.1 Testing Program

The testing program was carried out by two separate methods, namely, immersion testing and electrochemical testing.

Immersion Testing

Immersion test rigs were designed and constructed to enable a wide variety of materials to be subjected to exposure to water, both before and after chloramination. Two test rigs, each consisting of three exposure chambers were located at take off points along the Warren Trunk water main in South Australia. The first site was located 50 metres prior to the chloramination plant and the second 1400 metres downstream from it. Six sets of materials were assembled for installation in the exposure chambers where they were exposed for varying periods of time. The general arrangement of the samples and test rigs are shown in photographs 1 and 2. Flow through the rigs was set at a nominal 5 litres/minute.

Sets of specimens from before and after chloramination were removed after exposure periods of 189 days (0.52 years), 762 days (2.1 years) and 1175 days (3.22 years). Specimens were then assessed for any changes by one or more of the following methods,

- gravimetric (weight) changes
- dimensional changes
- depth of de-alloying
- visual assessment

Laboratory testing

Electrochemical methods were used to measure the corrosion rates of a selection of copper alloys in water from the same source as the field testing. Testing was carried out using both raw water and chloraminated water. This testing was carried out by CSIRO and full details of this work are reported in Appendix 1.

4.2 Test Materials

Selection of materials for this program was based on the likely and actual use of the material in water supply systems. In particular, because of the presence of ammonia and ammonium compounds, copper and copper based alloys were extensively tested. Many were also susceptible to corrosion from chlorinated waters and some were tested in previous work[1] . Where appropriate plastic washers were placed between samples to keep them both physically and electrically separated. This also had the effect of inducing a small crevice which in many materials can be the source of accelerated corrosion.

The materials can be split into four distinct categories.

Metallic - Non-ferrous.	These include copper and a selection of copper alloys used in general water supply and plumbing installations.
Metallic - Ferrous.	Various grades of stainless steels widely used in the water industry.
Plastics.	A range of plastic materials representative of those used in the infrastructure and consumer plumbing installations were chosen.
Elastomers.	A small number of elastomeric materials typically used for sealing rings, gaskets and liners were chosen.

Details of the materials and their compositions (where appropriate) are shown in Tables 1 - 4.

NON FERROUS MATERIALS		Actual Composition									
Alloy Description	Alloy	Cu	Pb	As	Sn	Al	Fe	Mn	Ni	Si	Zn
Aluminium - Silicon Bronze	1UA	89.80	0.01	-	0.01	7.40	0.69	-	-	1.98	0.10
Aluminium - Nickel Bronze	2UB	80.30	0.15	-	0.08	10.20	4.50	0.09	4.15	0.22	0.30
Leaded Aluminium Bronze (Free Machining)	3UC	88.10	1.21	-	0.01	9.60	0.17	0.51	0.04	0.16	0.20
Leaded 70/30 Arsenical Brass	4S	72.00	0.39	0.05	0.06	0.01	0.03	0.01	-	-	Rem
62/38 Wire Brass	5J	63.50	0.02	-	0.05	0.01	0.03	-	-	-	Rem
Leaded 63/37 Arsenical Brass	6SM	63.50	2.03	0.20	0.17	0.02	0.10	0.03	-	-	Rem
Leaded Arsenical Naval Brass	7SMH	61.10	2.18	0.21	1.02	0.01	0.15	0.03	0.01	-	Rem
Forging Brass	8D	58.50	1.66	0.01	0.29	0.15	0.12	-	0.09	-	Rem
Leaded High Tensile Brass	9XE	58.30	1.17	-	0.86	0.49	0.47	1.04	-	-	Rem
Free Machining Brass	10A	58.00	3.22	0.01	0.36	0.29	0.18	0.03	0.01	-	Rem
Copper Half hard	-	>99.90	-	-	-	-	-	-	-	-	-

Table 1 Actual composition of non-ferrous alloys

FERROUS MATERIALS		Nominal Composition				
Alloy Description	Alloy	C max	Cr	Ni	Mo	Others
Stainless Steel - Austenitic	304	0.05	18.50	8.50	-	-
Stainless Steel - Austenitic	316	0.05	17.00	11.00	2.20	-
Stainless Steel - Duplex	2205	0.03	22.00	18.00	6.20	Cu, N
Stainless Steel - Duplex	904L	0.02	20.00	25.00	4.20	Cu
Stainless Steel - Duplex	2304	0.03	23.00	4.00	-	N
Stainless Steel - Ferritic	3CR12	0.02	11.60	0.65	-	Ti

Table 2 Nominal compositions of Stainless Steels

PLASTICS	
Type	Component Use
Unplasticised PVC	Pipes & fittings
Plasticised PVC	Waterstops
Acetal Co-polymer	Plumbing fittings
Polybutylene	Pipe
Fibre Reinforced Polyester	Linings, structural components
Polyphenylene ether	Water meter components
Polystyrene 30% graphite	Water meter components
Nylon	Plumbing fittings

Table 3 Types and typical uses of plastic materials

ELASTOMERS	
Type	Use
Natural Rubber	Rubber rings, gaskets
Neoprene Rubber	Rubber rings
Chlorosulphanated polyethylene (Hypalon)	Liners and floating covers

Table 4 Types and typical uses of elastomers

4.3 Water Characteristics

Water samples both before and after chloramination were regularly sampled and analysed. The results are shown in Table 5. A pH correction facility installed to improve chloramination conditions increased the pH from a median of 7.4 to 7.8. This increased the Langelier Saturation Index from a median of -0.97 to -0.75. (The Langelier Saturation Index is an index calculated from the total dissolved solids, calcium concentration, total alkalinity, pH, and solution temperature that shows the tendency of a solution to precipitate (positive) or dissolve (negative) calcium carbonate). The median combined chlorine residual over the test period was 4.0 mg/L.

WATER QUALITY CHARACTERISTICS BEFORE AND AFTER CHLORAMINATION
Warren Reservoir Water

	pH	TDS mg/L	Cond. at25 C. uS/cm	Alkalinity as $CaCO_3$ mg/L	Bicarb mg/L	Calcium mg/L	Copper total mg/L	Langelier Saturation Index	Total Chlorine Residual mg/L
Before Chloramination									
Minimum	6.9	240	446	30	37	11	0.036	-1.99	< 0.1
Maximum	8.4	420	764	82	100	22	0.328	-0.18	< 0.1
Median	7.4	330	602	52	63	15	0.062	-0.97	< 0.1
After Chloramination									
Minimum	6.8	210	378	30	36	9.2	0.027	-1.97	0.1
Maximum	8.7	590	1080	89	107	24	0.327	0.23	7.5
Median	7.8	340	621	57	69	16	0.177	-0.75	4.0

Table 5 Water Quality details

5. Results

5.1 Testing Procedure

Prior to field exposure, all metallic samples were cleaned in ethyl alcohol and weighed to constant weight. All stainless steel samples were passivated with a 10% nitric acid solution prior to weighing. Where practical, non metallic samples were dimensionally measured. After removal all samples were examined and photographed as appropriate and then cleaned with a mild detergent. Metallic samples were then dried and reweighed to constant weight while non-metallic materials were remeasured to establish any changes in dimensions. Visual assessments at low power magnification was also made of all materials. For copper alloys susceptible to de-alloying, cross sections were cut from the specimens which were then mounted in bakelite and then polished. Any de-alloying was determined and measured. Where it was observed, the depth of measurement was carried out as described in AS 2345[7].

The testing procedure for electrochemical testing is detailed in Appendix 1.

5.2 Non Ferrous Alloys

Results of visual and gravimetric changes are detailed in Tables 6 and 7. Depths of de-alloying for each alloy are shown in Appendix 2 while the calculated corrosion rates are shown in Table 8. The corrosion rates were calculated by using the average and maximum depths of de-alloying as determined by measurement as described in AS 2345 at each exposure period. Corrosion rates for each of these periods were then calculated and averaged to give an indicative corrosion rate over the total exposure period.

Alloy Description	Alloy	Raw Water	Chloraminated Water
Aluminium-Silicon Bronze	**1UA**	Corrosion deposits on both surfaces, de-alloying below washers	Pitting on both surfaces, some crevice de-alloying below washer
Aluminium-Nickel Bronze	**2UB**	Dark bronze surface discolouration with corrosion deposits and severe pitting on exposed surfaces.	Dark green surface discolouration. Some de-alloying underneath washer.
Leaded Aluminium Bronze (Free Machining)	**3UC**	Slight pitting and corrosion deposits with severe de-alloying below washer.	Slight pitting on edges and de-alloying below washer. Mottled discolouration
Leaded 70/30 Arsenical Brass	**4S**	Black-green surface discolouration and minor corrosion deposits.	Black-green surface discolouration with some de-alloying underneath washer.
62/38 Wire Brass	**5J**	Black-green surface discolouration except under washer where some de-alloying has occurred	Dark bronze discolouration. Slight de-alloying under washer
Leaded 63/37 Arsenical Brass	**6SM**	Black-green surface discolouration	Dark bronze surface discolouration.
Leaded Arsenical Naval Brass	**7SMH**	Black-green surface discolouration	Black-green surface discolouration. Shallow pitting under washer
Forging Brass	**8D**	Black-green surface discolouration except below washer where slight de-alloying was evident	Mottled black colour. De-alloying and corrosion deposits below washer.
Leaded High Tensile Brass	**9XE**	Black-green discolouration with de-alloying below washer.	Heavy de-alloying below washer. High degree of surface corrosion.
Free Machining Brass	**10A**	Black-green discolouration with de-alloying below washer.	Dark bronze discolouration with shallow pit of approx 3mm diameter.
Copper - Half Hard	**-**	Black discolouration. Pitting corrosion under surface deposits	Black, green and purple discolouration

Table 6 Visual assessment of non ferrous alloys.

		% Weight Change					
		Raw Water			Chloraminated Water		
Alloy Description	Alloy	189 days	762 days	1175 days	189 days	762 days	1175 days
Aluminium-Silicon Bronze	1UA	-0.22	-0.49	-0.21	-0.04.	-0.10	-0.22
Aluminium-Nickel Bronze	2UB	-0.11	-0.33	-0.29	-0.02	-0.05	-0.10
Leaded Aluminium Bronze	3UC	-0.08	-0.23	-0.26	-0.02	-0.08	-0.45
Leaded 70/30 Arsenical Brass	4S	-0.11	-0.37	-0.41	-0.09	-0.42	-0.43
62/38 Wire Brass	5J	-0.48	-1.69	-2.10	-0.32	-1.75	-2.26
Leaded 63/37 Arsenical Brass	6SM	-0.15	-0.38	-0.48	-0.11	-0.37	-0.25
Leaded Arsenical Naval Brass	7SMH	-0.15	-0.53	-0.46	-0.12	-0.52	-0.62
Forging Brass	8D	-0.21	-1.69	-2.03	-0.26	-1.06	-2.95
Leaded High Tensile Brass	9XE	-0.27	-0.71	-1.19	-0.26	-1.23	-1.07
Free Machining Brass	10A	-0.21	-1.40	-0.81	-0.16	-0.89	-0.97
Copper - Half Hard	-	-0.44	-2.20	-2.52	-0.30	-1.77	-2.66

Table 7 Weight loss of Non Ferrous Alloys

Corrosion Rates in microns per year					
		Corrosion rates based on Average data		Corrosion rates based on Maximum data	
Alloy Description	Alloy	Raw Water	Chloraminated	Raw Water	Chloraminated
70/30 Arsenical Brass	4S	0	4	0	16
Aluminium Nickel Bronze *	2UB	5	8	15	47
63/37 Leaded Arsenical Brass	6SM	6	8	145	125
Aluminium Silicon Bronze	1UA	27	36	135	118
Leaded Naval Brass	7 SMH	28	27	113	237
Leaded Aluminium Bronze	3UC	147	298	259	853
Free Machining Brass	10A	158	181	336	317
Leaded High Tensile Brass	9XE	166	193	433	497
Forging Brass	8D	186	232	363	464
62/38 Wire Brass	5J	196	228	368	453
* Significant pitting					

Table 8 Corrosion rates in ascending order of copper alloys based on depth of de-alloying.

5.3 Ferrous Materials.

Some surface discolouration was evident on some of the stainless steel specimens but weight changes were such that they were less than the measurement error and as such were considered to be zero. Corrosion of the materials was also minimal. Some minor surface pitting was evident at 40X magnification on both 304 and 316 stainless steels with a higher incidence of pitting on type 304 stainless. There was no obvious difference between the raw and chloraminated water. Pitting was not observed on any of the other specimens.

5.4 Plastics.

All of the plastics exposed showed no visible effects of the chloramination when viewed up to 40X magnification.

5.5 Elastomers.

Dimensional and Shore Durometer A hardness changes of two of the elastomer compounds are shown in Table 9.

		Raw Water			Chloraminated Water		
Description		189 days	762 days	1175 days	189 days	762 days	1175 days
Neoprene	Dimensional (mm)	+0.2	+0.3	+0.2	+0.3	+0.6	+0.7
	Shore A hardness	68/69	69/70	72/73	69/70	70/71	73/74
Natural Rubber	Dimensional (mm)	+0.5	+0.7	+0.6	+0.6	+1.1	+1.3
	Shore A hardness	70/71	69/70	68/70	69/70	68/69	68/69

Table 9

Dimensional Changes and Hardness Values of Elastomeric Materials

Visible surface deterioration was apparent on the neoprene and natural rubber samples which had been exposed to chloramines. This consisted of surface roughening and in the case of neoprene, micro cracking/crazing (Photos 3 - 6). It was also possible to remove the surface of these samples by gentle rubbing with a cotton fabric. There were also significant effects of raw water on natural rubber in the form of surface cracking. There was no visible deterioration of the chlorosulphanated polyethylene (Hypalon) material in either raw or chloraminated water.

6. Discussion

6.1 Non Ferrous Materials

De-alloying and in some instances pitting corrosion of all copper alloys occurred in both the raw and chloraminated water. Corrosion rates, (Table 8) were calculated based on the depths of de-alloying using “average data” which was determined by using the methods specified in AS 2435 as well as the “maximum data” from the same set of information. With one exception, the average data showed that chloramination increased the rate of corrosion which in this case was the rate of dealloying.

Some of the early data, however, did not agree with the above results. Hence it was felt that electrochemical testing should also be carried out to further study the phenomena. The results of this testing confirmed that chloramination had the effect of increasing the corrosion rates.

In terms of exposure testing, the alloys with the best performance were the inhibited brasses and the Ni/Al and Si/Al Bronzes, although there was some significant pitting on the Ni/Al Bronze (photo 7). Non-inhibited brasses and Leaded Aluminium Bronze were the worst performers with levels of de-alloying in these alloys an order of magnitude greater than the best performers.

There was, however, no direct comparison between the corrosion rates obtained by electrochemical and exposure tests in this project. There is almost an inverse correlation between the extent of de-alloying and the measured corrosion rates indicating that the electrochemical corrosion rate measurement is not an effective measure of de-alloying. It is noteworthy that the arsenic containing materials were among those which had the higher electrochemical corrosion rates, including some dezincification in the case of sample No 6, (the Leaded 63/37 Arsenical Brass) whereas the materials which showed some of the most extensive dealloying in field testing, (sample 9-Arsenic Free High Tensile Brass) had the lowest electrochemical corrosion rate in chloraminated water. This is somewhat surprising since an electrochemical corrosion rate measurements in previous work by Nicholas[3] provided good correlation between electrochemical and metallographic data. However, Nicholas[8] has pointed out that the good agreement between electrochemical corrosion rate measurements and dezincification was found in waters with effectively nil residual disinfectant. He has pointed out that results for heavily chlorinated waters showed a serious underestimate of de-alloying rates , which is consistent with the present work.

There is no doubt, however, that chloramination had the effect of increasing the de-alloying rates of the copper alloys, especially those alloys with no dezincification resistance imparted by the addition of arsenic and/or structural modification.

The results for copper follow a similar pattern, with increases in corrosion from chloramination evident in both electrochemical and weight loss measurements. Both of these methods rated copper as having the highest corrosion rate however weight loss measurements for copper showed only minor variations in the corrosion levels.

Chloramines are oxidising agents, and hence the increase in the corrosion of copper and copper alloys is not unexpected. Similar increases in corrosion have been observed with the more common disinfectant, chlorine. However, there is now data which suggests that some copper corrosion, (blue water and pitting) is a consequence of microbiological induced corrosion (MIC). Elimination of these microbiological influences by disinfection has also been shown to reduce some of the copper corrosion problems. Herein lies the dichotomy of the effects of disinfectants on corrosion rates and highlights the complexity of the corrosion of these materials.

The de-alloying phenomena, which can also be accelerated by chlorination, was recognised as a major problem with brass fittings, and in the mid 1980's measures were undertaken to address this situation by the mandatory use of dezincification resistant brasses. AS2345 was published originally as a test method but more recently has been revised to provide both a test and performance standard. The ongoing use of this performance standard as a requirement for use in chloraminated systems is reinforced by the results of this project.

Whilst no comparative rates between the effects of chloramination and chlorination are available the lower oxidising capacity of chloramines is likely to have a lesser impact than chlorination.

6.2 Ferrous Materials

Stainless steels are becoming widely specified and adopted as an economical material in the water/wastewater industry especially in water and wastewater treatment plants. The various types of stainless steel tested in this program are all used to varying extents, with the most common being types 304 and 316. The only evidence of corrosion on any of these materials was very minor pitting, which was only observable at 40x magnification with raw and chloraminated water exposure on both 304 and 316.

The chloride content has the most influence on the performance of stainless steels and given the relatively low levels in this supply (104 mg/L min. 161 max. 136 median) it is a little surprising to see even minor attack. It was also most surprising to observe the good performance of type 3CR12 (a basic 11% chromium ferritic stainless steel). This alloy's performance is also not in line with general field performance where crevice and pitting corrosion in aqueous environments has occurred, and this alloy should still not be recommended for continuous immersion applications.

The performance of the higher alloyed duplex stainless steels was excellent with no sign of any corrosion, which is an expected result.

A precautionary note on the interpretation of this data. The specimens of stainless steel, as exposed, were in the ideal state for the minimisation of corrosion. They were all weld free and fully passivated. In field applications welding and other forms of fabrication are always present which if not carefully treated[9], can result in premature failures due to surface contamination, non removal of welding residues and heat tinting. These aspects are commonly overlooked in specifying stainless steel fabrications and result in failures.

6.3 Plastics

No observable deterioration of any of the plastic materials was evident, which is not in agreement with the results found by Reiber[10] which showed that there was significant attack on an Acetal type plastics in both chlorine and chloramine solutions. This variation may be related to the levels of chloramines used in the testing. Concentrations of 240-268 mg/L of chloramines were used by Reiber in an accelerated test program compared to a median of 4.0 mg/L in this series of tests. While high concentrations can act as an accelerated test, they can also produce environments which are much more aggressive and unrealistic. In those circumstances extrapolation of performance is not necessarily valid. The plastics that were tested are widely used in the water industry and there have been few if any reported examples of failures as a result of chemical attack. Reiber also showed that chlorine also has a detrimental effect at high concentrations, but the lack of failures in the more extensive chlorinated water systems at low concentrations suggests that the accelerated testing using high concentrations is unrepresentative of field performance. The present results are therefore supported, and there will be little effect of chloramines on the common plastics used in the water industry.

6.4 Elastomers

Only two true elastomers were tested, the third, chlorosulphanated polyethylene is a "hybrid" and was included in this instance as an "elastomer" due to its physical properties. There were no observable effect on this material. By contrast there was considerable effect on both natural and neoprene rubbers. This is consistent with Reiber[10] who also found that chloramines had a significant effect on some elastomeric materials.

Deterioration was also evident on natural rubber when exposed to raw water, however the attack by the chloramines was more of a chemical attack as shown by surface swelling, roughening and tackiness of the surfaces. Microbiological attack and failures of natural rubber rings has been reported in some parts of Australia (QLD, NT and SA) and this appears to be related to the quality of the original rubber compound, in particular the use of regrind and reclaimed rubber. This deterioration has been reported from the "soil" side of the joints, but there is little field evidence to suggest deterioration from the "water" side of the joints.

Reiber[10] reported significant attack by chloramines on elastomers, especially those with natural isoprenes (rubber) or synthetic isoprene derivatives. The newer completely synthetic polymers, developed for their chemical resistance, performed well. This work was carried out using accelerated tests at high levels of chloramines (300 mg/L target). As previously suggested, accelerated testing does not always result in data which can be extrapolated to indicate field performance but is very useful for comparative testing. In the case of the elastomers, the long term tests at low levels provided similar results, and of the two materials tested, the ranking would be the same as that reported by Reiber[10] ie natural rubber is more affected than neoprene.

Chloramines have been used in parts of the Brisbane water supply since 1936. In 1983, testing and evaluation of rubber rings in the Brisbane water supply system showed no evidence of failure due to chloramines[11]. Attack on rubber components in Brisbane domestic plumbing installations has been attributed to chloramine attack, but these components are usually more exposed to the chloramines or other disinfectants than a rubber ring for instance. Rubber rings used in water reticulation pipes are well encapsulated within the joint and direct access to chloramines or any other disinfectant is limited. The levels of disinfectants in these areas would be expected to be lower than the mainstream pipe line and hence any direct attack on the rings themselves could be expected to be low. However in light of this work and that of Reiber, further work is planned by Brisbane Water to further assess further rubber rings and their field performance in water reticulation mains.

The effects of chloramines on elastomers can in most instances be markedly reduced by the selection of suitable compounds and formulations. To ensure the use of appropriate materials, a performance standard is required which could be incorporated into Australian Standards. Work has already started on such a standard and is being considered. Refer Appendix 3.

7 Summary and Recommendations

As shown by the long term testing of metallic and non-metallic materials, at chloramination levels of up to 4 mg/L have been shown to:

- Increase de-alloying of copper based alloys particularly in non-dezincification resistant materials. "DR" materials showed slight increases in de-alloying but the levels were well within acceptable limits.

- Increase corrosion rates of copper, especially when determined electrochemically, although there was only minor differences in field samples.

- Significantly attack natural rubber (stock sheet) and Neoprene rubber (stock sheet) with natural rubber being effected the worst. The natural rubber also showed considerable deterioration in raw water.

- Have negligible effect on a range of stainless steels and plastic materials.

Which leads to the following recommendations:

1. The ongoing mandatory use of DR materials for use in water supplies, regardless of the type of disinfection, should continue.

2. Develop a test method and performance requirements for chloramine resistance for incorporation into AS1646 - "Elastomeric seals for waterworks performance". This requirement should also be used as a requirement for elastomeric seals used in domestic applications.

3. Determine the performance of rubber rings in existing chloraminated water supplies.

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References

[1] B I Dillon & W Yeo, Dezincification Study - Port Augusta, Amdel report No 1105 March 1976.

[2] Darlington et al, Dealloying phenomena in potable waters - the effects of chlorination. 6th International Congress on Metallic Corrosion, Sydney 1975.

[3] Nicholas D, Dezincification of Brasses in Potable Waters, Urban Water Research Report No 84, August 1994.

[4] P M Thomas, Chloramination of Water Supplies, Urban Water Research Association Report No 15, pp 4 - 7.

[5] U. Kaeding, Australian Water Quality Centre, Private Communication.

[6] P M Thomas, Chloramination of Water Supplies, Urban Water Research Association Report No15, pp 20 - 23.

[7] AS 2345 - 1992, Dezincification Resistance of Copper Alloys.

[8] Nicholas D, Hunter Water , Private Communication.

[9] AS 1556 Part 6 Welding Stainless Steels for Structural Purposes.

[10] S Reiber, Chloramine Effects on Distribution System Materials, AWWA Research Foundation.

[11] A Krumins, Brisbane Water Corporation, Private Communication.

INVESTIGATION OF THE INFLUENCE OF CHLORAMINATION ON THE ELECTROCHEMICAL CORROSION BEHAVIOUR OF COPPER-BASED ALLOYS

by

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SUMMARY

1. Electrochemical methods were used to measure corrosion rates of eight copper-containing alloys in water from the Warren reservoir in the untreated (raw) state and after treatment with monochloramine.

2. All materials studied had low mean corrosion rates in raw Warren water, with the leaded high-tensile brass having a much lower value than the others.

3. The corrosion rates of all materials were increased on exposure to chloraminated water. The differences between materials were not great, a factor of four separating the lowest and the highest. The order of decreasing corrosion rate based on corrosion current density was:

(Highest corrosion rate)
    Copper
    Leaded 70/30 As-brass, leaded As-naval brass, forging brass.
    Leaded 67/37 As-brass, free-cutting brass
    Forging brass
    Leaded high-tensile brass
(Lowest corrosion rate)

4. No clear correlation appeared to exist between the electrochemical corrosion rate and the extent or depth of dezincification although there was a tendency to an inverse correlation.

INTRODUCTION

In a previous report[1], the influence of chloramine dosing of Adelaide tap water was investigated for a number of copper alloys and stainless steels using mass-loss measurements of coupons which had been immersed for 189 days in flowing mains water prior to and following a chloramination plant. The report found that chloramination had reduced the corrosivity of water due to the increase in pH which accompanies this treatment. The work was carried out at a mean residual chloramine concentration of 5.6 mgl^{-1}.

A second report[2] included assessment of the extent and nature of dezincification of the copper-based alloys after up to 38 months immersion. These measurements showed wide variations within the eight sample types which were studied for different immersion times.

It is the purpose of this study to use electrochemical methods to measure the effect of chloramination on corrosion rates of copper and its alloys.

EXPERIMENTAL PROCEDURE

Materials tested

In all, eight samples were tested, one being phosphorus deoxidised copper and the other seven copper-based alloys having compositions as listed in Table 1.

Table 1: Copper alloys tested in this study

Sample	EM* Designation	Common name
1	UA	Aluminium - silicon bronze
4	S	Leaded 70/30 arsenical brass
6	SM	Leaded 63/37 arsenical brass
7	SMH	Leaded arsenical naval brass
8	D	Forging brass
9	XE	Leaded high-tensile brass
10	A	Free-cutting brass
Cu	Cu	Phosphorus-deoxidised (PDO) copper

Note: * EM = Extruded Metals

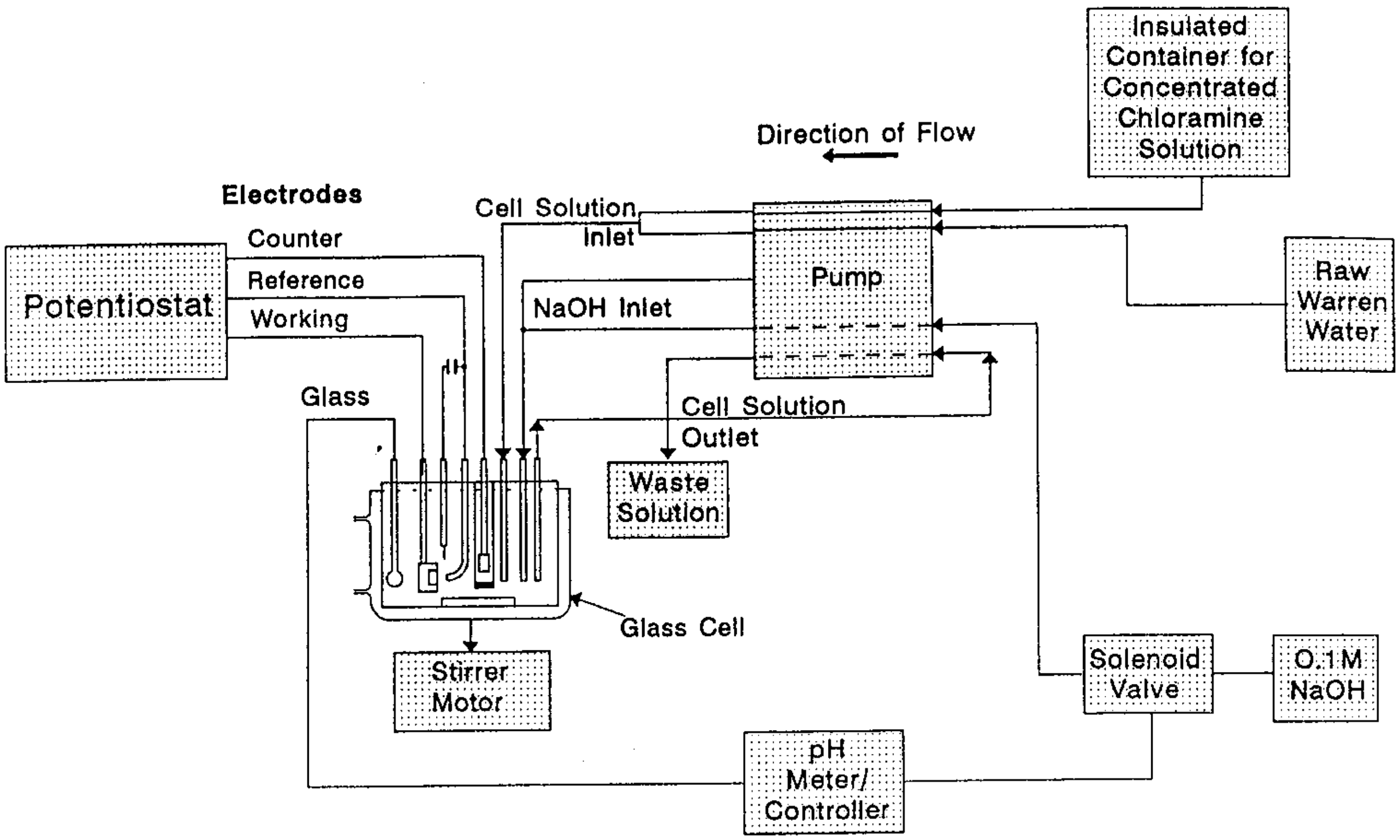


Figure 1 Schematic of test assembly

Samples 4,6,9 and 10 were subjected to more intensive investigation than the others on advice that they were the more important of the group. Samples 1,7,8 and phosphorus deoxidised copper were tested to obtain qualitative preliminary data.

Specimen Preparation

Machined cylindrical samples 11.28mm diameter and 10mm high were supplied by the Engineering and Water Supply Department of South Australia (E&WSD). Electrical connection to each sample was provided via an M3 brass bolt which was screwed into a hole which was tapped in the back of each cylindrical sample. The specimen was then degreased and mounted in Ciba Geigy epoxy resin LC 191 and hardener LC 226. The mounted specimens were oven-cured at 50oC for 2 hours and ground to a 600-grit finish prior to testing.

Test Assembly

Figure 1 is a schematic of the test assembly used. The tests were performed in the water-jacketed glass electrochemical cell in which the test specimen was the working electrode. The cell also contained a saturated calomel reference electrode (SCE) in a Luggin capillary, a platinum counter electrode separated from the test solution by a sintered glass frit, a supplementary platinum reference electrode coupled to the SCE via a $1\mu F$ capacitor to stabilise the electrochemical system against electrical oscillation, a glass electrode for pH measurement and inlet and outlet tubes for the test solution.

The pH was automatically controlled using a pH-stat which consisted of a teflon solenoid valve which was operated by a relay in the pH module (an Amalgamated Instrument Co. Model PM4) which was programmed to introduce 0.1 M NaOH solution via a peristaltic pump when the pH fell below 8.4. The cell was continually stirred with a magnetic stirrer to ensure complete mixing.

Initial experiments were performed without temperature control, but since the stirring heated the cell, subsequent experiments were conducted at a constant temperature of 25°C which was maintained by circulating water from a thermostatically-controlled bath through the water-jacketed glass cell.

Corrosion rate measurements

Electrochemical corrosion rate measurements were performed using a Princeton Applied Research Model 273 Potentiostat controlled by PAR M352 software. Each measurement involved a 2 mVs^{-1} scan of potential over a +30 mV range about the corrosion potential (E_{corr}). The corrosion rate was obtained by a curve-fitting procedure which was included in the M352 software package. The good correlation for copper alloys between corrosion rate measurements and weight-loss has been demonstrated by Nicholas.[3]

Chloramine Solution

The total chlorine level specified for testing was between 1 and 2 mg/l, with 1.5 mg/l being preferred. The chlorine source, in which the major chlorine species was monochloramine, was a concentrated chloramine (CLA) solution of approximately 500 mg/l which was prepared as follows:

1. The pH of 0.5 litre of distilled water was adjusted to approximately 8.0 using 0.1 M NaOH
2. 0.45g of ammonium chloride crystals were added with vigorous stirring
3. While stirring, 6.5 ml of 125g/l sodium hypochlorite solution (AJAX chemicals UN No. 1791) were added slowly
4. The pH was adjusted to 8.40 using 0.1M NaOH
5. The solution was stored in a brown glass container at 4°C

Chloramine analysis

Solutions were analysed for total residual chlorine using a procedure based on a standard method [4] which involved the use of the following solutions:

pH 6.5 buffer
N,N-diethyl-1,4-phenylene diamine sulphate (DPD)
ferrous ammonium sulphate (FAS)
barium diphenylamine sulphonate
potassium dichromate

The methods used are set out in Attachment 1.

Methods of chloramine dosing

1. Batch Approach

In initial experiments, concentrated CLA solution was added to the cell to give an initial available chlorine concentration of 1-1.2 mg/l. and then corrosion rate measurements were performed. It was not possible to maintain this chlorine level during a measurement run lasting several days due to loss of available chlorine by evaporation and reaction with oxidisable material in the water.

2. Continuous Dosing

To overcome the decay in CLA concentration, a peristaltic pump with an 8-channel pump-head was used to continually feed the cell with raw Warren water and CLA solution, and to simultaneously pump solution out of the cell. The CLA solution was contained in a sealed bag of the type used for collecting blood (A blood bag, obtained from Tuta Pty Ltd) which was stored in an insulated, cooled container. Tubing was selected so that the ratio of inflows (raw Warren water : CLA solution) was about 20:1. By appropriate selection of flow rates and CLA concentration it was possible to maintain a reasonably steady state concentration of CLA in the test solution.

As each batch of water had its own biochemical oxygen demand the following approach was used to calculate the appropriate bag concentration. At the steady state, and assuming that the consumption of CLA follows first order kinetics,

Equation 1:

CLA flow rate in = CLA flow rate out + CLA consumption rate

i.e.

Equation 2:

$[\mathrm{CLA}]_{\mathrm{bag}} \times \mathrm{vol.flow\ in} = [\mathrm{CLA}]_{\mathrm{soln}} \times \mathrm{vol.flow\ out} + [\mathrm{CLA}]_{\mathrm{soln}} \times k$

where k is the rate constant for CLA consumption.

If the rate constant for CLA consumption, k, is determined from the steady state conditions, then the concentration of CLA concentrate required to produce a given steady state CLA concentration in the test solution may be calculated. For example, for a particular set of steady state conditions taken from a previous run):

$[CLA]_{soln} = 0.92$ mg/l; $[CLA]_{bag} = 1.67$ mg/l

Volume flow of chlorine in = 2.924 ml/hr

Volume flow of raw water in = 60.86 ml/hr.

Volume flow of water out = 2.92 + 60.86 = 63.78 ml/hr

Equation 2 then becomes:

$$33.4 \times 2.924 = 0.92 \times 63.78 + 0.92 \times k$$
$$= 0.92\ (63.78 + k)$$
$$\therefore k = 42.3 \text{ ml/hr}$$

In other words, the rate of CLA loss is equivalent to an additional flow rate out of 42.3 ml/hr.

The bag concentration required to maintain a concentration of 1.5 mg/l in solution may be calculated from Equation 2 using the measured value of k:

$$[Cl_2]_{bag} = \frac{1.5\ (63+k)}{20 \times 2.924} = 2.72\ mg/l = z$$

To achieve this new steady state concentration the original CLA solution was used as follows:

1) The CLA solution was diluted by 1/9. by adding 55 ml to standard flask and making up to 500 ml.
2) 5 ml of this solution was titrated to give the available chlorine concentration (x).
3) The volume, y, of CLA solution required to achieve the desired bag solution concentration was found using the following expressions:

   55 ml → x mg/l

   y ml → desired bag concentration (z)

   $\therefore y = (z \times 55)/x$
4) Prepare the bag solution by adding y ml of the original CLA solution and diluting to 500 ml.
5) Check pH and adjust to 8.40.

Even within a batch of water, variations in the steady state CLA concentration were observed for a fixed bag concentration indicating variation in the biochemical oxygen demand (BOD) of the water. As a result, monitoring and adjustment as described above were required for each run. Control of chlorine concentration was by no means simple. It was not possible to conduct all runs at the same level which necessitated normalisation of corrosion rates measured by dividing the mean corrosion rate by the mean CLA concentration.

Corrosion Rate Measurement Procedure

Each of samples 4,6,9 and 10 was subjected to two test conditions:

1) raw Warren water
2) dosed Warren water (dosed with CLA)

The testing produced graphs of current density versus potential. Curve-fitting of the data in such plots gave the corrosion rate of each material over time. This allowed a comparison between dosed and undosed water to determine the effect of chloramination on the corrosion rate of the specimen.

Testing was carried out for between two and five days depending on the CLA level and reliability of the results. Corrosion rate measurements were usually taken every 2 or 4 hours. If a constant CLA level and constant corrosion rate was observed the experiment was stopped after a few days. The CLA level of the cell and bag solutions were monitored regularly on samples taken each morning and afternoon using the titrimetric methods already described in Attachment 1. If the CLA concentration fell below an acceptable level, either additional CLA was added to the cell, with or without replacement of the bag solution, or in cases when [CLA] dropped due to interruption of CLA flow, the experiment was stopped.

The bag solution titration followed the same procedure as for the cell solution but 5 ml of solution was used instead of 100 ml and 95 ml of distilled water was placed in the conical flask before titration started.

The available [CLA] was calculated using the following expression:

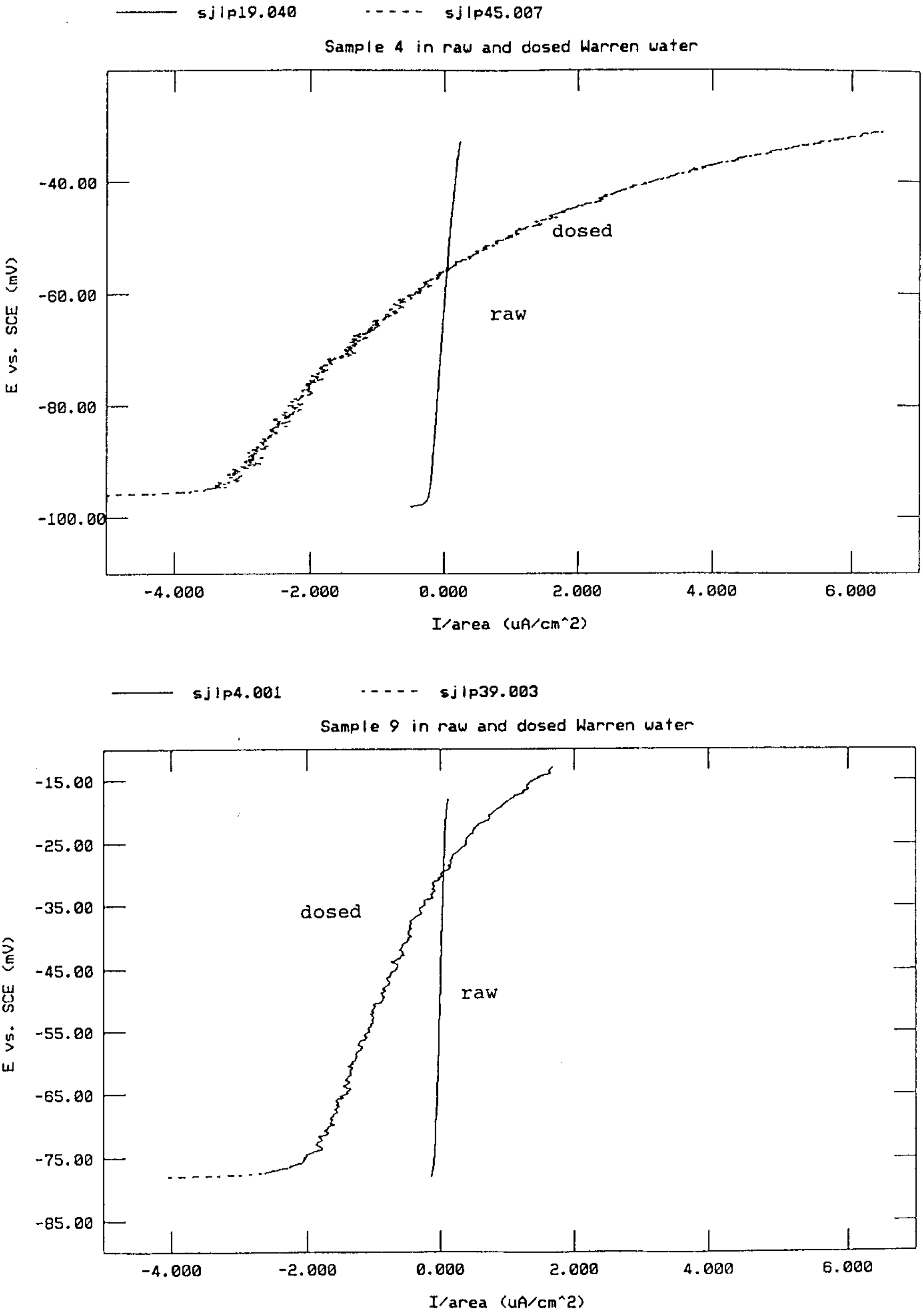


Figure 2. Current-potential curves in raw and dosed water for (a) Sample 4 and (b) Sample 9

$$\textit{available chlorine} = \textit{titre (ml)} \times \frac{\textit{normality}}{0.00282}$$

where normality is found by the standardisation of FAS solution. Again this procedure is found in Attachment 1.

RESULTS AND DISCUSSION

All current-potential curves for the alloys tested had similar appearances and features; Two representative results are shown in Figures 2a and b. In each Figure the almost vertical curve is for raw water and the curve at larger currents is for dosed water. The shape of each curve is determined by the mechanisms of both the anodic metal oxidation process and the cathodic oxygen and/or chloramine reduction processes. The corrosion rate is calculated from the slope of the curve at zero current and a parameter derived from the shape of the curve.

Table 2 is a summary of the corrosion rates measured in this project. Some values are for preliminary runs which were aborted, usually due to a lack of control of [CLA]. For corrosion rate (i_{corr}) measurements in raw and dosed water, both maximum and mean values are included for each run. There is also a column for the mean chloramine dosing level, and one which contains a normalised corrosion rate obtained by dividing the mean corrosion rate by the mean chloramine concentration.

Corrosion rates in raw Warren water - samples 4,6,9,10, Cu.

The corrosion rates of all samples in raw water approached low values over time. A steady state corrosion rate was established within two to four hours after immersion for samples 4,9 and Cu For sample 6 higher rates were observed for the first 16 hours and for sample 10 the corrosion rate decayed over a period of several days. The high initial rate for sample 6 is close to the maximum possible for diffusion-controlled corrosion by dissolved oxygen and indicates that the surface is initially very active towards corrosion.

The limiting values approached by the alloys are all considered to be low, with sample 9 showing exceptionally good performance. Samples 1,7,and 8 were not tested in raw water.

Corrosion rates in chloraminated Warren water - all samples

The corrosion rates of all samples tested were higher in water which had been dosed with chloramine. The samples will be discussed in the following order:

- Samples 9,10,6,4 which were studied in more detail, being the more important of the materials, presented in order of increasing corrosion rate.
- Samples 7,8,1 and Cu which were studied in less detail.

Sample 9: Leaded high-tensile brass

Sample 9 had the lowest rate in dosed water, consistent with its good performance in raw water. In Runs 1 and 3 the [CLA] control was good and the indicated rates fluctuated but relaxed to a low level with Run 3 having a slightly higher mean value than Run 1. Run 2 had few data points and poorer [CLA] control but followed a similar pattern to Run 1. The normalised corrosion rates in column 7 were found by dividing the corrosion current in μAcm^{-2} by the [CLA] in mgl^{-1}, giving units of $\mu Acm^{-2}mg^{-1}l$; **these units will not be quoted in reports of normalised rates in the text.**

Sample 10: Free-cutting brass

In an initial trial (Run 1), the system used for the raw water measurement for Sample 10 was dosed with CLA to about 1 mgl^{-1} after 5 days exposure to raw water. The result was a momentary increase in corrosion rate, and then a decline to about 0.14 μAcm^{-2} when [CLA] had decayed to 0.7 mgl^{-1}. In all other tests CLA dosing was applied from the start.

In a second preliminary measurement, Run 2, the corrosion rate decayed rapidly to a mean value of 0.35 μAcm^{-2} after a maximum of 1.7 μAcm^{-2} while the [CLA] remained greater than 1.3 mgl^{-1}. The steady state mean normalised corrosion rate was 0.26.

The measurements in Run 2 beyond 2000 minutes are difficult to interpret because of the uncertainty in [CLA]. The test solution was adjusted to 1 mgl^{-1} after 5800 minutes whereupon the rate also increased, only to decay as [CLA] also decayed, indicating acceleration of the corrosion process by CLA.

In other tests, better [CLA] control was achieved. In Run 3 the rate decreased gradually over a period of 3 days and then increased to plateau at 1.2 μAcm^{-2}. The normalised value for the minimum i_{corr} prior to 4300 minutes (~3 days) is 0.18, whereas the value after the rate increase is 0.79. Run 4 lasted 1.7 days over which the mean rate was 0.8 μAcm^{-2}.

There is clearly scope for longer investigations of Sample 10 to establish whether this rate increase occurs predictably, and may indicate a change in mechanism, possibly the onset of dezincification which was not observed in micrographs (see later).

Sample 6: Leaded 63/37 arsenical brass

Two quite reproducible runs were recorded for sample 6 in which the corrosion rates decayed to mean values of 1.2 and 1.4 μAcm^{-2} for Runs 1 and 2 respectively, with corresponding normalised rates of 0.75 and 0.7, quite similar to those for Sample 10.

Sample 4: Leaded 70/30 arsenical brass

The first trial run for this sample was subject to large fluctuations in [CLA], however instantaneous measurements taken after replenishment with CLA indicated maximum rates of the order of 2 μAcm^{-2} which converted to normalised rates of 0.8 and 1.0, slightly greater than those for the Samples 6 and 10. In Run 2, over one day, the rates were less than the values measured for undosed water thereby indicating unusually high passivity. A single measurement after dosing to 3.6 mgl^{-1} caused a corrosion rate increase to a normalised value of 0.4.

The measurement taken with effective control of [CLA], Run 3, showed a fairly constant corrosion rate with a normalised value of 1.1 which is significantly higher than the those for the previous three Samples 9, 10 and 6.

Samples 1: Aluminium-silicon bronze
7: Leaded arsenical naval brass
8: Forging brass

These samples were tested sequentially in a common electrolyte in order to obtain tentative data. Sample 7 was tested first and the corrosion rate rose rapidly to a limiting value of 2.3 μAcm^{-2}. Sample 8 was tested next over three days and the corrosion rate decayed over the first 1.5 days to a limiting value of 0.85 μAcm^{-2}. Sample 1 behaved almost identically to

Sample 8. The normalised rates, shown in the Table, were high for samples 1 and 7, and low for sample 8.

Phosphorus-deoxidised copper sample

The corrosion rates measured on PDO-copper in two separate batches of raw water were typical of those measured in this laboratory for copper in a range of waters. Corrosion rates of copper in other waters have been found to be extremely reproducible, so the differences between the rates for the two waters are considered to be significant.

The corrosion rate measurements in the first batch of dosed water were performed immediately after and in the same water was used for Sample 1. The mean corrosion rates were highest recorded for any material tested in this study.

Chloramination of the second batch was complicated by the fact that the rate of decay of [CLA] in the second batch was substantially greater than that in the first batch. As a consequence, it was necessary to increase the bag concentration of CLA by almost 50% in order to maintain the required [CLA]. Dosing was commenced after 22 hours exposure to raw water and once again high corrosion rates were measured. The normalised corrosion rates for PDO copper were higher than any other alloy tested.

In a recent report[5], the corrosion rate of copper in water containing 100 ppm HCO_3^- was 0.1 - 0.2 μAcm^{-2} and increased following chlorination at 0.5 mgl^{-1} to 1.7 - 1.9 μAcm^{-2}. In the same environment, the corrosion rate of ductile cast iron did not appear to be affected by chlorination probably because any small increase was masked by the much higher corrosion rate (35 - 48 μAcm^{-2}) in raw water.

MICROSCOPY

After corrosion of samples 4,6,9 and 10 for 2, 6.6, 4.3 and 4.3 days respectively, their exposed faces were sectioned using a diamond saw and one half section was mounted and polished for microscopic examination across the 11.25 mm diameter. The results are included in the third column from the right in Table 2.

Sample 9 showed about 35 small 1-2 μm thick copper-coloured regions and several larger copper-coloured grains 10-35 μm deep across the diameter indicating that significant dezincification had occurred during exposure to chloramine-treated water.

Sample 6 had two major regions of dezincification 18 and 35 μm across, and 7 mm deep. There were some small dezincified areas close to the wider of the two regions.

By contrast, samples 4 and 10 showed no sign of dezincification whatever.

There is an almost inverse correlation between the extent of dezincification and the measured corrosion rates for these four alloys, indicating that corrosion rate measurement may not be an effective measure of dezincification. This is not surprising since a corrosion rate measurement gives no indication concerning the distribution of corrosion but is simply an average value.

It is noteworthy that the arsenic-containing materials were among those which had the higher corrosion rates, including some dezincification in the case of sample 6, the leaded 63/37 arsenical brass. However, the material which showed most extensive dezincification was sample 9, the arsenic-free leaded high-tensile brass which had the lowest corrosion rate in chloraminated water. A recent paper has reported more rapid dezincification and possibly more rapid cracking of arsenical brass[6] indicating that dezincification of brasses is an extremely complex phenomenon.

CORRELATION WITH PREVIOUS TESTS

It is not possible to compare corrosion rates measured in this study with those derived from the mass change measurements in the previous studies because in that work corrosion products were not removed prior to weighing after exposure. Thus, no account was taken of **soluble** corrosion products which there must have been otherwise a **weight gain** would have been observed. Normal practice would have involved the use of deaerated 50 vol% hydrochloric acid[7]. It may still be possible to determine total weight losses if the samples have been saved and stored in a dry condition.

In the right-hand column of Table 2 there are figures derived from the previous study (Ref 2) in which depths of dezincification were measured. Once again, there is a tendency to an inverse correlation with corrosion rate, with the lowest normalised mean rate coinciding with the deepest dezincification.

CONCLUSIONS

1. All materials studied had low mean corrosion rates in raw Warren water, with the leaded high-tensile brass having a much lower value than the others.

2. The corrosion rates of all materials were increased on exposure to chloraminated water. The differences between materials were not great with a factor of four separating the lowest and the highest. The order of decreasing corrosion rate based on corrosion current density was:

(Highest corrosion rate)
Copper
Leaded 70/30 As-brass, leaded As-naval brass, forging brass.
Leaded 67/37 As-brass, free-cutting brass
Forging brass
Leaded high-tensile brass
(Lowest corrosion rate)

3. No clear correlation appeared to exist between the electrochemical corrosion rate and the extent or depth of dezincification although there was a tendency to an inverse correlation.

4. Further experiments would be necessary to determine more quantitatively the corrosion performances of these materials.

Future work

This small project has probably created as many questions as it has answered. Further investigations of this complex question may be directed towards the following:

1. Perform corrosion product removal on samples from previous investigations and recalculate corrosion rates.
2. Use larger samples and simultaneous replicate measurements
3. Feedback control for chloramine concentration.
4. Variation in [CLA] to check reaction order - this study assumed it was first order.
5. Also perform measurements on surfaces after stabilising in raw water.
6. Investigate the effects of intermittent CLA dosing and peak dosing
7. Perform all measurements in the same solution to ensure identical conditions of exposure.
8. Perform more microscopy
9. Measure corrosion rates over a longer period of time, in situ.
10. Perform scanning reference electrode studies to indicate *in situ* the distribution of areas of corrosion.

Table 2 Corrosion rate measurements in raw and dosed Warren water

Sample /Run	Raw Warren water		Dosed Warren Water				Start date	Extent of DZ	Time H(ours) D(ays)	DZ Depth µm (Ref 2)
	max i_{corr} μAcm^{-2}	mean i_{corr} μAcm^{-2}	max i_{corr} μAcm^{-2}	mean i_{corr} μAcm^{-2}	mean [CLA] mgl^{-1}	$\frac{\text{mean } i_{corr}}{\text{mean [CLA]}}^{ncr}$ $\mu Acm^{-2}mg^{-1}l$				
9 /1	0.067	0.026	1.4	0.4	1.5	0.27	9/10	* 35 areas	4.3D	251
/2			1.0	0.3	1.2	0.25	29/10		1D	
/3			1.0	0.3	1.4	0.29	4/11		2.2D	
10 /1			0.67	14	i.d.	i.d.	5/8		6D	220
/2			1.67	0.35	1.35	0.26	3/9		4D	
/3			2.4	0.25^m	1.4	0.18(0.79)	16/10	* nil	4.3D	
/4	0.85	0.42	0.88	0.8	1.9	0.42	30/9		1.5D	
6 /1	4.5	0.35	1.98	1.2	1.6	0.75	21/10	* two areas	6.6D	21
/2			2.60	1.41	2.0	0.7	24/11		3.2D	
4 /1			2.19	0.45			25/8		4D	25
/2	0.14	0.13	1.28	0.18	>2.2	n.a.	2/9		20H	
/3			1.79	1.60	1.5	1.1	14/10	* nil	2D	
7 /1	n.t.	n.t.	2.32	1.95	1.9	1.03	27/11	n.t.	3D	210
8 /1	n.t.	n.t.	2.78	0.85	1.8	0.47	30/11	n.t.	3D	203
1 /1	n.t.	n.t.	2.28	1.95	1.9	1.03	3/12	n.t.	3.75D	-
Cu $/1^{B1}$	0.35	0.24	4.3	2.7	2.0	1.35	7/12	n.a.	18H	-
Cu $/1^{B2}$	0.73	0.45	3.3	2.1	1.4	1.5	10/12	n.a.	3.2D	-

Notes:

n.t.	Not tested	i.d.	Insufficient data for calculation	B1	Batch 1
n.a.	Not applicable	m	Minimum value	B2	Batch 2
*	Sample sectioned	ncr	Normalised corrosion rate	DZ	Dezincification

REFERENCES

1. Moore, G.C. (1989) Effects of chloramination of potable water on the corrosion resistance of materials, Progress Report No 1., Engineering and Water Supply Department, September 1989.

2. Donaldson, K. (1991), Effects of Chloramination on the corrosion resistance of materials, 22nd February, 1991.

3. Nicholas, DMF, Private communication

4. American Public Health Association (1985) "Standard methods for examination of water and wastewater" 16th Edition American Public Health Association, Washigton, DC.

5. Shahrabi, T., Newman, R.C. and Sieradzki, K. (1993) J. Electrochem. Soc. **140** 348-352.

6. ASTM G1 "Preparing, cleaning and evaluating corrosion test specimens", 1986 Annual Book of ASTM Standards, Vol 03.02, American Society for Testing and Materials.

Attachment 1

METHOD FOR THE FORMATION OF A MONOCHLORAMINE SOLUTION

1. APPLICATION

This method produces a monochloramine solution of approximately 1000 mg/L, with a chlorine to ammonia ratio of 3.4:1 (w/w). The solution is stable for one month if refrigerated.

2. PRINCIPLE

Chlorine when added to ammonia forms chloramines, either monochloramine, dichloramine, trichloramine or a combination. Monochloramine formation is favoured if the pH of the solution is greater than 8.0, with the optimum pH being 8.4.

3. REAGENTS

3.1 General Requirements

Use only reagents of recognised analytical grade, unless otherwise specified, and deionised or distilled water.

3.2 Ammonium Chloride
(NH_4Cl) crystals

3.3 Sodium Hypochlorite
solution, about 10%

Use commercial grade sodium hypochlorite solution (swimming pool chlorine).

3.4 Sodium Hydroxide
solution, about 1N

4. APPARATUS

4.1 pH meter and glass electrode.

5. PROCEDURE

5.1 To 1 litre deionised water add sodium hydroxide solution dropwise until the solution reaches a ph of 8.0.

NOTE: The addition of sodium hypochlorite solution should bring the pH to near the optimum of 8.4

5.2 To the pH corrected water add 0.90 g of ammonium chloride crystals. Stir vigorously.

5.3 While still stirring vigorously, slowly add 10 mL of 10% sodium hypochlorite solution.

5.4 Store the solution at 4°C in a glass container.

METHOD FOR THE TITRIMETRIC DETERMINATION OF CHLORINE IN POTABLE WATERS

1. SCOPE

Free chlorine, chloramine species [monochloramine (NH_2Cl), dichloramine ($NHCl_2$), nitrogen trichloride (NCl_3)] and total chlorine in potable waters can be determined by titration.

2. APPLICATION

The method is applicable to concentrations, in terms of chlorine (Cl_2) from 0.03 to 5 mg/L total chlorine and at higher concentrations by dilution of samples. For interfering substances see Sections 6 and 8.

3. PRINCIPLE

N,N-diethyl-p-phenylene diamine (DPD) is used as an indicator in the titrimetric procedure with ferrous ammonium sulphate (FAS) at a pH 6.2 to 6.5. The colour change is from red to colourless.

The procedure can be simplified to give only free and combined available chlorine or total residual available chlorine.

Free available chlorine reacts instantly with DPD indicator to produce a red colour. Subsequent addition of a small amount of iodide acts catalytically to cause monochloramine to produce colour. Addition of excess iodide causes a rapid response from dichloramine. Nitrogen trichloride is included with dichloramine, however, if iodide is added before DPD, a proportion of the nitrogen trichloride appears with free available chlorine.

4. REAGENTS

4.1 General Requirements

During the analysis use only reagents of recognised analytical grade and deionised or distilled water which meets the specification of 4.2.

4.2 Water Free From Chlorine and Reducing Substances

Deionised or distilled water the quality of which can be checked as follows:

Into two 250 mL conical flasks place, in order,

(a) in the first: 100 mL of the water to be checked and about 1g of potassium iodide (4.12), mix, and after 1 min add 5 mL buffer solution (4.5) and 5 mL of DPD reagent (4.6).

(b) in the second: 100 mL of the water to be checked and one or two drops of sodium hypochlorite (4.9), then, after 2 min, 5 mL of buffer solution (4.5) and 5 mL of DPD reagent (4.6).

No colouration should appear in the first flask whereas a light pink colouration must appear in the second flask.

In the case of a water not having the desired quality, it must be chlorinated and after a suitable contact period, dechlorinated (see 4.3 below).

4.3 Preparation of Chlorine Demand Free Water

To obtain dilution water of the desired quality, deionised or distilled water is first chlorinated to a level of about 10 mg/L and stored in a well-stoppered carboy for at least 16 hours. The water may then be dechlorinated by exposure to UV irradiation, sunlight for several hours or activated carbon. Finally check the quality using the procedure as in 4.2.

4.4 Disodium Ethylene Diamine Tetra Acetic Acid Dihydrate (EDTA) [$C_{10}H_{14}N_2O_8Na_2.H_2O$] solution, 8 g/L

Dissolve 8g of disodium EDTA dihydrate in deionised water and dilute to 1 litre.

4.5 Buffer Solution pH, 6.5

Dissolve 24g anhydrous disodium hydrogen phosphate (Na_2HPO_4) and 46g anhydrous potassium dihydrogen phosphate (KH_2PO_4) in deionised water. Add 100 mL of 8 g/L disodium ethylenediaminetetra acetic acid (disodium EDTA dihydrate $C_{10}H_{14}N_2O_8Na_2.2H_2O$) solution or 0.8g of the solid form. Check pH. Add 0.02g of mercury (II) chloride ($HgCl_2$) to prevent mould growth and interference in the free available chlorine test caused by any trace amounts of iodide in the reagents. Dilute to 1 litre.

4.6 N,N-diethyl-1,4-phenylene diamine sulphate (DPD) [NH_2-C_6H_4-$N(C_2H_5)_2.H_2SO_4$], solution 1.1 g/L

Sparge 1 litre of deionised water with nitrogen for 15-30 minutes. Dissolve 1.1g DPD sulphate in 800 mL of this water, add 25 mL of 8 g/L EDTA solution (or 0.2g of the solid form) and 2 mL concentrated sulphuric acid. Dilute to 1 litre.

Store in a dark bottle protected from heat. Discard if a pink colour develops or after one month, whichever comes first.

Note: The presence of EDTA provides virtually complete suppression of dissolved oxygen errors by prevention of trace metal catalysis.

4.7 Ferrous Ammonium Sulphate (FAS)
$Fe(NH_4)_2(SO_4)_26H_2O$ titrant, 1.106 g/L (0.00282N)
(1 mL is equivalent to 100 ug chlorine)

4.7.1 Preparation of Solution

Dissolve 1.106g ferrous ammonium sulphate in deionised water containing 0.25 mL concentrated sulphuric acid. Dilute to 1 L. If this solution should become turbid, discard at once. Store in a dark bottle. Stable for one month. This solution should be standardised frequently by the method outlined in 4.7.2.

4.7.2 **Standardisation of Solution**

Place, in a 250 mL conical flask, 100 mL of the FAS solution, 2 mL concentrated sulphuric acid, 5 mL concentrated phosphoric acid and 2 mL of a 0.1% barium diphenylamine sulphonate indicator (4.10). Titrate with 0.100 N potassium dichromate (4.11). The end-point is reached when one drop produces an intense purple coloration which persists for 30 seconds. The FAS titrant is equivalent to 100 ug Cl as Cl_2/1 mL.

$$\text{Normality} = \text{Titre (mL)} \times \frac{0.1}{\text{sample aliquot (ml)}}$$

4.8 **Sodium Arsenite**
($NaAsO_2$) solution, 5 g/L

Dissolve 5.0g sodium arsenite in deionised water and dilute to 1 L.

4.9 **Sodium Hypochlorite**
solution, about 0.1 g/L

Prepare by dilution of concentrated sodium hypochlorite solution.

4.10 **Barium Diphenylamine Sulphonate**
solution, 1 g/L

Dissolve 0.1g barium diphenylamine sulphonate [$(C_6H_5-NH-C_6H_4-SO_3)_2Ba$] in 100 mL water.

4.11 **Potassium Dichromate**
standard solution, 0.100 N

Dissolve 4.904g of anhydrous (previously dried at 105-120°C) potassium dichromate ($K_2Cr_2O_7$) in deionised water and make up to 1 L.

4.12 **Potassium Iodide**
(KI) crystals

4.13 **Potassium Iodide**
(KI) solution, 5 g/L

Dissolve 0.5g potassium iodide in deionised water and dilute to 100 mL. Store in brown bottle and discard when solution becomes yellow.

5. PROCEDURE

5.1 Test Portion

A 100 mL sample is normally used. If the concentration of total available chlorine exceeds 5 mg/L, it is necessary to take a smaller volume of test sample diluted with deionised water to 100 mL.

5.2 Determination of Free Available Chlorine and Chloramines

5.2.1 Free Available Chlorine

Place rapidly in a titration flask in this order : 5 mL of buffer solution (4.5), 5 mL of DPD reagent (4.6) and mix. Add 100 mL sample or diluted sample and mix.

Titrate rapidly to a colourless end-point with ferrous ammonium sulphate solution (4.7).

Note the volume reading (V_1).

Note: If the total concentration of available chlorine is likely to exceed 5 mg/L, the sample volume should be correspondingly less than 100 mL. The difference between 100 mL and the volume taken should be made up with chlorine free water.

Note: In the case of an unknown water, possibly very acid or very alkaline or with a high salt concentration, it is advisable to verify that the volume of buffer solution added is sufficient to bring the sample to pH 6.2 to 6.5. If not, use a greater volume of the buffer solution.

Too low a pH in the first step tends to make the monochloramine show in the free chlorine step and the dichloramine in the monochloramine step. Too high a pH causes dissolved oxygen to give a colour.

Note: The order of addition of the solutions is critical.

Note: Higher temperatures increase the tendency for chloramines to react and leads to increased apparent free chlorine results. Complete measurements rapidly, particularly at higher temperatures.

5.2.2 Monochloramine

To the titrated solution of 5.2.1, add 3 drops of potassium iodide solution (4.13) and mix. Continue titration until red colour is again discharged.

Note the volume reading (V_2).

5.2.3 Dichloramine

To the titrated solution of 5.2.2 add about 1g of potassium iodide crystals and mix to dissolve. Allow to stand for 2 minutes and then continue titration until the red colour is again discharged (V_3). In the case of very high dichloramine concentrations, a further 2 minutes standing may be required if colour drift-back indicates slightly incomplete reaction.

5.2.4 Simplified Procedure for Free and Combined Available Chlorine or Total Available Chlorine

Omit stage 5.2.2 above so as to obtain monochloramine and dichloramine together as combined available chlorine. To obtain total available chlorine in one reading, add 1g of potassium iodide at the start with the specified amounts of buffer reagent and DPD indicator and titrate after 2 minutes standing.

5.3 Determination of Nitrogen Trichloride

The absence of colour in 5.2.1 indicates the absence of nitrogen trichloride, since this compound exists in water only in the presence of free chlorine. Use the following procedure if its presence is suspected.

Place 3 drops potassium iodide solution in a titration vessel. Add 100 mL sample and mix. Add contents to a second flask containing 5 mL each of buffer reagent and DPD solution. Titrate rapidly with standard FAS titrant until red colour is discharged (V_4).

6. CORRECTION OF INTERFERENCE DUE TO THE PRESENCE OF OXIDISED MANGANESE

Place test portion in titration vessel, add 1 mL sodium arsenite solution (4.8). Add 5 mL buffer solution and 5 mL DPD reagent. Titrate in the case of oxidised manganese interference immediately to a colourless end-point.

Note the volume (V_5) corresponding to the oxidised manganese.

7. CALCULATION AND EXPRESSION OF RESULTS

Results are expressed in mg/L as chlorine (Cl_2).

7.1 Method of Calculation

For a 100 mL sample, 1.00 mL standard FAS titrant = 1.00 mg/L available residual chlorine.

Determination	NCl_3 Absent	NCl_3 Present
Free Cl_2	V_1	V_1
Monochloramine	V_2-V_1	-
Dichloramine	V_3-V_2	V_3-V_4
NCl_3	-	$2(V_4-V_1)$
Combined Cl_2	V_3-V_1	$V_3+V_4-2V_1$
Total Cl_2	V_3	$V_3+V_4-V_1$

In the unlikely event that monochloramine is present with nitrogen trichloride, it will be included in reading V_4, in which case nitrogen trichloride is obtained from $2(V_4-V_1)$.

Chlorine dioxide if present is included in reading V_1 to the extent of one fifth of its total available chlorine content.

7.2 Repeatability and Reproducibility

7.2.1 Repeatability

The USA-EPA (3) evaluated the titrimetric method with the following results:

For distilled water samples at concentrations of 0.34, 0.65 and 3.45 mg/L total chlorine, the standard deviations were 0.019, 0.003 and 0.003 respectively (RSD of 5.6%, 0.5% and 0.5%). Using drinking water containing 0.98 mg/L total chlorine, the standard deviation was 0.012 (RSD 1.2%)

Results published by the British DOE (4) showed for total chlorine concentrations of 1.0 and 5.0 mg/L, standard deviations of 0.014 and 0.044 respectively (RSD of 1.4% and 0.88%).

7.2.2 Reproducibility

Inter-laboratory comparisons carried out by USA-EPA (5) showed that 6 laboratories obtained means of 0.82 (SD 0.09) and 1.17 (SD 0.08) for free chlorine residuals in distilled water of 0.80 mg/L and 1.10 mg/L respectively.

8. INTERFERENCES

Two types of interference may be noted.

8.1 Interference by Other Chlorine Compounds

A fraction of any chlorine dioxide that might be present is measured as free chlorine. This interference may be corrected by measuring the chlorine dioxide in the water.

8.2 Interference by Compounds Other Than Chlorine Compounds

Oxidation of N,N-diethyl-1,4-phenylene diamine (DPD) is not specifically caused by chlorine compounds. The following substances may be mentioned in particular: bromine, iodine, bromoamines, iodoamines, ozone, hydrogen peroxide, oxidised manganese, nitrite, iron (III) ions and copper ions. In the case of ionic copper (<8 mg/L) and ionic iron (III) (<20 mg/L), the interference is suppressed by the disodium EDTA and a correction for oxidised manganese and chromate is listed in part 6.

9. REFERENCES

(1) Palin A.T. Methods for the determination in water of free and combined available chlorine dioxide and chlorite, bromine, iodine and ozone, using diethyl-p-phenylene diamine. J.Inst.Water Engrs., 21, 1967 : 537.

(2) Draft International Standards Organisation Standard ISO/DIS 7393/1. Determination of free chlorine and total chlorine Part 1 - Titrimetric method using N,N-diethyl-1,4-phenylene diamine.

(3) Bender D.F. Comparison of methods for the determination of total available residual chlorine in various sample matrices. Report No. EPA-600/4-78-019. US Environmental Protection Agency, 1978.

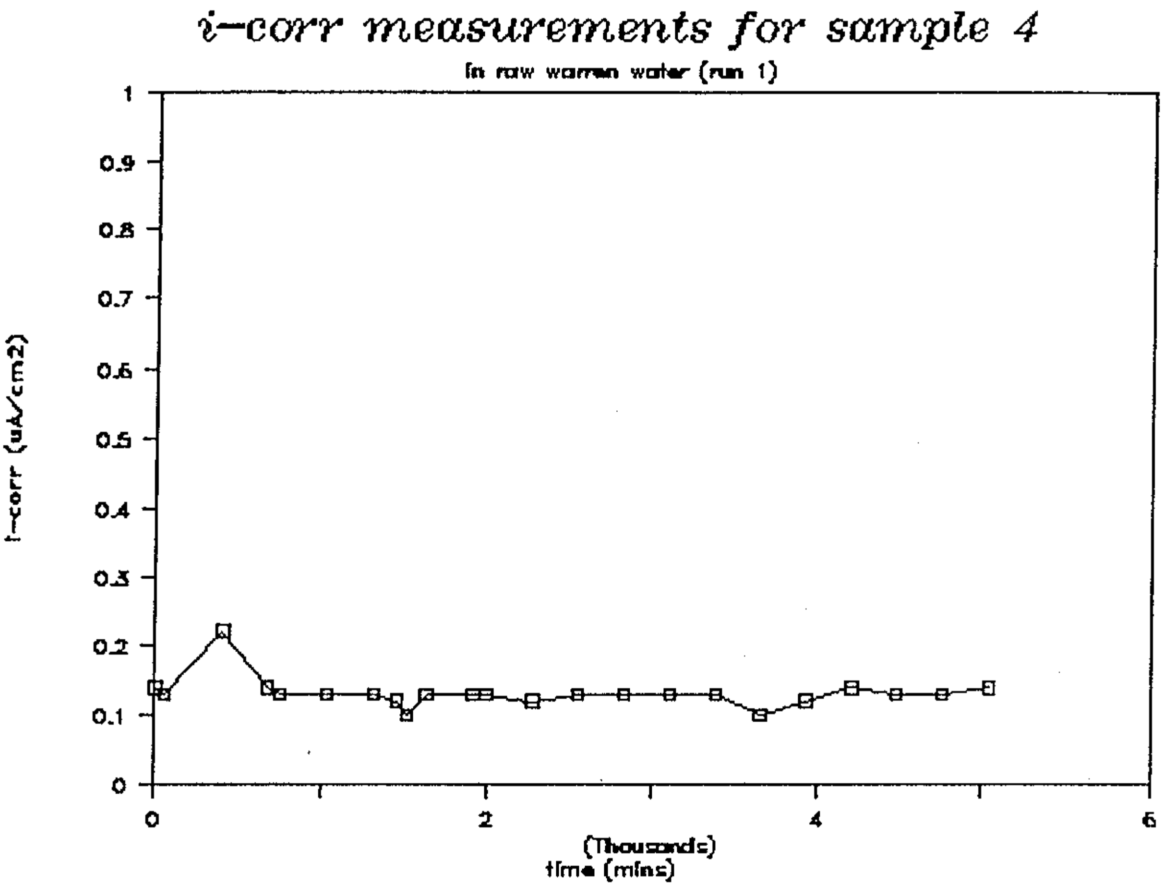
(4) Chemical disinfecting agents in waters and effluents and chlorine demand, methods for the examination of waters and associated materials. London, UK, HMSO, 1980.

(5) Studies WS007 and WS008, Quality Assurance Branch, Environmental Monitoring and Support Laboratory, Office of Research and Development, US Environmental Protection Agency, 1980.

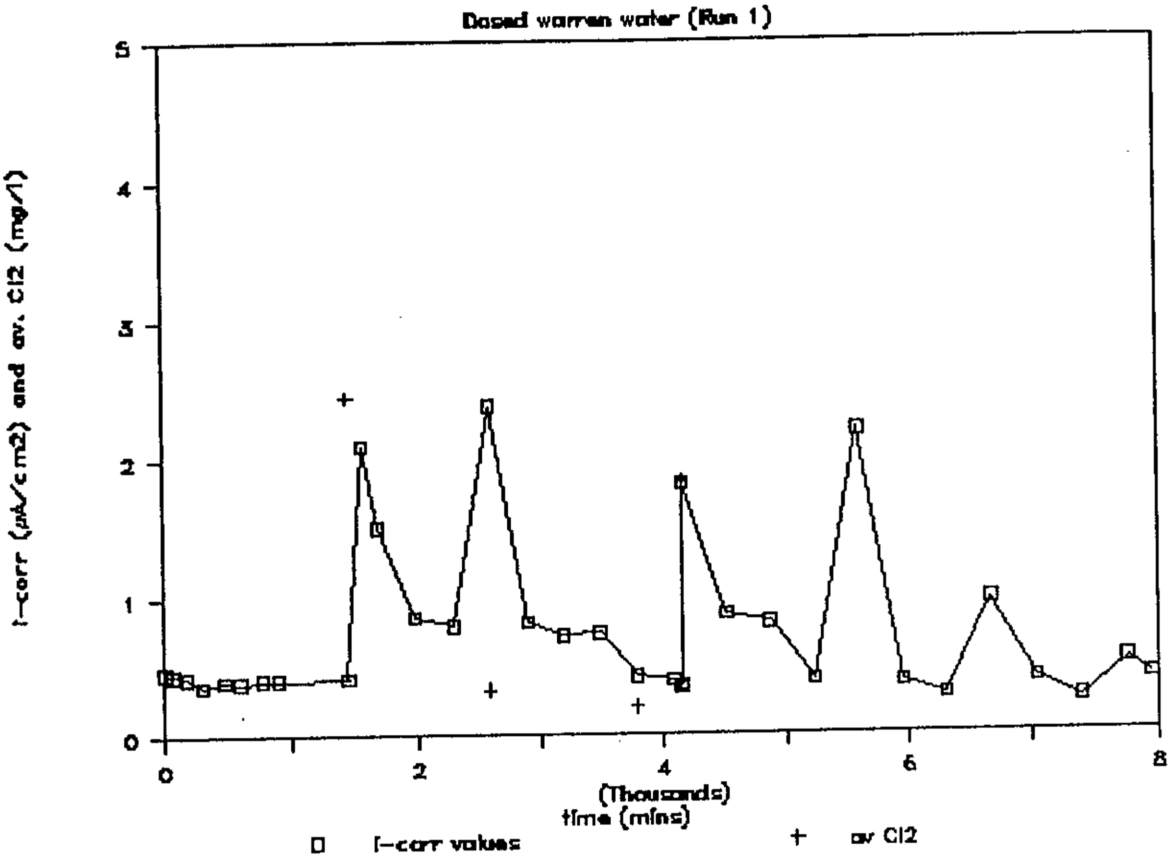
(6) Department of the Environment. Chemical disinfecting agents in water and effluents. HM Stationery Office, London, 1980.

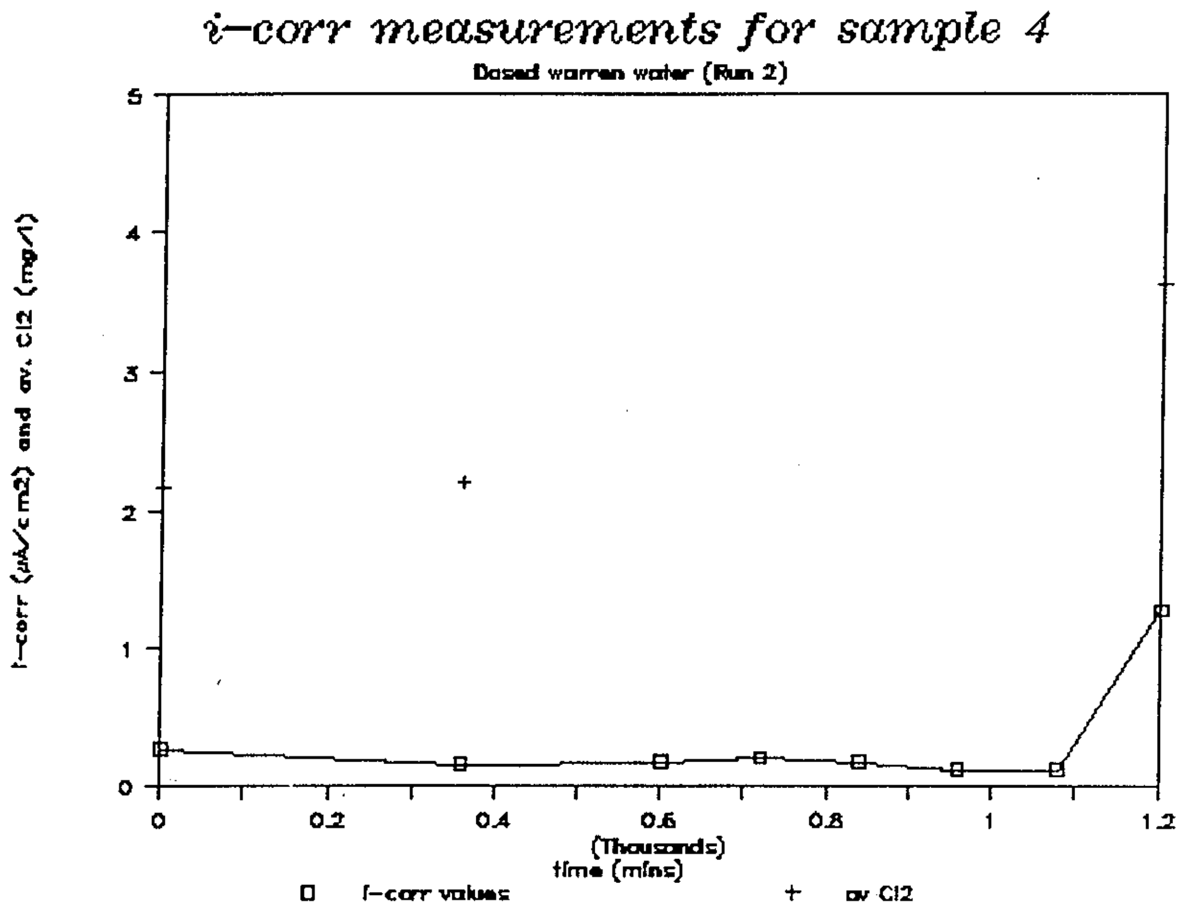
Attachment 2

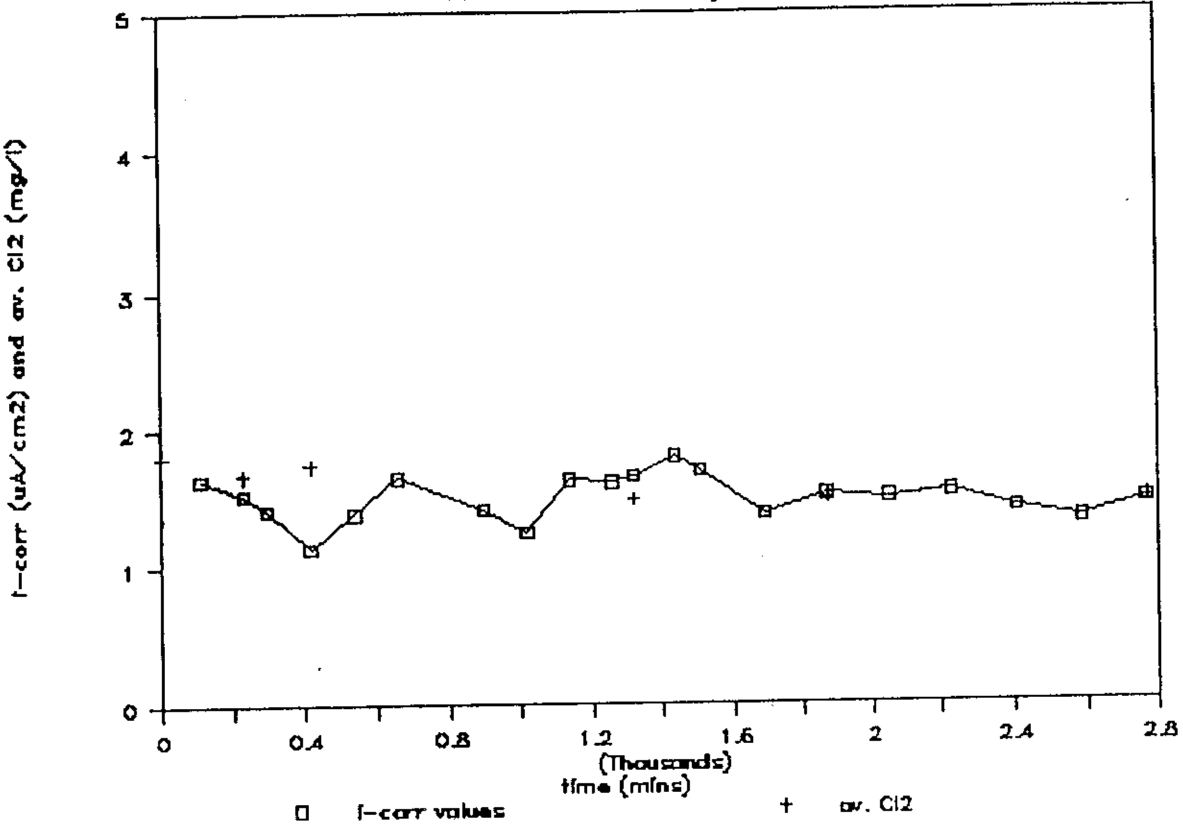
PLOTS OF I_{CORR} AND [CLA] VERSUS EXPOSURE TIME FOR ALL TEST RUNS


i–corr measurements for sample 4
in raw warren water (run 1)
i–corr (uA/cm2)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
2
4
6
(Thousands)
time (mins)

i–corr measurements for sample 4

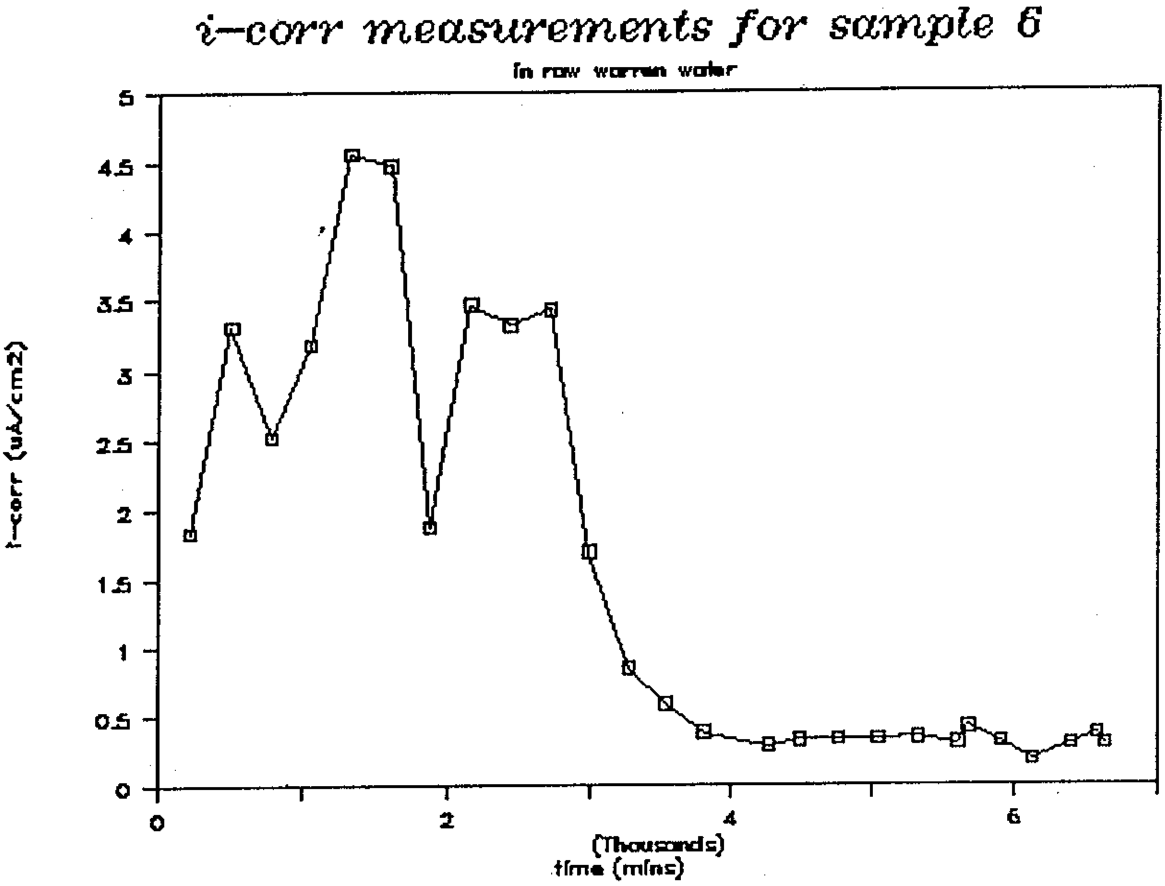



i-corr measurements for sample 4
Dosed warren water (Run 2)
i-corr (µA/c m2) and av. Cl2 (mg/l)
0
1
2
3
4
5
0
0.2
0.4
0.6
0.8
1
1.2
(Thousands)
time (mins)
□ i-corr values
+ av Cl2



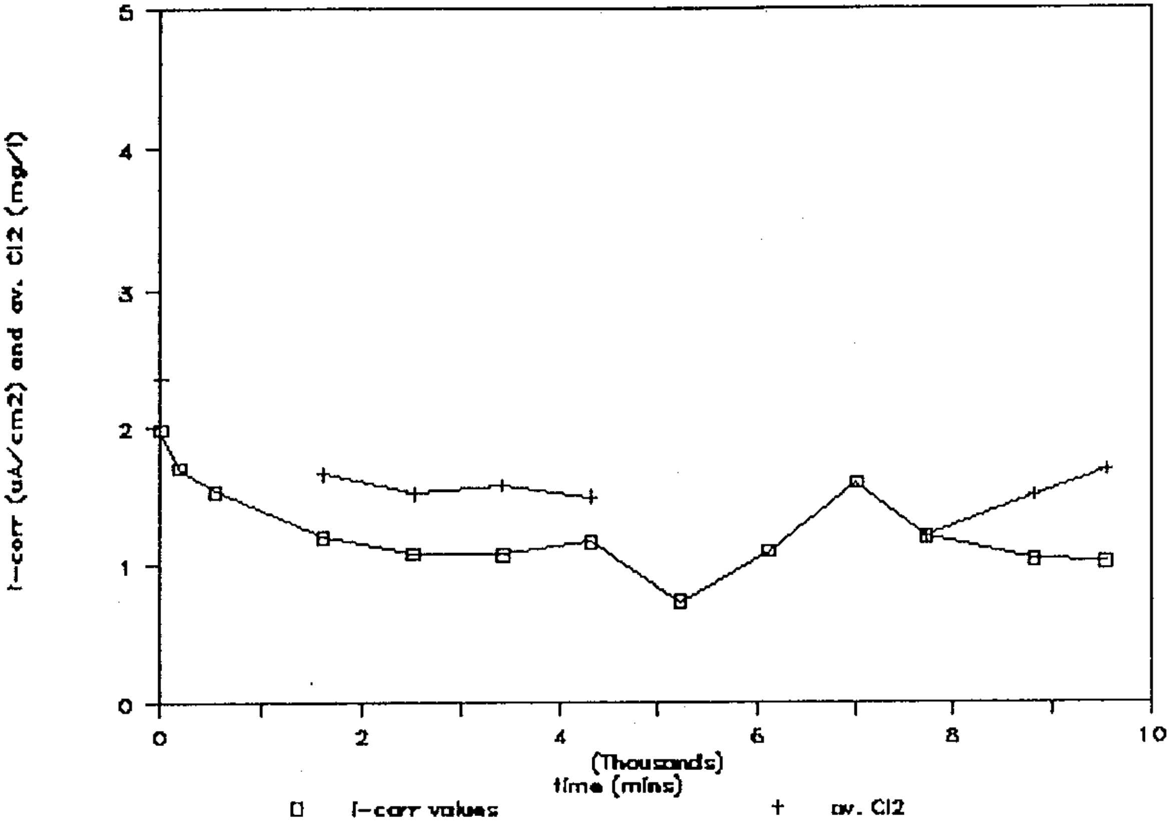
i-corr measurements for sample 4

in dosed warren water (run 3)


i-corr measurements for sample 6
in raw warren water
i-corr (uA/cm2)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
2
4
6
(Thousands)
time (mins)

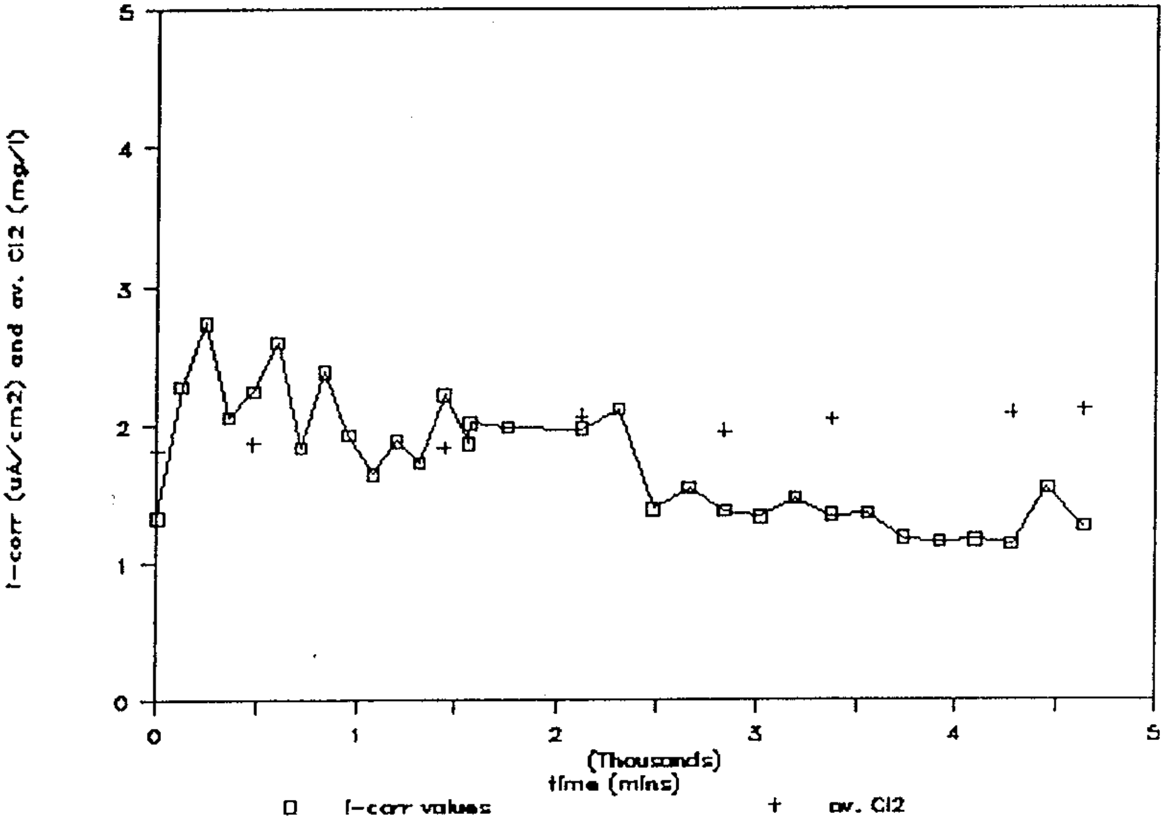
i-corr measurements for sample 6

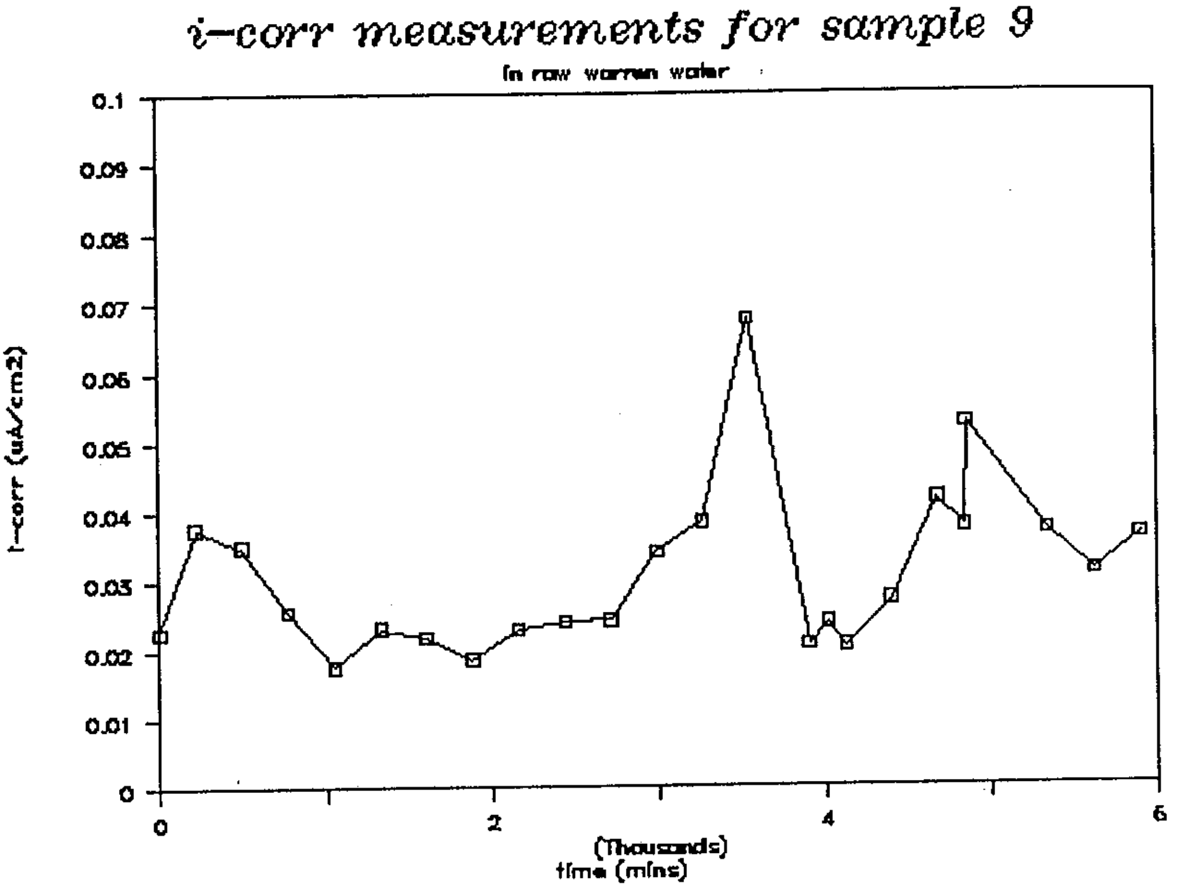
in dosed warren water (run 1)



i-corr measurements for sample 6

In dosed warren water (run 2)



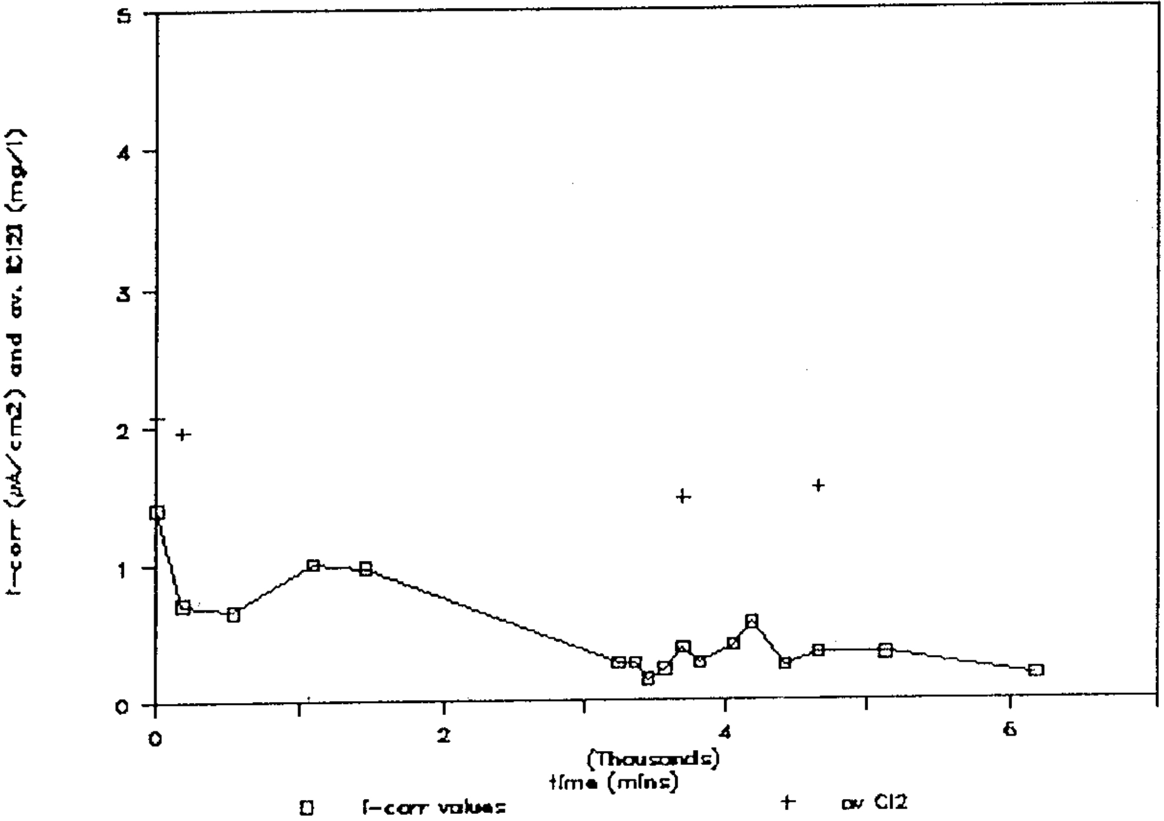


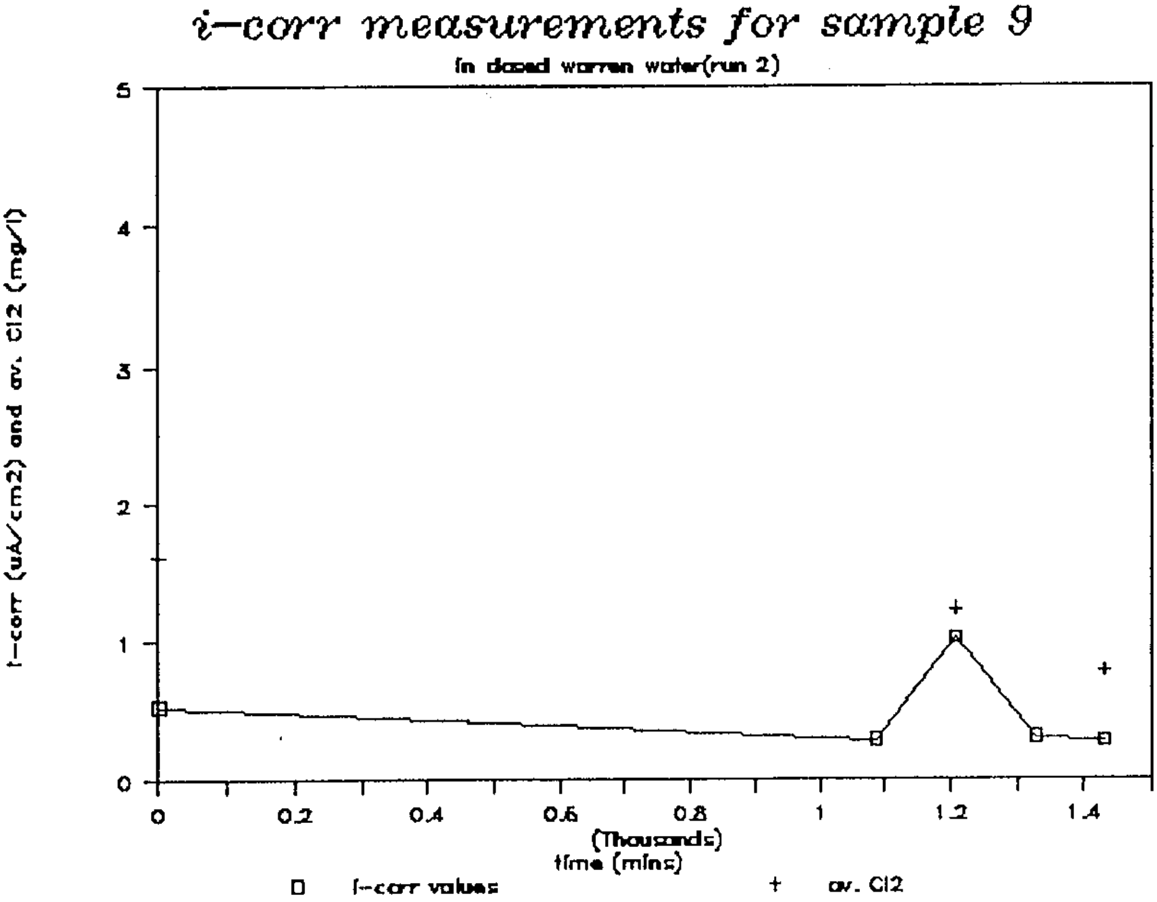
i-corr measurements for sample 9

In raw warren water

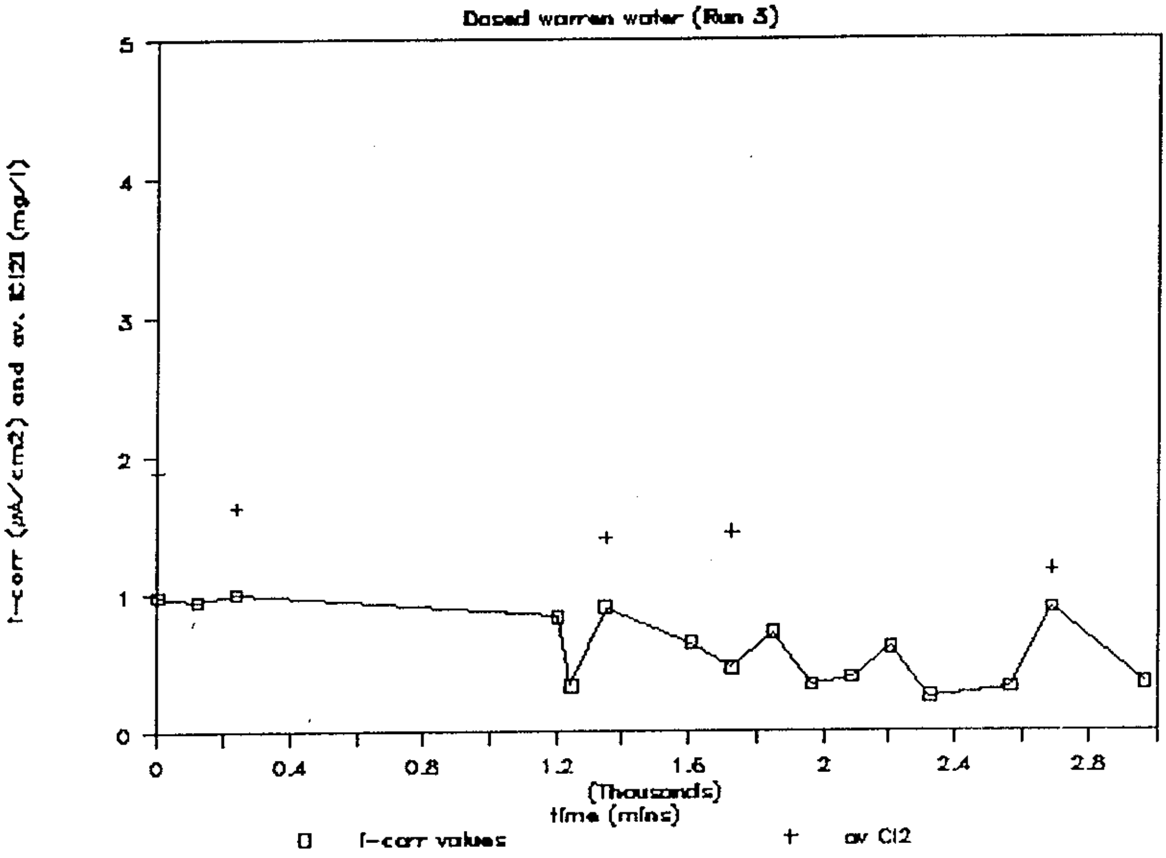
i-corr measurements for sample 9

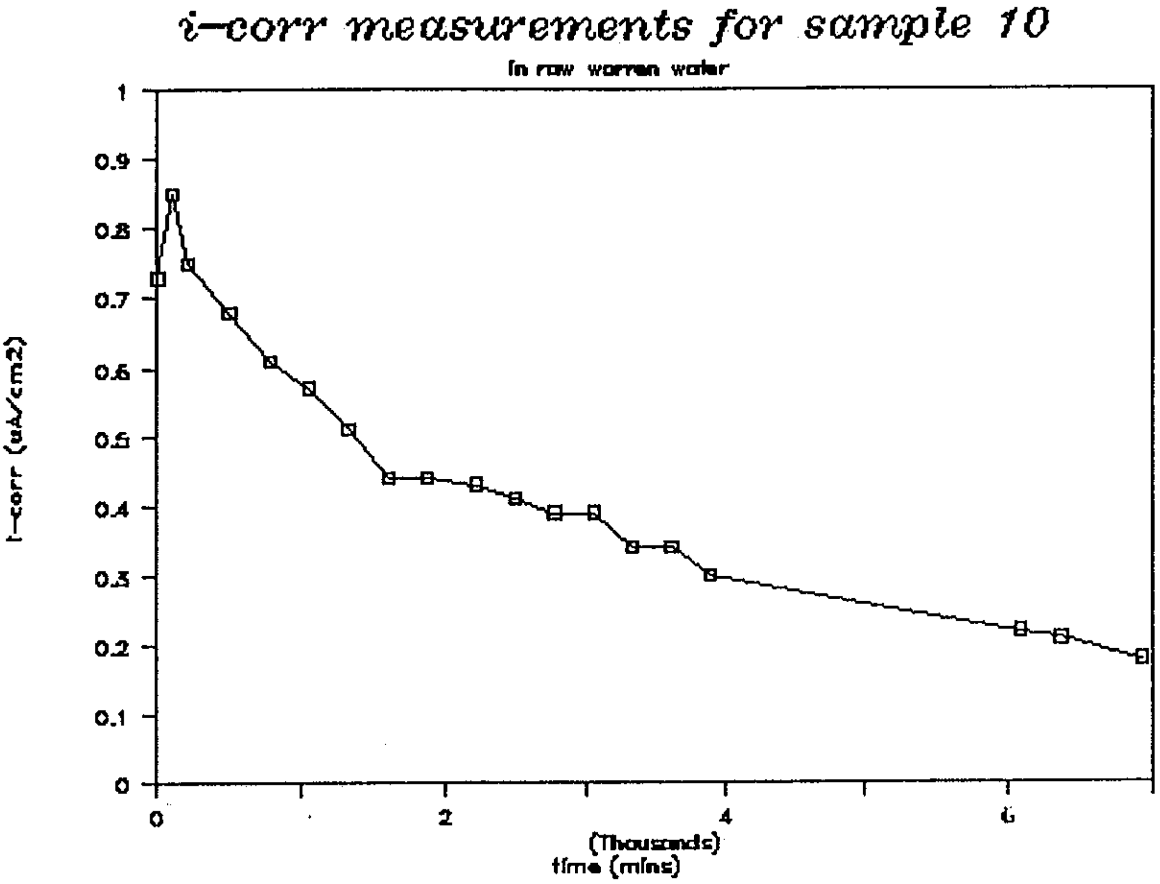
Dosed warren water (Run 1)



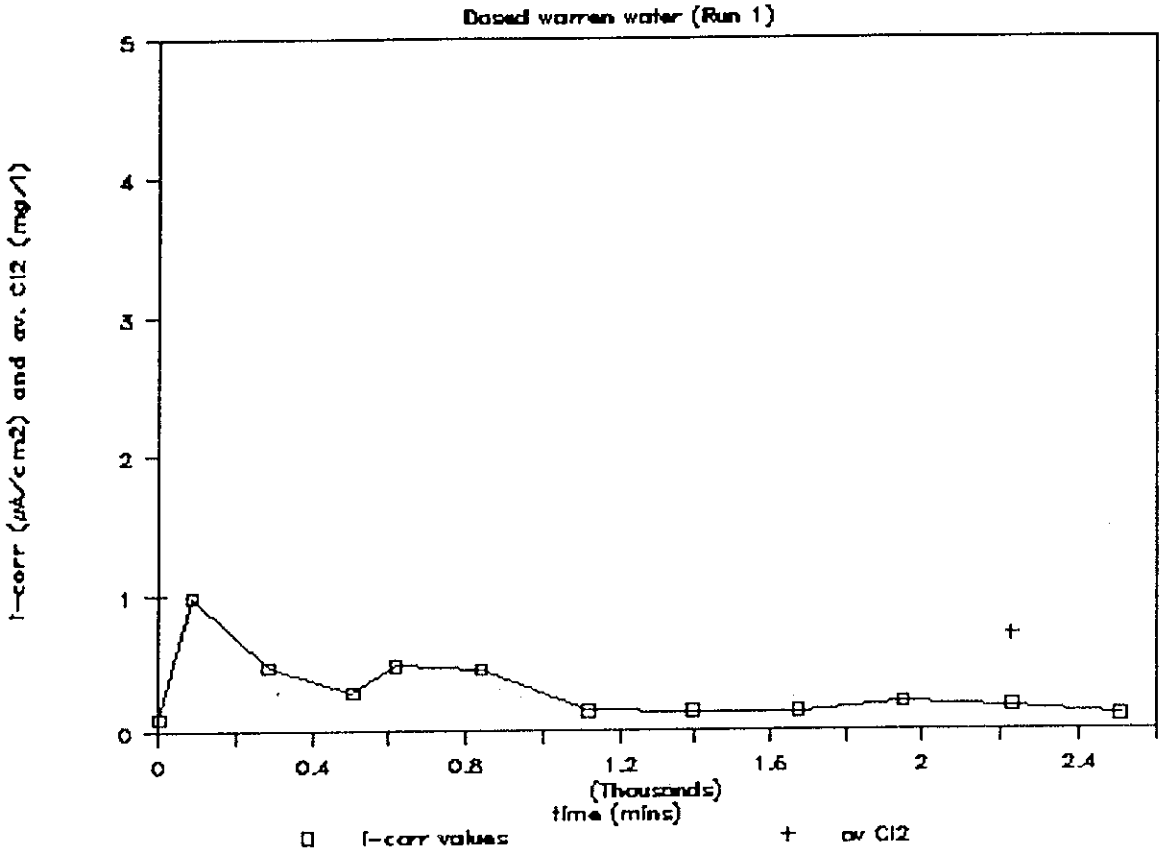

i–corr measurements for sample 9
in dosed warren water(run 2)
i–corr (uA/cm2) and av. Cl2 (mg/l)
0
1
2
3
4
5
0
0.2
0.4
0.6
0.8
1
1.2
1.4
(Thousands)
time (mins)
□ i–corr values
+ av. Cl2

i–corr measurements for sample 9



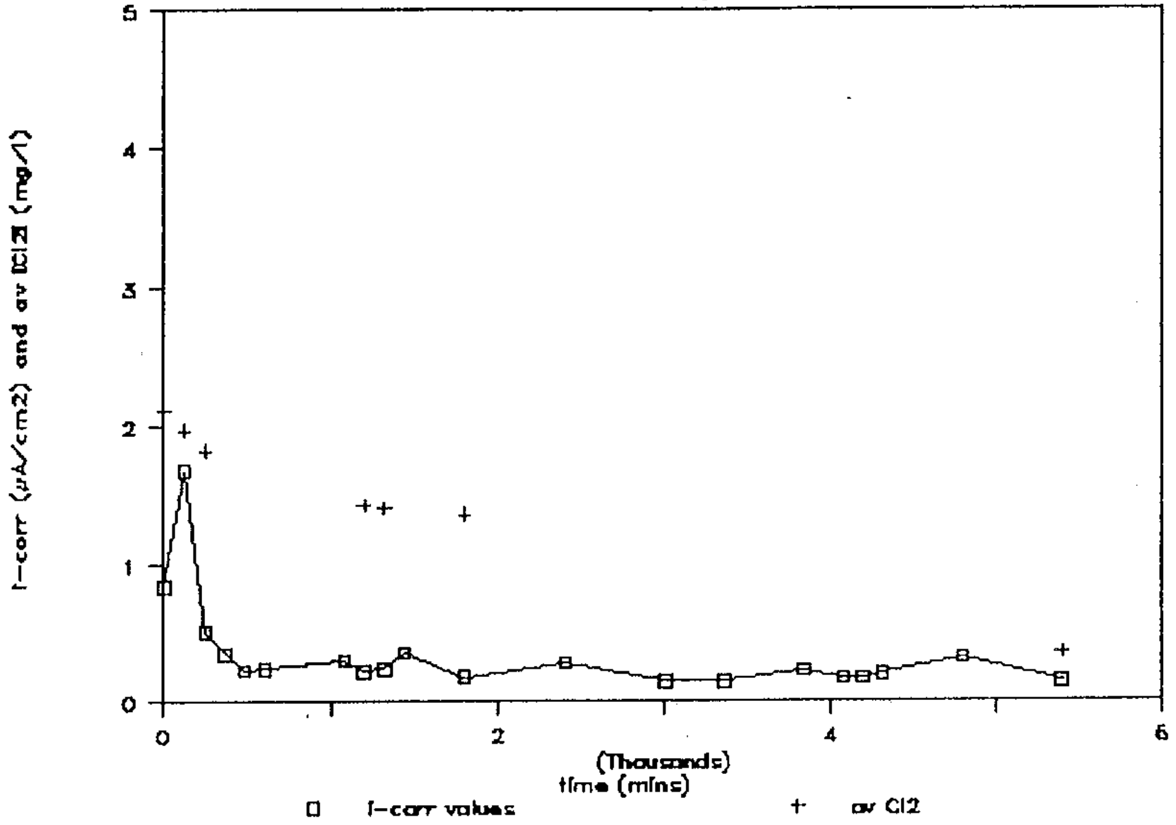

i-corr measurements for sample 10
In raw warren water
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
i-corr (uA/cm2)
0
2
4
6
(Thousands)
time (mins)

i-corr measurements for sample 10



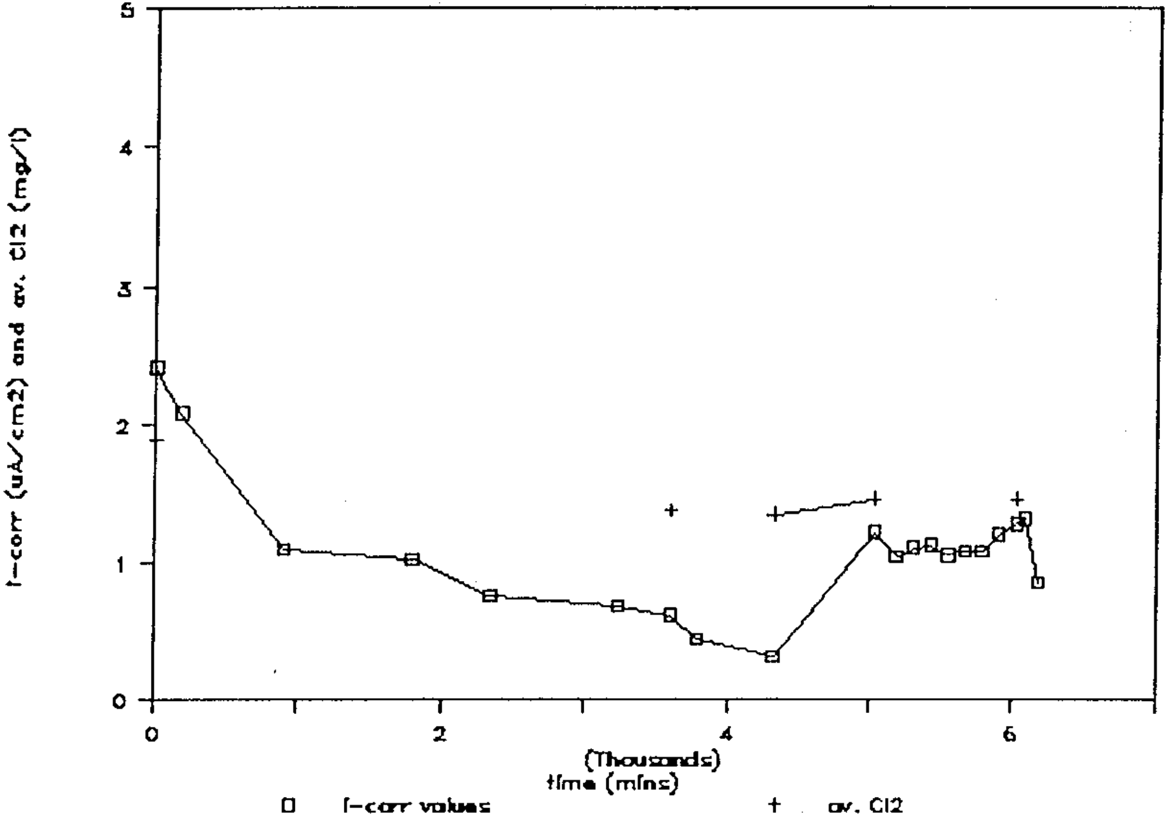
i-corr measurements for sample 10

Dosed warren water (Run 2)

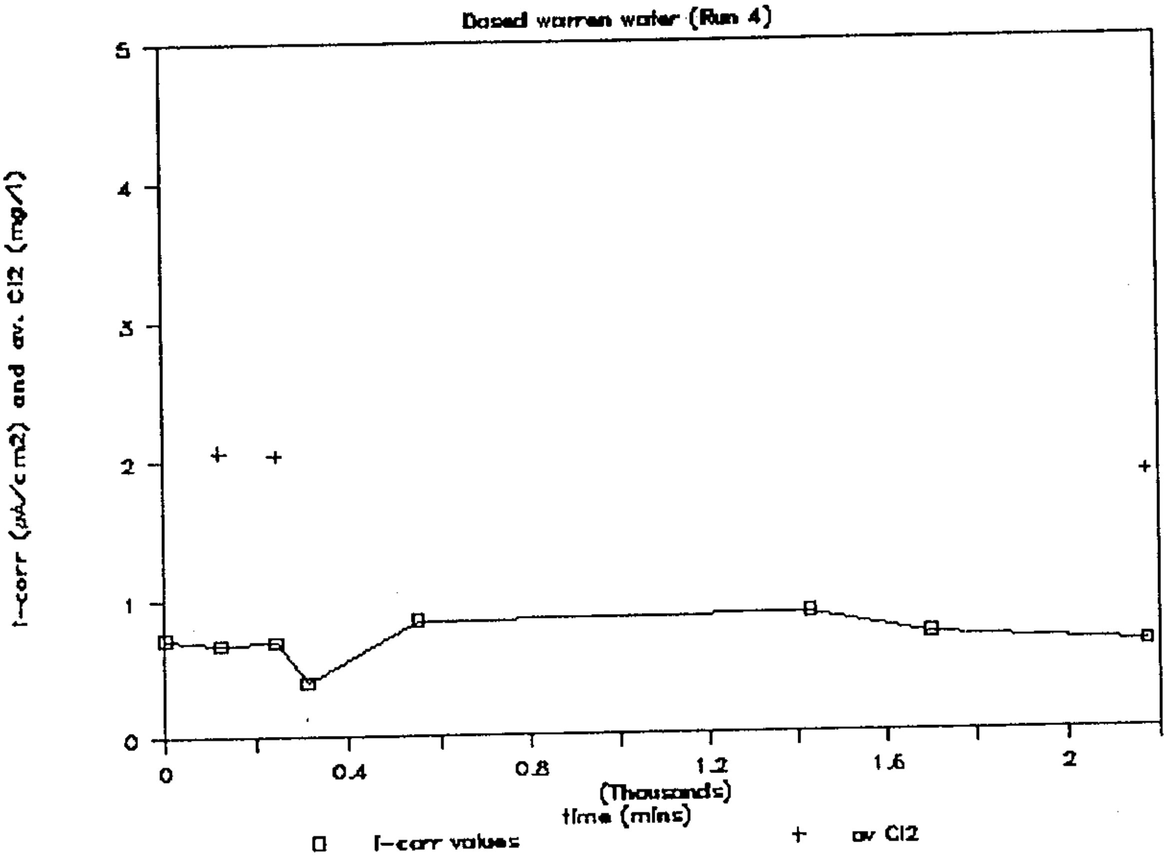


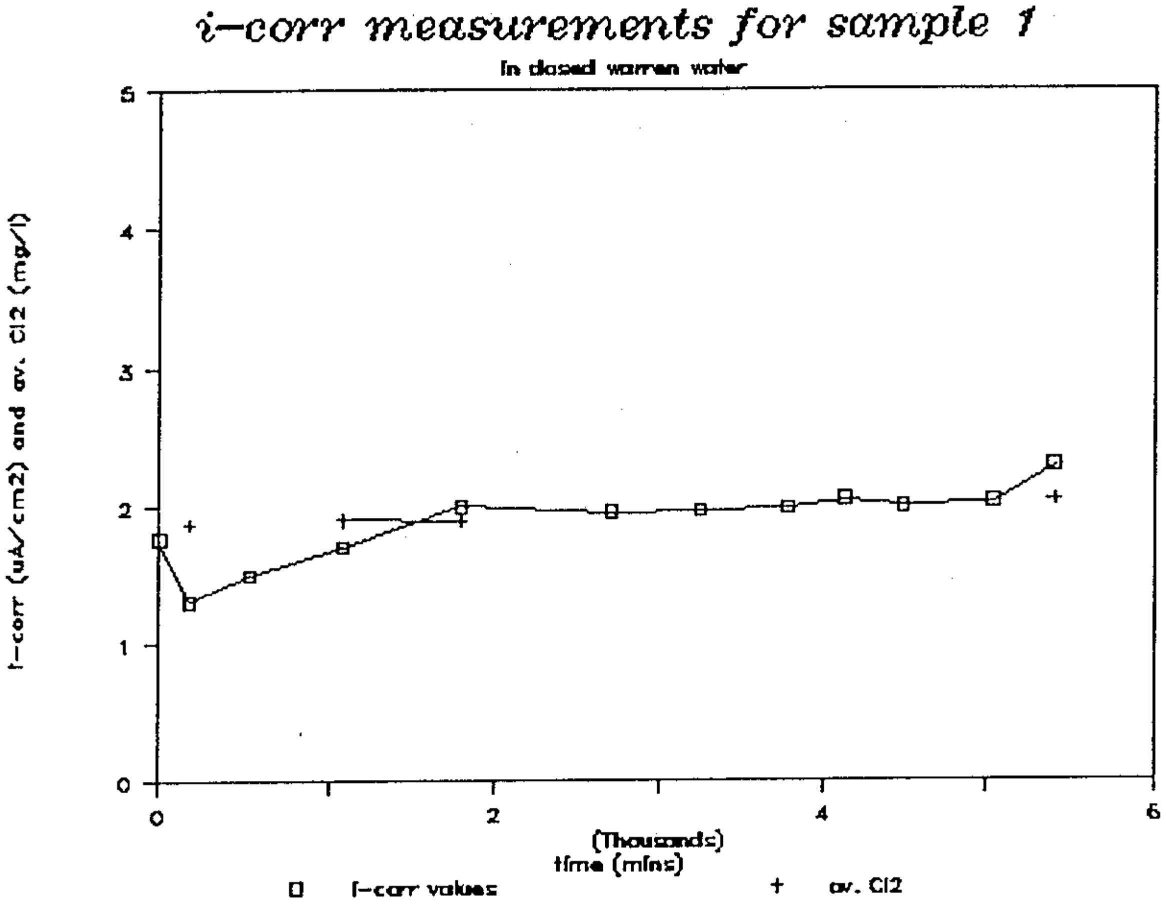
i–corr measurements for sample 10

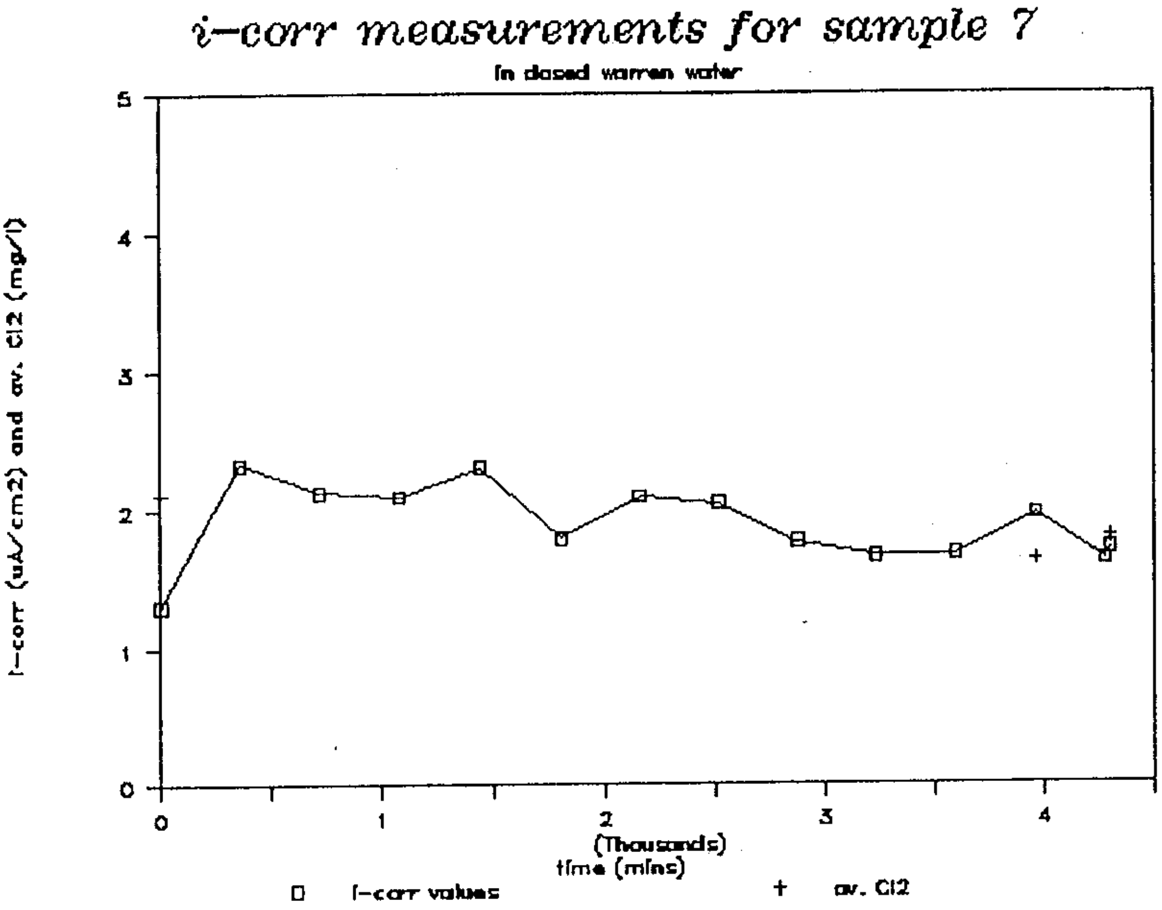
in dosed warren water (run 3)

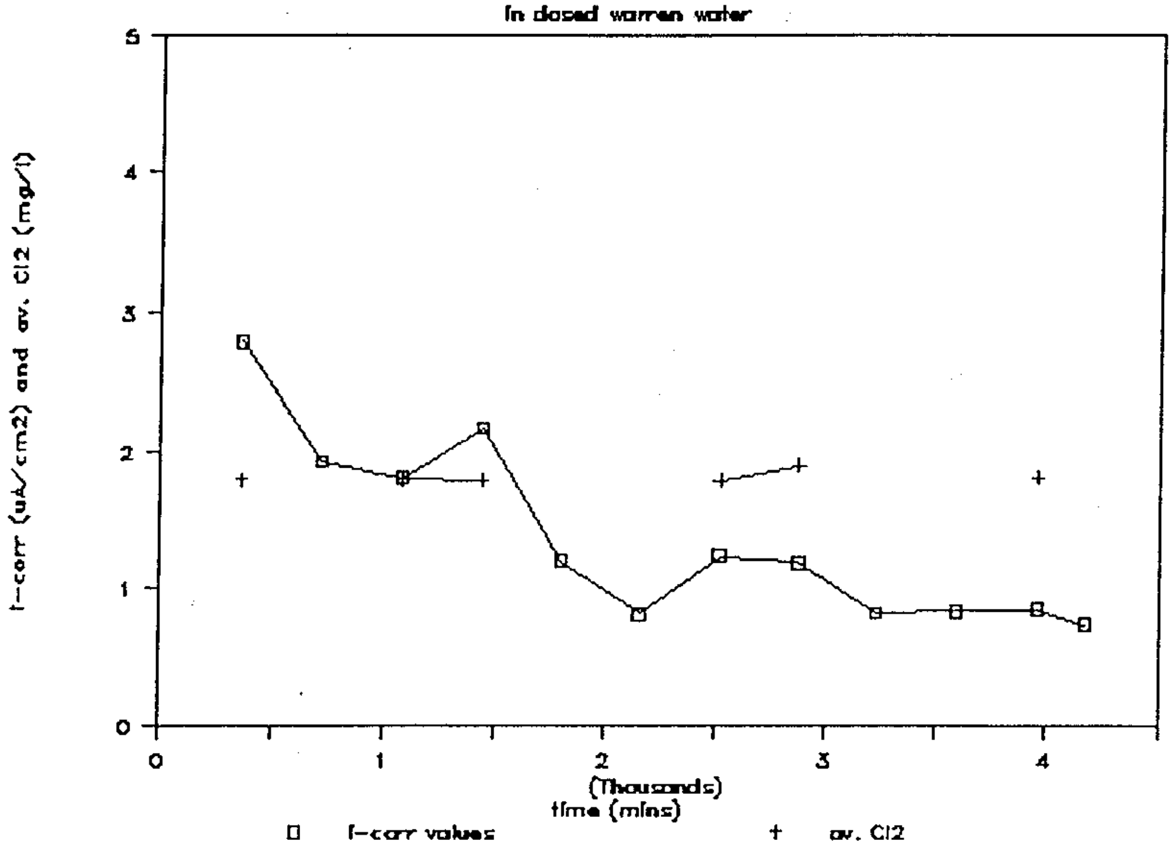


i-corr measurements for sample 10



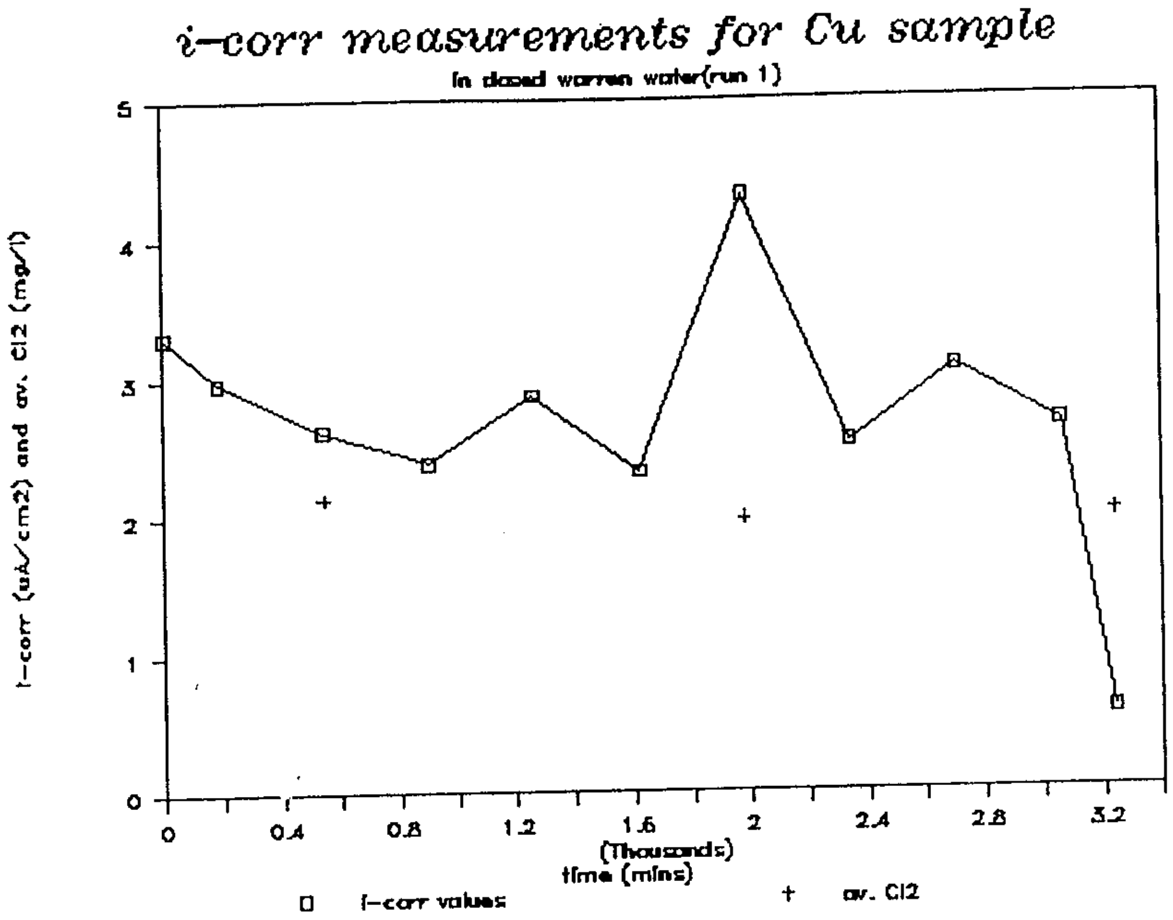

i-corr measurements for sample 1
In dosed warren water
i-corr (uA/cm2) and av. Cl2 (mg/l)
0
1
2
3
4
5
0
2
4
6
(Thousands)
time (mins)
□ i-corr values
+ av. Cl2

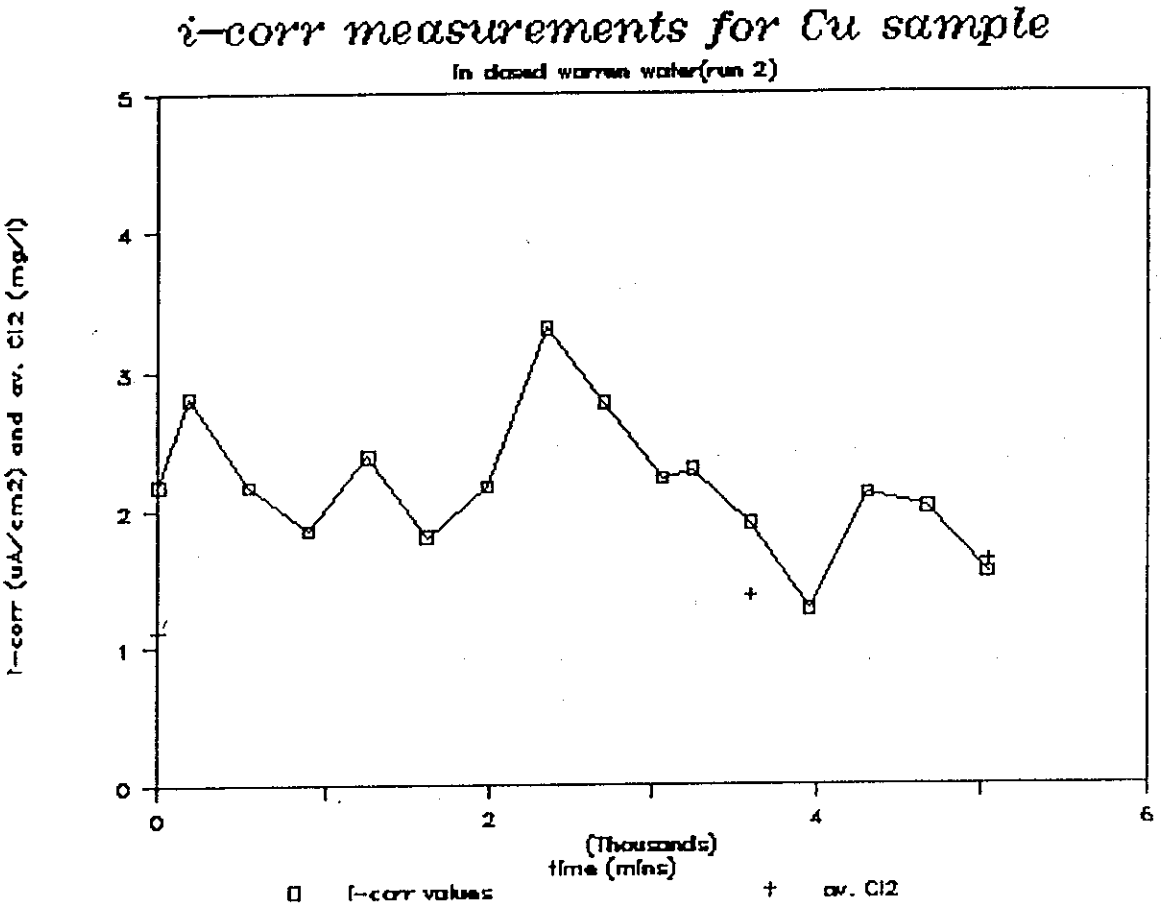

i-corr measurements for sample 7
in dosed warren water
i-corr (uA/cm2) and av. Cl2 (mg/l)
0
1
2
3
4
5
0
1
2
3
4
(Thousands)
time (mins)
□ i-corr values
+ av. Cl2



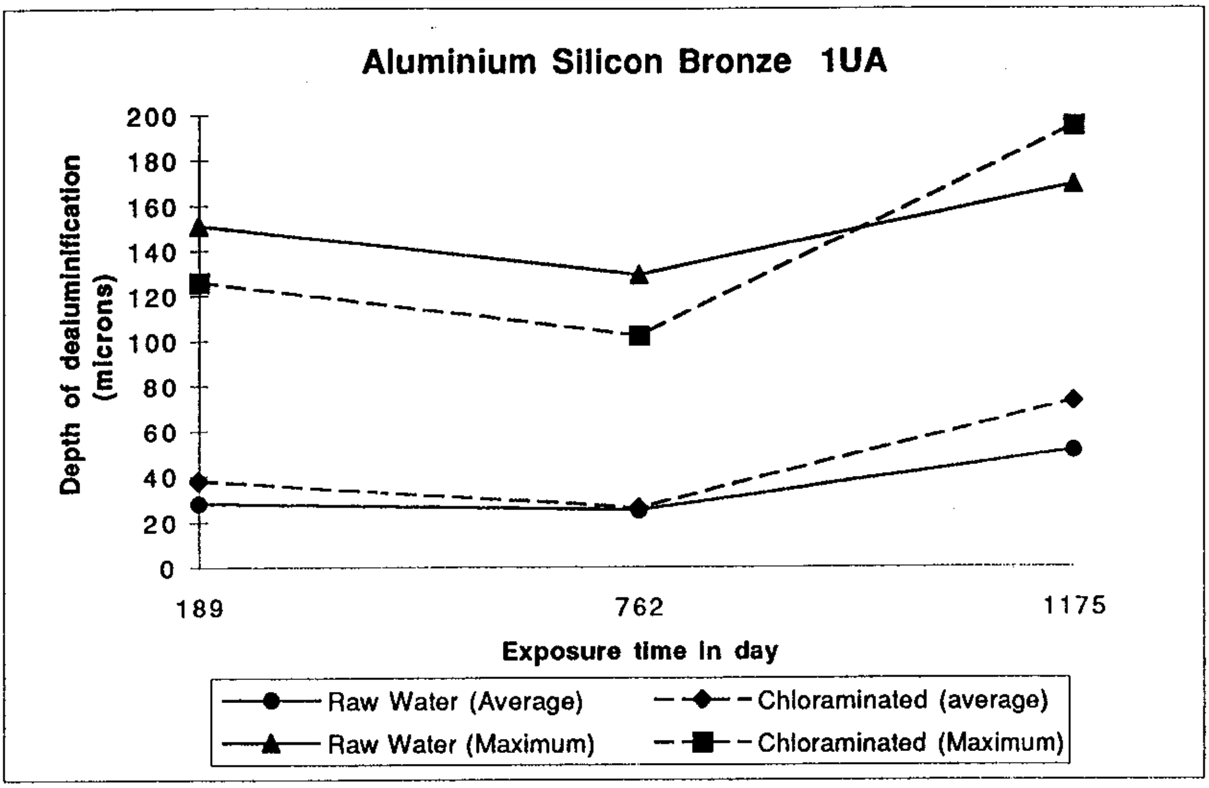
i-corr measurements for sample 8

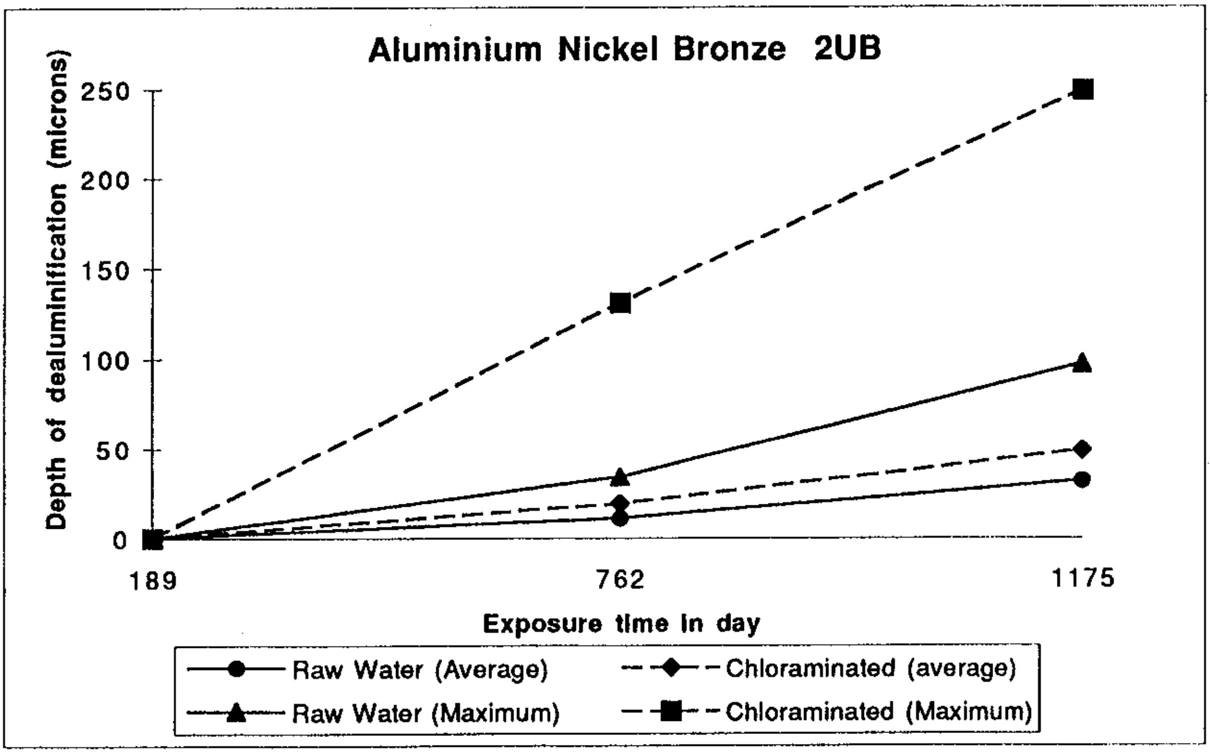
In dosed warren water

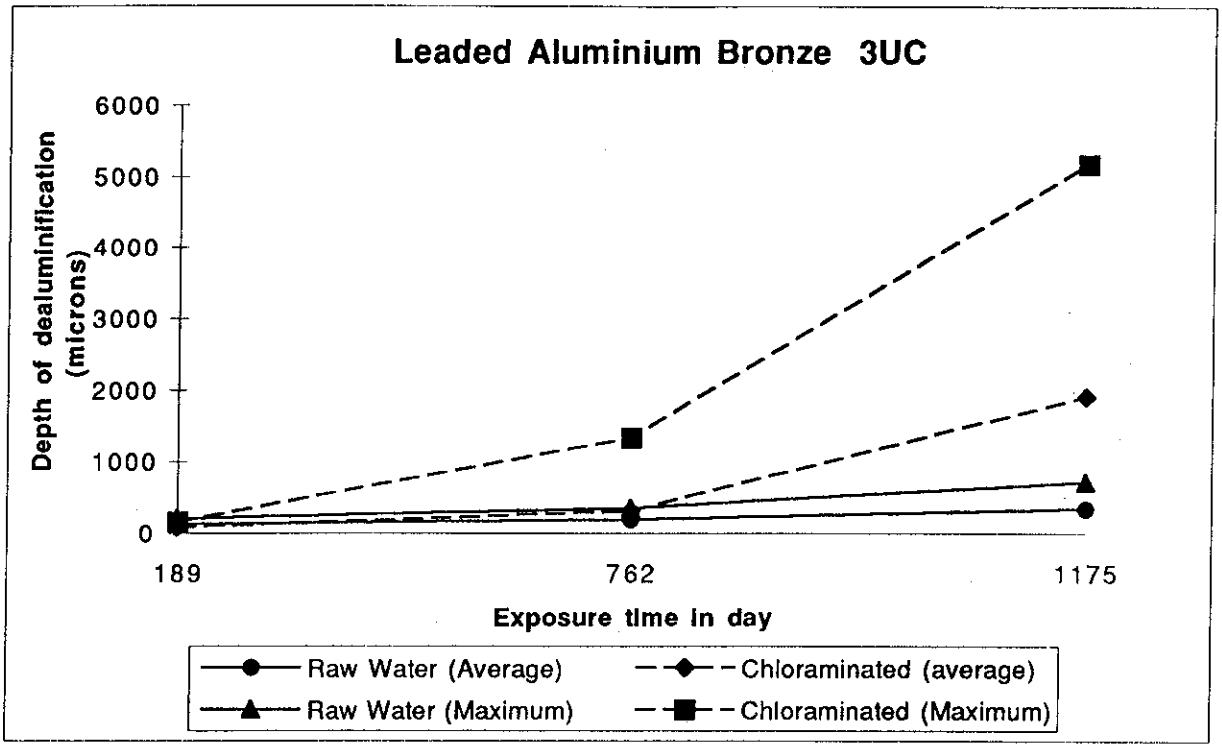

i-corr measurements for Cu sample
In dosed warren water(run 1)
i-corr (uA/cm2) and av. Cl2 (mg/l)
0
1
2
3
4
5
0
0.4
0.8
1.2
1.6
2
2.4
2.8
3.2
(Thousands)
time (mins)
□ i-corr values
+ av. Cl2

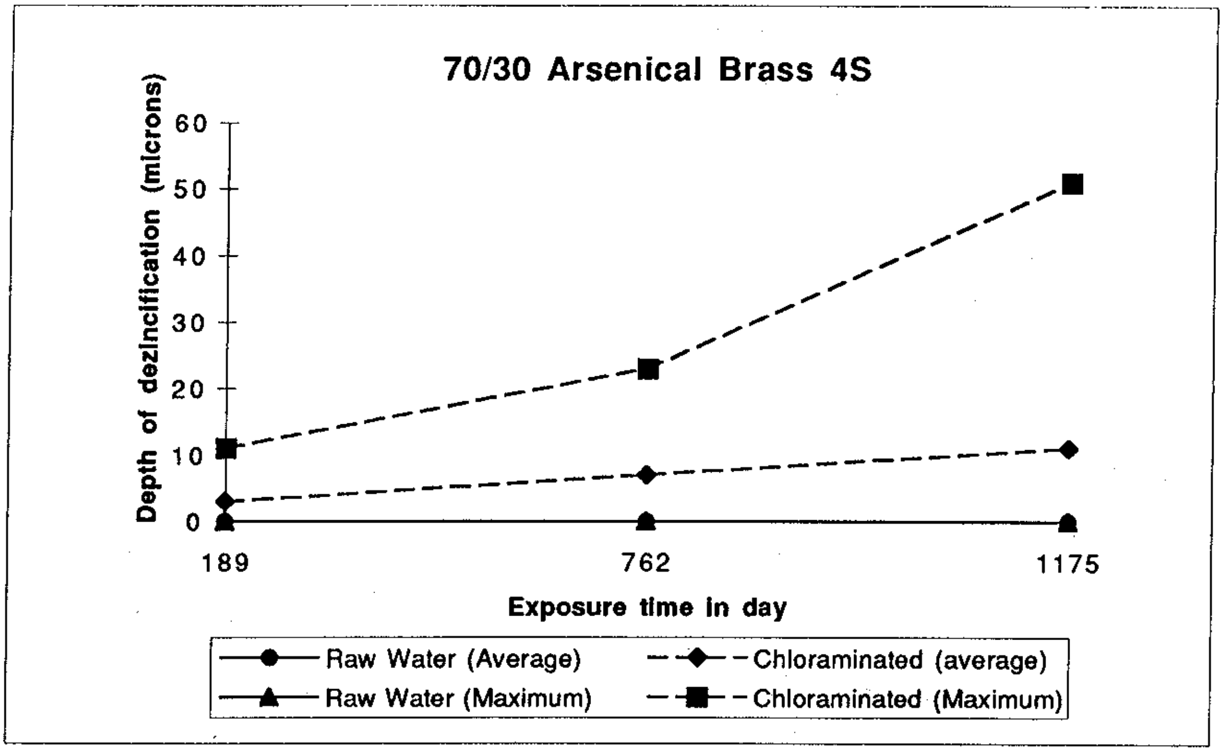

i–corr measurements for Cu sample
In dosed warren water(run 2)
i–corr (uA/cm2) and av. Cl2 (mg/l)
0
1
2
3
4
5
0
2
4
6
(Thousands)
time (mins)
i–corr values
av. Cl2

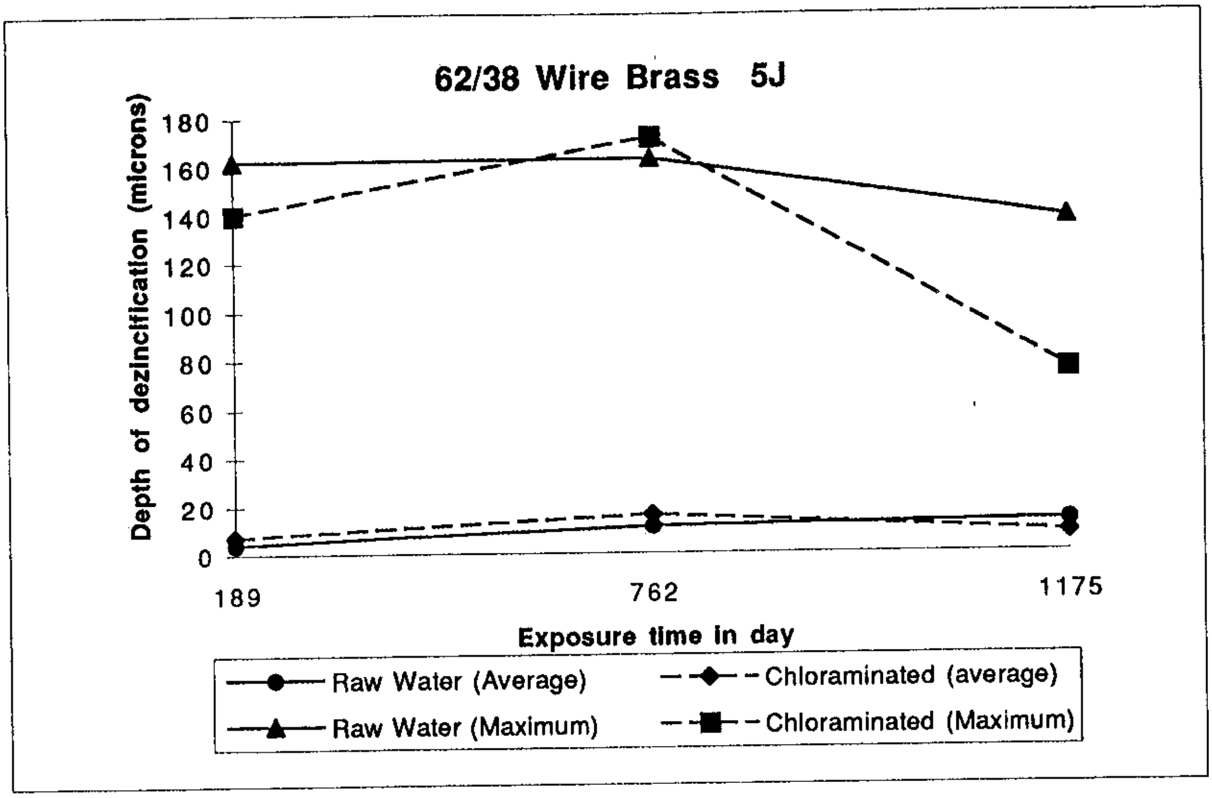
APPENDIX 2

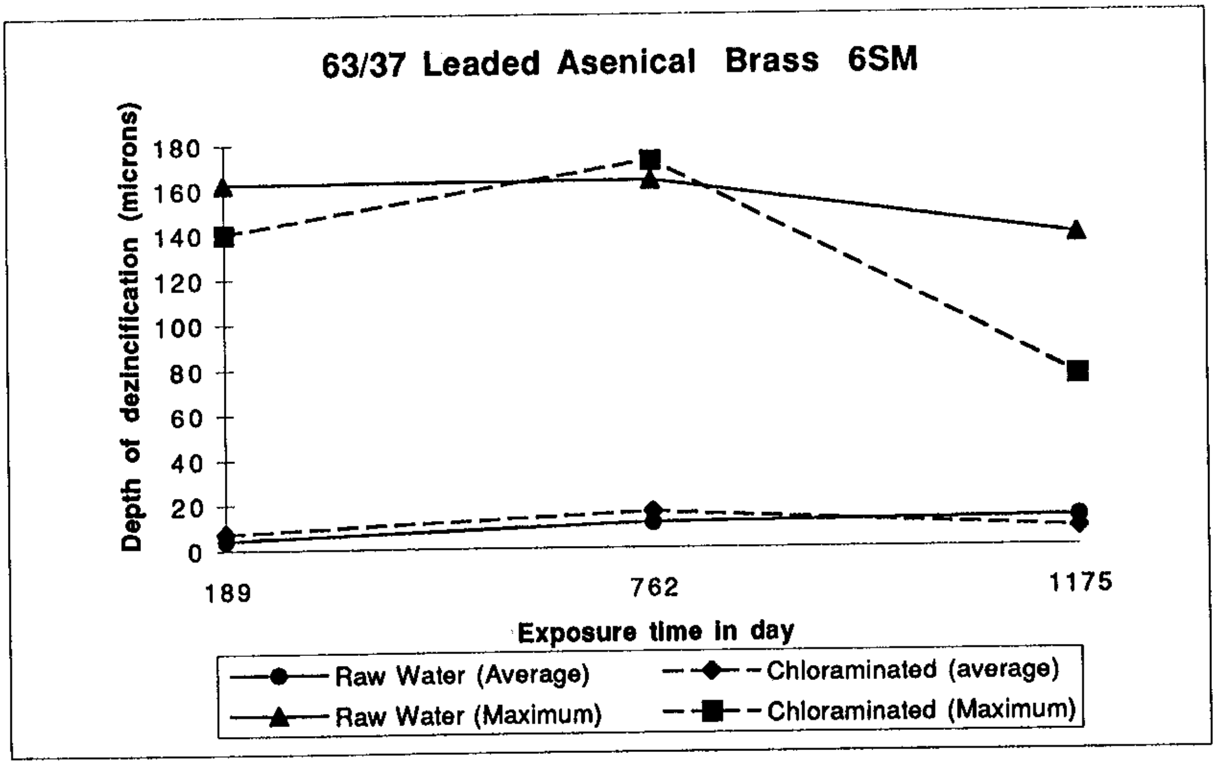

Aluminium Silicon Bronze 1UA
Depth of dealuminification (microns)
200
180
160
140
120
100
80
60
40
20
0
189
762
1175
Exposure time in day
Raw Water (Average)
Raw Water (Maximum)
Chloraminated (average)
Chloraminated (Maximum)

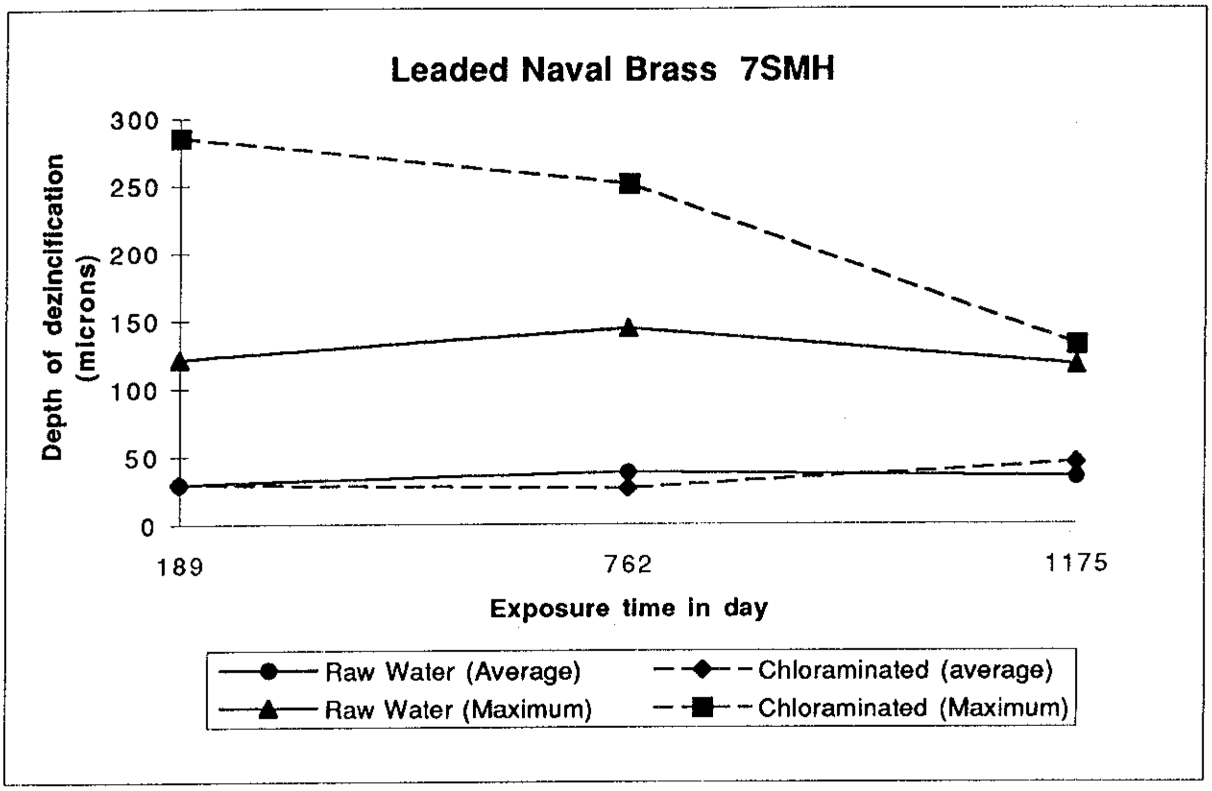

Aluminium Nickel Bronze 2UB
Depth of dealuminification (microns)
250
200
150
100
50
0
189
762
1175
Exposure time in day
Raw Water (Average)
Raw Water (Maximum)
Chloraminated (average)
Chloraminated (Maximum)

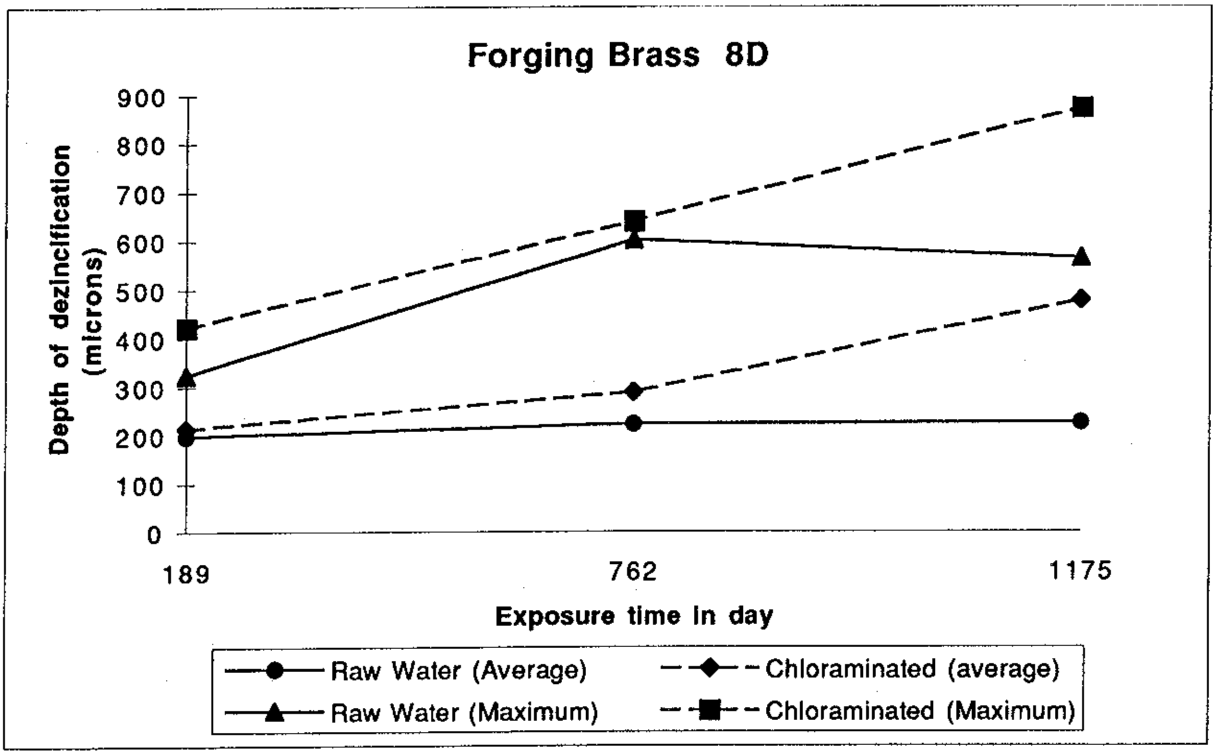

Leaded Aluminium Bronze 3UC
Depth of dealuminification (microns)
6000
5000
4000
3000
2000
1000
0
189
762
1175
Exposure time in day
Raw Water (Average)
Raw Water (Maximum)
Chloraminated (average)
Chloraminated (Maximum)

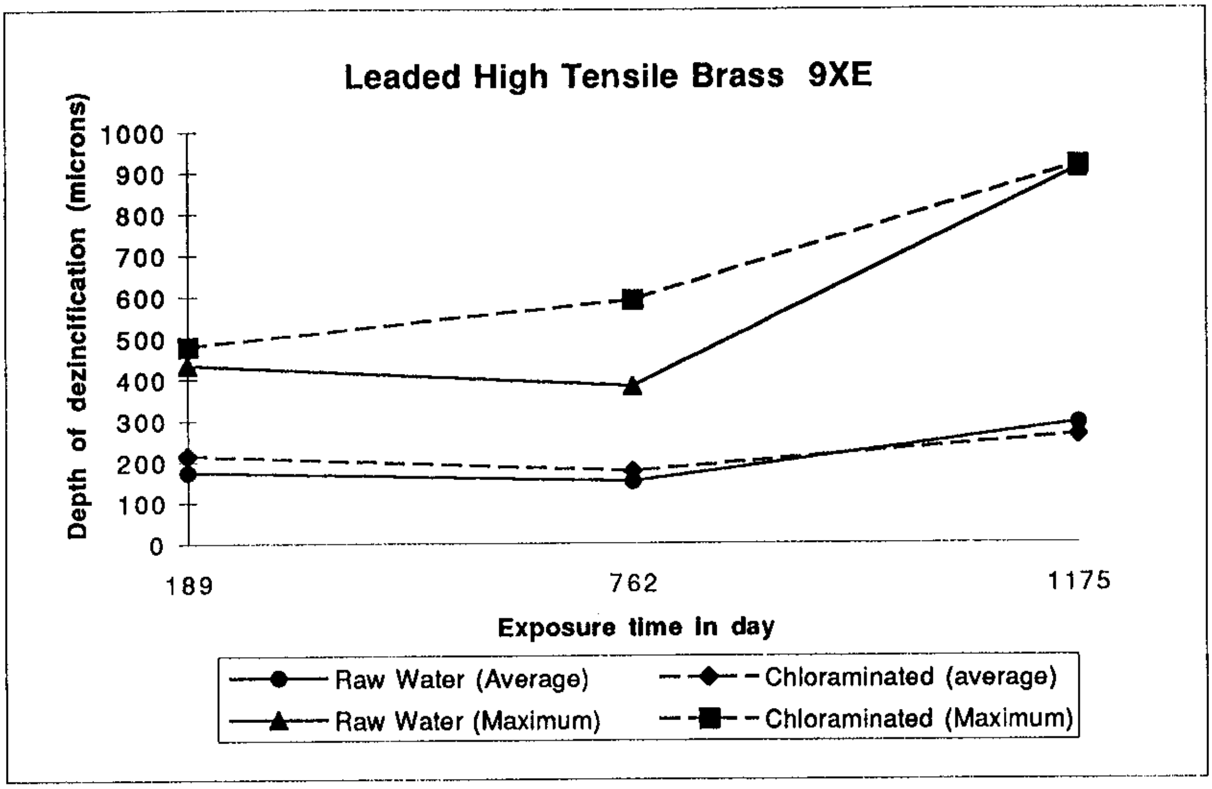

70/30 Arsenical Brass 4S
Depth of dezincification (microns)
60
50
40
30
20
10
0
189
762
1175
Exposure time in day
Raw Water (Average)
Raw Water (Maximum)
Chloraminated (average)
Chloraminated (Maximum)

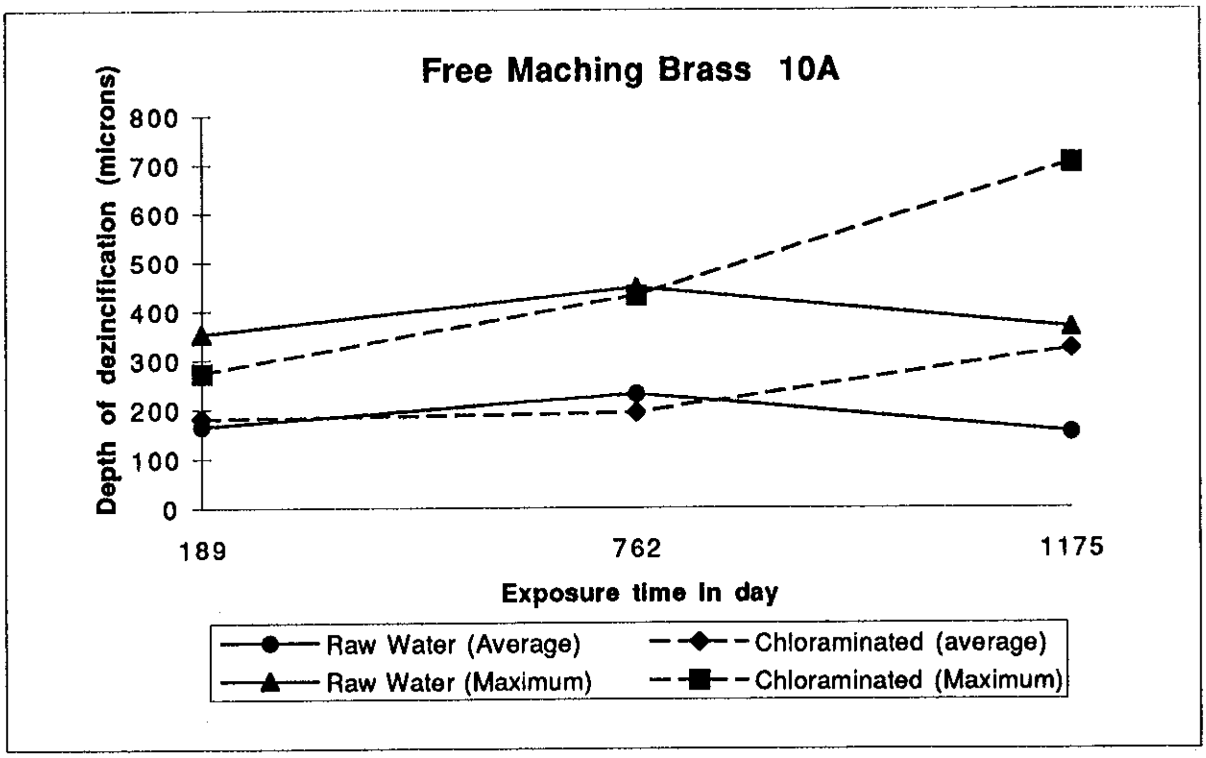

62/38 Wire Brass 5J
Depth of dezincification (microns)
0
20
40
60
80
100
120
140
160
180
189
762
1175
Exposure time in day
Raw Water (Average)
Raw Water (Maximum)
Chloraminated (average)
Chloraminated (Maximum)


63/37 Leaded Asenical Brass 6SM
Depth of dezincification (microns)
0
20
40
60
80
100
120
140
160
180
189
762
1175
Exposure time in day
Raw Water (Average)
Raw Water (Maximum)
Chloraminated (average)
Chloraminated (Maximum)


Leaded Naval Brass 7SMH
Depth of dezincification (microns)
300
250
200
150
100
50
0
189
762
1175
Exposure time in day
Raw Water (Average)
Raw Water (Maximum)
Chloraminated (average)
Chloraminated (Maximum)


Forging Brass 8D
Depth of dezincification (microns)
900
800
700
600
500
400
300
200
100
0
189
762
1175
Exposure time in day
Raw Water (Average)
Raw Water (Maximum)
Chloraminated (average)
Chloraminated (Maximum)


Leaded High Tensile Brass 9XE
Depth of dezincification (microns)
1000
900
800
700
600
500
400
300
200
100
0
189
762
1175
Exposure time in day
Raw Water (Average)
Raw Water (Maximum)
Chloraminated (average)
Chloraminated (Maximum)


Free Maching Brass 10A
Depth of dezincification (microns)
800
700
600
500
400
300
200
100
0
189
762
1175
Exposure time in day
Raw Water (Average)
Raw Water (Maximum)
Chloraminated (average)
Chloraminated (Maximum)

DRAFT 4

Designation: ASTM Dxxxx

Standard Test Method for
Rubber Property — Effect of Aqueous Available Chlorine and Chloramine Solutions

1. Scope

1.1 This test method covers the procedures for evaluating the ability of rubber and rubber-like compositions to withstand the effects of aqueous chlorine and chloramine solutions. It is intended to compare the effects on rubber articles of chlorine compounds present in potable water due to disinfection procedures. It is designed for testing specimens of vulcanized rubber cut from standard sheets (see Practice D3182).

1.2 Test solutions will be designed to include the following chlorine compounds:

Available Chlorine {which includes: Hypochlorous Acid(HOCl) and, Hypochlorite Ion(OCl^-)}
Monochloramine (NH_2Cl)

1.3 This test method includes the following:

Change in Volume (after immersion)	*Section 9*
Change in Hardness (after immersion)	*Section 10*
Change in Visual Appearance and Surface Condition (after immersion)	*Section 11*
Calculation (of test results)	*Section 12*

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*
D471 Test Method for Rubber Property—Effect of Liquids[1]
D1193 Specification for Reagent Water[2]
D2240 Test Method for Rubber Property—Durometer Hardness[1]
D1253 Standard Test Method for Residual Chlorine in Water[2]

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[1] *Annual Book of ASTM Standards, Vol. 09.01*
[2] *Annual Book of ASTM Standards, Vol. 11.01*

Designation: ASTM Dxxxx

Standard Test Method for
Rubber Property — Effect of Aqueous Available Chlorine and Chloramine Solutions

3. Summary of Test Method

3.1 This test method provides procedures for exposing test specimens to aqueous chlorine and chloramine solutions under definite conditions of temperature and time. The resulting deterioration is determined by changes in volume, hardness and specimen surface conditions after immersion in the test liquid.

4. Significance and Use

4.1 Rubber articles may be exposed to chlorine compounds as a result of potable water disinfection. The exposure may be continuous or intermittent and may occur at various temperatures.

4.2 Properties of rubber articles can deteriorate during exposure to these liquids, affecting the performance of the rubber part, which can result in premature failure.

4.3 This test method attempts to simulate service conditions through controlled accelerated testing, but may not give any direct correlation with actual part performance, since service conditions vary too widely. It yields comparative data on which to base judgment as to expected service quality.

4.4 This test method is suitable for specification compliance testing, quality control, referee purposes, and research and development work.

5. Test Conditions

5.1 *Temperature and Immersion Periods*— Unless otherwise specified, between end user and supplier,, the test temperature shall be 70 ± 2°C (158 ± 4°F) and the immersion period shall be as indicated in Table 1.

5.1.1 When the temperature of the testing room is other than the standard 23 ± 2°C (73 ± 4°F) the room temperature and any effect on the temperature of the test solution shall be reported.

5.1.2 To obtain information on the rate of deterioration it is necessary to make determinations after several immersion periods. The tolerance for any immersion period shall be ±15 minutes or ±1% of the immersion period, whichever is greater.

5.1.4 Acceptable immersion periods.

TABLE 1 Test Immersion Periods

Immersion Periods, hours
22
46
70
166
334
502
670
1006
1342
2182
4366

6. Standard Test Liquids

6.1 Reagent Water and one or more test solutions, prepared as described in Tables 3 and 4, may be specified by the end user.

6.1.1 TABLE 2 Reagent Water Test Solution

Solutions to be prepared in amber glass jars of sufficient volume to contain 1900 cm^3 of water.

1. Heat 1900 cm^3 distilled/deionized water (ASTM D1193,Type III or purer) to 70 ± 2°C(158 ± 4°F) in a sealed amber glass jar.
2. Pour finished solution into test vessel.

6.1.2 TABLE 3 Available Chlorine Test Solution

Solution strength based on 50 ppm Chlorine $\approx$ 0.0007M

Solutions to be prepared in amber glass jars of sufficient volume to contain 1900 cm^3 of water.

1. Heat 1900 cm^3 distilled/deionized water (ASTM D1193,Type III or purer) to 70 ± 2°C(158 ± 4°F) in a sealed amber glass jar.
2. Add 0.89 cm^3 Sodium Hypochlorite (NaOCl) Solution with 10% minimum available chlorine.[3]
3. Add 7.00 cm^3 Phosphate Buffer Solution, pH 7.0. [4]
4. Return jar to oven and reheat for 10 ± 1 minutes.
5. Pour finished solution into test vessel.

6.1.3 **TABLE 4 Monochloramine Test Solution**

Solution strength based on 50 ppm Chlorine ≈ 0.0007M
Ammonia based on ≈ 0.0014M

Solutions to be prepared in amber glass jars of sufficient volume to contain 1900 cm^3 of water.

1. Heat 1900 cm^3 distilled/deionized water (ASTM D1193,Type III or purer) to 70 ± 2°C(158 ± 4°F) in a sealed amber glass jar.
2. Add 0.89 cm^3 Sodium Hypochlorite ($NaOCl$) Solution ,10% minimum available chlorine. [3]
3. Add 4.00 cm^3 Phosphate Buffer Solution, pH 7.0. [4]
4. Return jar to oven and reheat for 10 ± 1 minutes.
5. Add 2.68 cm^3 Ammonium Hydroxide (NH_4OH) Solution,1N. [5]
6. Add 8.00 cm^3 Phosphate Buffer Solution, pH 7.0. [4]
7. Return jar to oven and reheat for 10 ± 1 minutes.
8. Pour finished solution into test vessel.

NOTE——— An acceptable alternative method is to use a glass container of sufficient volume to prepare one large batch of test solution. Heat enough water to fill all the necessary test vessels with1900 cm^3 per vessel. Before proceeding further, the water should be stirred and checked with an immersion thermometer to insure it has reached the specified temperature throughout. Solutions shall be prepared as described above, with appropriate adjustments made to quantities of reagents.

NOTE——— Chloramine-T is never an acceptable replacement for any of the reagents specified in this document.

6.2 Fresh test solutions shall be prepared on a daily basis. At no time, throughout the entire immersion period, shall test specimens be allowed to remain in the same solution for more than 48 hours. [6]

6.3 Total chlorine levels, of at least one chlorine and one chloramine solution shall be checked by a method agreeable with ASTM D1253 weekly. Solutions prepared as specified in Tables 3 and 4, should yield 50±5 ppm Total Chlorine.

[3] *Mallinckrodt, Inc. — Catalog no. 7216*

[4] *Hach Company — Catalog no. 27002*

[5] *Mallinckrodt, Inc. — Catalog no. V044*

[6] *If the test period is to be 166 hours or greater, the test solutions may be left unchanged for one day per week. solution concentrations should not be doubled on these occasions.*

7. Preparation

7.1 Except as otherwise specified, specimens shall be prepared in accordance with the requirements of Practices D 3182 and D 3183.[7]

7.2 The dimensions of the standard specimens shall be:

Type	Length, mm(in.)	Width, mm(in.)	Thickness, mm(in.)
1	50.0±0.1(2.000±0.004)	25.0±0.1(1.000±0.04)	1.0±0.1(0.040±0.04)
2	50.0±0.1(2.000±0.004)	25.0±0.1(1.000±0.04)	2.0±0.1(0.040±0.04)
3	50.0±0.1(2.000±0.004)	25.0±0.1(1.000±0.04)	4.0±0.1(0.040±0.04)

7.3 If parts or non-standard specimens are used, procedure shall be adjusted so that a minimum volume of 20 cm^3 of test solution per cm^2 of specimen surface area is maintained. Data obtained on test specimens having different original thickness' are not comparable.

NOTE—— Type 1 specimens are preferred for accelerated testing. Type 2 or Type 3 specimens nay be specified by mutual agreement between producer and purchaser, depending upon anticipated service conditions.

8. Apparatus

8.1 A three-neck distillation flask with a capacity of 2000 cm^3 [8], shall be mounted in a heating mantle[9] of sufficient size and wattage to maintain specified immersion temperature throughout the test solution. The center neck of the flask is to be used for adding and removing test specimens and shall be fitted with a removable glass stopper. The other necks of the flask shall be tightly fitted with an immersion thermometer and a Graham Condenser[10] with continuous water supply.

NOTE—— Proprietary test procedures utilizing continuous monitoring of test solutions and automatic addition of reagents may produce results dramatically different than those obtained utilizing the procedure outlined in this standard.

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[7] *Type 2 specimens shall be cut from a standard vulcanized sheet prepared in accordance with D3182. Sheets for Type 1 and Type 3 specimens shall be vulcanized in molds modified for cavity depth, but otherwise having cavity dimensions as shown in D3182; Fig. 1,2,3 or 4.*

[8] *Coming No. 4960-2L*

[9] *Electrothermal No. EM-2000C*

[10] *Coming No. 2560-500*

9. Procedure for Change in Volume

9.1 Test three specimens of a single composition. Calculate the test results of the three specimens (see 12.1, Eq 1) and average the results. Weigh each specimen in air to the nearest 1 mg and record as M_1. Remove all air bubbles clinging to the test specimens. Weigh each test specimen in distilled water (or methanol)[11] and record as M_2. Quickly blot each specimen dry with of lint-free paper. Mount the three test specimens on a glass rod so that a minimum separation of 6 mm is maintained between individual specimens. Place glass rod with specimens in immersion apparatus described in 8.1 so that all specimens are entirely immersed.

NOTE——— Six Type 1 specimens are required to meet thickness requirements for hardness testing. Tester may either record volumes of all six or record volumes on three specimens and indelibly mark the other three specimens as; for hardness testing only.

9.1.1 Fresh test solutions shall be prepared daily (except as noted in footnote 3). When the fresh solutions reach the specified test temperature, the old solutions shall be discarded and the fresh solutions added to the flasks described in 8.1. Test specimens only need to be removed from the immersion apparatus for testing.

9.1.2 The temperature of the test liquid shall be monitored by means of an immersion thermometer as described in 8.1.

9.2 At the end of the required immersion period, note any change in the color of the test solution and remove each specimen from the flask. Cool the specimens to room temperature by transferring them to a cool, clean portion of the test liquid for 30 minutes. Lightly blot the specimen dry with lint-free paper and place in a tared, stoppered weighing bottle. Weigh and record the mass as M_3. Remove each specimen from the bottle, weigh in distilled water (or methanol)[11], and record the mass as M_4 in immediate consecutive order to determine the displacement after immersion.

9.3 Return the test specimens to the cool clean portion of the test liquid before proceeding to hardness and visual tests. It is important that each manipulation following removal of the test specimen from the test medium take place promptly with the least possible lapse in time.

[11] When methanol is used; 12.1, Eq 2 shall be used for all calculations

10. Procedure for Change in Hardness

10.1 *Original Hardness* —The same samples(see section 7) shall be used for volume change, hardness change and visual rating. Three standard rectangular specimens (see Note in Section 7) shall be plied for measuring hardness before and after immersion. Hardness measurements shall be made as close as possible to the center of the specimen. Measure the hardness of the top specimen then place it at the bottom of the stack. Repeat on the next two specimens. Record the median of the three readings as the original hardness (H_o).

10.2 *Hardness After Immersion* —Remove the specimens from the cool-down solution and blot them dry with lint-free paper. Ply the specimens and measure the hardness as described in 10.1. Record the median of the three specimens as hardness after immersion (H_i). The time interval between removal from the cool solution and testing shall be not less than 2 nor more than 3 minutes.

10.3 Proceed immediately to visual rating.

11. Procedure for Visual Rating

11.1 Visual inspection shall be done with the naked eye. Changes to the specimen surface should be noted and recorded.

11.2 If consecutive testing is desired, the specimens shall be mounted on glass rods (see 9.1) and immersed in fresh test solution which is at the specified test temperature.

12. Calculation

12.1 Calculate the percent change in volume as follows (Section 10):

$$\Delta V, \% = \frac{(M_3 - M_4) - (M_1 - M_2)}{(M_1 - M_2)} \bullet 100 \qquad (1)$$

$$\Delta V, \% = \frac{[\,(M_3 - M_6) \bullet a\,] - [\,(M_1 - M_5) \bullet a\,]}{[\,(M_1 - M_5) \bullet a\,]} \bullet 100 \qquad (2)$$

where:
ΔV = change in volume, %
M_1 = initial mass of specimen in air
M_2 = initial mass of specimen in water
M_3 = mass of specimen in air after immersion
M_4 = mass of specimen in water after immersion
M_5 = initial mass of specimen in methanol
M_6 = mass of specimen in methanol after immersion
a = the inverse of the density (d) of the methanol: (1/d)

12.2 Calculate hardness change after immersion in hardness units

$$\Delta H = H_i - H_o \qquad (3)$$

where:
ΔH = change in hardness after immersion, units
H_o = original hardness, units
H_i = hardness after immersion, units

13. Report

13.1 State that the test was conducted in accordance with Test Method Dxxxx and report the following:

13.1.1 Description of the sample and its origin
13.1.2 Temperature of the testing room (see 5.1)
13.1.3 Duration, temperature and date of vulcanization of test specimens
13.1.4 Temperature of exposure
13.1.5 Duration of exposure
13.1.6 Visible changes to specimen surfaces.
13.1.7 Results calculated in accordance with Section 12
13.1.8 Which test method was used for determination of hardness
13.1.9 Any deviations from standard test methods

14. Precision and bias

To be determined

15. Keywords

15.1 plumbing; potable water; disinfection; chlorine; available chlorine; chloramine.

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