Oxidation Kinetics of Silver Thin Films for Antimicrobial Applications in the Health Care Industry

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Approval Page

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Table of Contents

Abstract……Pg. 1

Introduction……Pg. 1

Experimental Procedure……Pg. 2

Results……Pg. 4

Discussion……Pg. 5

Conclusions & Recommendations……Pg. 6

Works Cited……Pg. 6

Appendix A……Pg. 7

Appendix B……Pg. 8

List of Tables

Table I: Fixed Parameters……Pg. 3

Table II: Testing Matrix……Pg. 3

Table III: Master Water Quality……..Pg. 3

Table IV: Oxidation Corrosion – Ionic Silver Concentrations……..Pg. 4

List of Figures

Figure 1:Ionic Silver Concentration plots a) & b)……Pg. 4

Figure 2: Surface Plot of Ag. Conc. vs TDS, pH ……Pg. 5

Figure 3: SEM Micrograph……Pg. 5

KEY WORDS

Silver, thin film, anti-microbial, staph, linen, treatment

Abstract

To determine if varying city water qualities from around the United States can support a developing “oxidation corrosion of silver thin films” method of creating aqueous ionic silver solutions for the anti-microbial treatment of healthcare linens, a test was devised holding all variables constant with the exception of water quality parameters. This corrosion style test was done in order to asses a pass/fail criteria of 25 ppb ionic silver concentration in the aqueous solutions which resulted from the corrosion of silver thin film coated substrates. Above 25 ppb being a pass, below 25 ppb being a fail. While varying the levels of total dissolved solids (TDS) and pH from 200 ppm - 500 ppm and 6 – 8 respectively, all water qualities produced ionic silver concentrations above 25 ppb. The trend observed was that increasing pH and decreasing TDS resulted in increasing ionic silver concentrations.

Introduction

The antimicrobial behavior of ionic silver has been documented as early as ancient Greek times. Hippocrates, who is often considered the father of modern medicine, noted in the 4th century BC that silver had beneficial healing and anti-disease properties[1]. Within the past 20 years there has been a resurgence in the use of ionic silver to kill harmful microbes and also to inhibit their future growth. Because silver is a heavy metal, it has a residual biocidal effect on human pathogens which follows the Oligodynamic Effect. This is what allows ionic silver in particular to exhibit the residual biocidal effect not seen in current cleaners and treatments.

Staphylococcus aureus (S. aureus), commonly known as Staph. is a bacterium that is carried naturally by 20% - 30% of the human population. It is harmful to people with open wounds and/or weakened immune systems. In some cases S. aureus is treatable with antibiotics, however many people who contract the bacterial infection have immune systems that are too weak for prescribed antibiotics[2]. Also, methicillin-resistant *S. aureus* (MRSA) is a form of Staph. which is resistant to antibiotics[3]. All forms of Staph. are spread by direct contact or contacting contaminated surfaces[4]. Although there is no current national data on the Staph. infection rates of the entire American population, in 2005 a study was done by *Resources for the Future* and *National Institutes of Health* that showed a total of 477,927 people were hospitalized by S. aureus[3].

Ionic silver has been proven to kill S. aureus and inhibit its future growth[5].
By developing a way to create aqueous ionic silver solutions for cleaning and coating purposes, S. aureus contraction through contacting contaminated surfaces could be reduced or nearly eliminated. Every health care patient would benefit from the implementation of ionic silver cleaners and coatings. The fewer Staph. bacteria present in health care settings, the less likely sick patients are to contract the bacterial infection.

While anti-microbial ionic silver treatments have many possible beneficial applications in the consumer and health care industries, the area of interest is in the treatment of hospital linens during the laundering process. This treatment falls under the category of a health care application due to the fact that hospital patients will be the ones directly benefitting from the treated linens’ anti-microbial performance. However, hospital linens generally are not laundered on-site. Instead they are trucked to and from large industrial laundry facilities belonging to linen provider companies.

In the past companies such as Samsung® have used electrolysis of anodic and cathodic silver ingots submerged under inlet laundry wash water to create anti-microbial aqueous ionic silver laundering solutions. This technology is built right into their washing machines. A new process for creating aqueous ionic silver solutions exists which uses corrosion of silver coated substrates in inlet laundry wash water to create the anti-microbial aqueous ionic silver washing solutions.

One area of study which has not been made available is what the quality of the incoming inlet wash water has on the ability of specific washing machines or devices to produce consistent ionic silver

concentrations for aqueous anti-microbial silver solutions. The lowest ionic silver concentration confirmed to exhibit anti-microbial properties in linen treatment is 25 parts per billion (ppb) (Appendix A).

Experimental Procedure

Many healthcare linen providers maintain intellectual property (IP) on their specific laundering processes and techniques. The laboratory testing procedure described below is a result of one such IP protected process, however background testing was done to establish correlations between laboratory testing and the actually laundry application itself. These differences arise due to differences in environmental factors between the laboratory and the laundry application.

The IP protected washing conditions of one specific linen provider's facilities dictated the testing parameters used to study oxidation-corrosion reactions of silver and oxygen underwater. The oxidation-corrosion reaction yields aqueous ionic silver solutions which can be used in the laundering of hospital linens as anti-microbial treatments as previously stated.

In order to evaluate whether the effects of inlet wash water quality on aqueous oxidation corrosion of silver thin films would prevent the creation of 25 ppb ionic silver concentration solutions, an experiment was devised holding time, temperature, and water volume constant (Table I) while varying water qualities based on those found from 23 test sites across the United States (Appendix B).

Fixed sized samples of silver thin film coated substrates were placed into a beaker containing 200ml of water, then at the conclusion of each 3 minute testing trial the silver thin film coated substrates were removed, disposed of, and new ones were used for following testing trials. The exact specifications of these silver thin film coated substrates cannot be discussed due to IP protection held by an industrial laundry equipment manufacturer currently exploring silver technology.

After collecting water quality reports from around the United States, nine separate corrosion tests were determined to be run. The three-by-three testing matrix (Table II) varies pH and Total Dissolved Solids (TDS) based on the range of these parameters found across the nation divided into three equal increments across both ranges. Each combination of pH and TDS comprised the nine 200ml water test samples. Three trials of each test were run in order to be able to observe variation in the results.

All nine solutions were created from a beginning solution of well water (Master solution). The high mineral content of the Master solution made it possible to dilute each water test sample to the proper TDS levels using "rule of mixtures" with distilled water assumed to have 0 ppm TDS. pH was varied to 6,7 and 8 at each of the three TDS levels using 0.6 mol HCl to lower pH and 95% solid NaOH to elevate pH. In summary – the testing inputs were pH and TDS; the output for all tests was ionic silver concentration measured in the resulting solutions after the silver thin film coated substrate was removed from 200ml water samples.

Upon removal of the silver thin film coated substrate from the water, the resulting water samples were considered aqueous ionic silver solutions. Each aqueous ionic silver solution was then poured into separate sample collection bottles containing 1-2 ml of concentrated nitric acid ($HN0_3$). The concentrations of the aqueous ionic silver solutions were measured using an inductively coupled plasma spectrometer (ICP). By lowering the pH inside the sample collection bottle via addition of nitric acid, the aqueous ionic silver solutions were able to be measured more accurately by the ICP.

Table I: Fixed Parameters

Time (s)	180
Temperature (K)	323
Volume (ml)	200

Table II: Testing Matrix

	200 ppm TDS			350 ppm TDS			500 ppm TDS		
pH Level	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3
6									
7									
8									

Table III: Master Water Quality

Analyte	**Units**	**Well Water**
Total Recoverable Calcium	ppm	0.91
Total Recoverable Magnesium	ppm	3.4
Total Recoverable Sodium	ppm	230
Total Recoverable Potassium	ppm	2.4
Bicarbonate	ppm	420
Carbonate	ppm	<2.5
Hydroxide	ppm	<1.4
Alkalinity as $CaCO_3$	ppm	350
Chloride	ppm	73
Fluoride	ppm	0.33
Nitrate/nitrite as NO3	ppm	<0.44
Sulfate	ppm	45
Total Cations	meq/L	10
Total Anions	meq/L	9.9
Hardness as $CaCO_3$	ppm	16
pH	-log(H+)	7.78
Electrical Conductivity @ 25°C	umhos/cm	964
Total Dissolved solids @ 180°C	ppm	775
Nitrate as N	ppb	<50

In a lower pH environment, corroded silver is more likely to remain in its ionic form and less likely to form a compound and precipitate out of solution. ICP's atomize minute water samples using a plasma torch then analyze the emitted light waves using absorption spectroscopy. If a silver ion were to photocatalyze into an atom or form a compound with a negatively charged ion also in the water sample, that silver ion/atom would not be detected by the ICP due to the irregular light emission during atomization as compared to a completely dissociated silver ion. Low pH (<2) substantially lowers the risk of precipitation. A specialized glass bottle is used to store the samples before ICP analysis to avoid photocatalyzation.

Results

The ionic silver concentrations of the anti-microbial solutions measured in ppb using an ICP are summarized using a populated testing matrix (Table IV).Table IV varies from the testing matrix seen in Table II because pH of 7 was not properly achieved at each of the three TDS levels. pH levels 6 and 8 were achieved within pH +/- 0.01 at all TDS levels.

In order to represent how both of the input variables of TDS and pH affect silver ion concentration two-dimensional plots were created (Fig.1)

Table IV: Oxidation Corrosion – Ionic Silver Concentrations

	200 ppb			350 ppb			500 ppb		
pH Level	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3
6	78	28	36	64	47	64	55	45	28
7.19	140	47	66						
7.49				51	81	54			
7.56							76	74	58
8	92	110	120	76	39	58	44	65	49

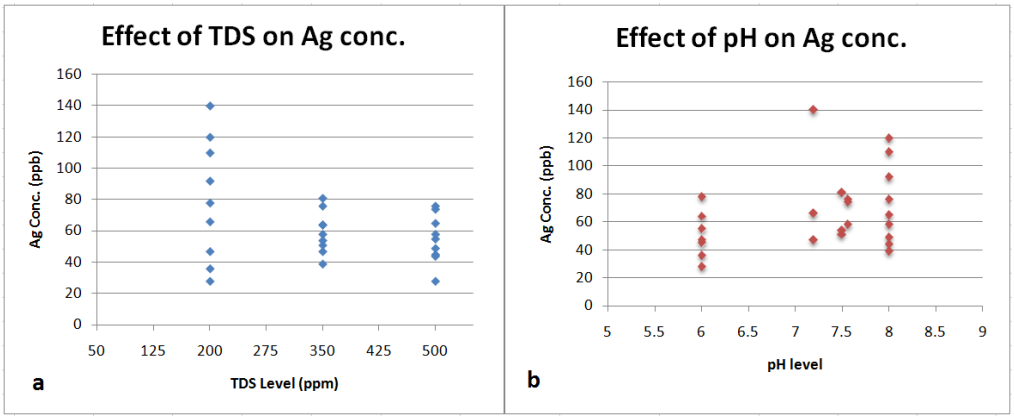

Figure 1: a) displays how ionic silver concentration varies as a function of varying TDS, b) displays how varying pH affects ionic silver concentration

The greatest variance found in the effect of TDS on ionic silver concentration in the 200 ml samples was seen at 200 ppm TDS. At a level of 200 ppm TDS, both the highest (120 ppb) and lowest (28 ppb) ionic silver concentrations were observed. The smallest ionic silver concentration variance, 17 ppb, was observed at a TDS level of 350 ppm.

The effect of pH on ionic silver concentration in the 200 ml water samples has more than three input variable levels. There are five pH input levels which can also be found in Table IV. pH 6 has the lowest variance in ionic silver concentration of 50 ppb. In order to evaluate how the combination of both input variables affected ionic silver concentration, a three dimensional surface plot was created (Fig.2). The general trend observed in the surface plot, is that elevated ionic silver concentrations resulted from increasing pH and decreasing TDS. This is consistent with both plots a) and b) from Figure 1. Although not confirmed with statistical analysis, the dominant factor appears to be pH.

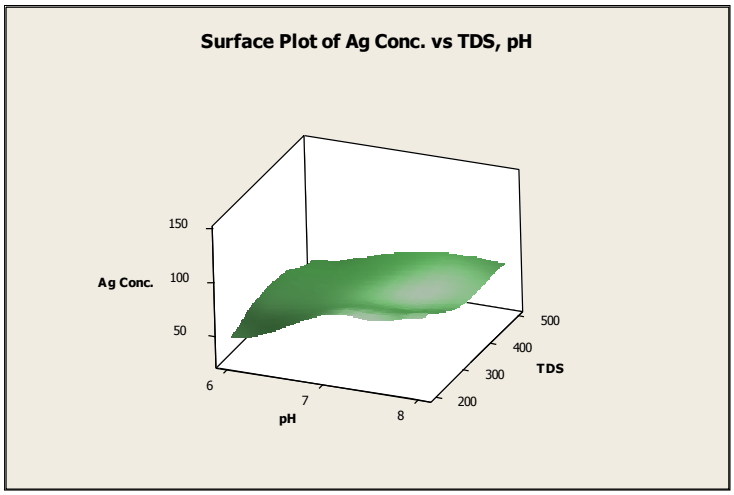

Figure 2: surface plot which depicts how the combination of varying pH and varying TDS affect ionic silver concentration in 200ml water samples.

Discussion

TDS was chosen as one of the input variables because a general inverse relationship was established between ionic silver concentrations produced and TDS levels existing in the 200 ml water test samples. Higher TDS was observed to produce lower ionic silver concentrations. TDS can be directly tied to the thermodynamic driving force for oxidation corrosion of silver. Water has a certain solubility limit at every temperature. As equilibrium solute concentrations are approached, the driving force to push more solids into solution decreases. Water samples with high TDS levels exhibit this relationship because they are closer to the overall solubility limit of the water sample than that of those water samples with lower TDS levels at the same temperature. During preliminary testing it was hypothesized that if TDS levels were above 700 ppm, not only would silver oxidation corrosion not take place, but dissolved solids within the water samples would plate out onto the silver thin film coated test samples (Fig.3).This behavior was observed during preliminary testing using the Master water supply without dilution or adjusted pH.

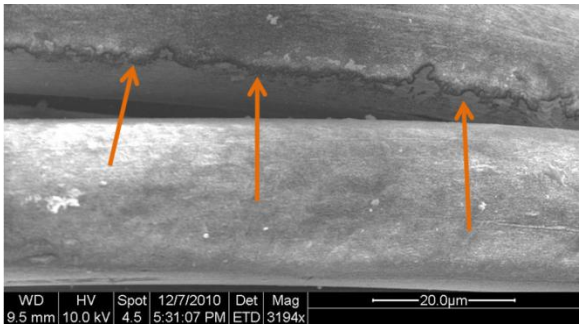

Figure 3: SEM micrograph of a crevice in silver thin film coated substrate which appears to exhibit mineral plating similar to hard water deposit.

The arrows point the edge of what looks to be a deposited layer on top of a crevice within the surface of the silver thin film coated substrate. Energy Dispersive X-Ray Spectroscopy (EDS) was used to attempt to determine what type of plating occurred in the above micrograph. However, due to the limitations of the accuracy of the particular EDS process used on nano-films, no conclusive data was able to be obtained pertaining to the chemical make-up of what appears to be mineral plating.

While the exact chemical make-up of what appears to be a mineral plating remains unknown, a correlation was established between what appears to be mineral plating and zero ionic silver concentration – any time plating was thought to be seen, the ionic silver concentration in the corrosion water sample was between 0 ppb - 5 ppb.

pH is often mentioned when discussing the factors affecting corrosion. pH is generally a relative measure of the reactivity of an electrolyte. Any corrosion study hinges on the relationship between the electrolyte and corrosion specimen. Generally what is expected is to observe lower pH electrolytes to have more corrosive properties. The results of this experiment are opposite of what is generally expected in a corrosion environment. The higher pH water samples proved more corrosive. Both are equally important. This is theorized to be due to the fact that pH was elevated using NaOH. Upon dissolution of NaOH the OH^- ions likely readily formed silver oxide compounds. All silver oxides are soluble in water at high enough temperatures. The abundance of oxygen provided by the OH^- ions facilitated the formation of silver oxides while the elevated temperature (50°C) provided the necessary kinetics to dissolve the silver oxides.

Conclusions and Recommendations

The “inlet wash water silver oxidation corrosion” study was successful.

- Corrosion was measured in 200 ml water samples which resulted from corrosion testing.
- 200 ml water samples were analyzed using ICP to determine ionic silver concentrations within the samples.
- All samples had concentrations above the pass/fail criteria of 25 ppb
- The lowest concentration found in a sample was 28 ppb and the highest concentration found in a sample was 120 ppb
- Increasing pH and decreasing TDS levels produced increasing ionic silver concentrations in the water test samples

Other methods of varying pH need to be explored for this test. Also, the effects of chloride ions are subject for a different study. Another field of interest would be to investigate the cementation (or reclamation) of silver using copper or brass to lower the concentrations ultimately ending up in sewer systems.

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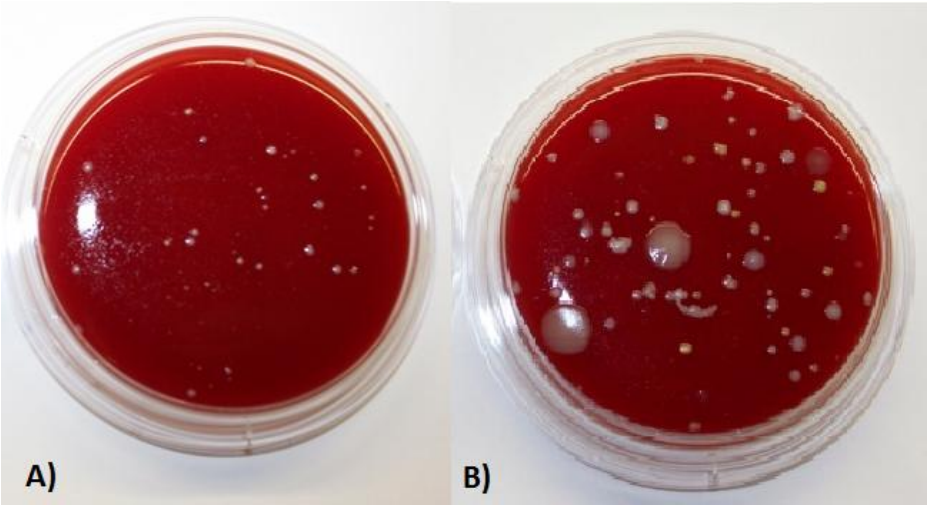
Appendix A

The figure below shows two petri dishes, A) and B) that have been touched to silver treated with a 25 ppb aqueous ionic silver solution (A) and untreated (B) linens. Both of these linen samples were slept on by the same person. The results shown below represent the bacterial growth pulled from the linens by touching the petri dishes to the bed linens after one night's sleep. Petri A displays a 70% reduction of bacterial growth as compared to petri B.



Appendix B

General Minerals Analysis										
Analyte	**Units**	**Corbett**	**Napa**	**Fresno Facility**	**Bolton, TX**	**Eagle Mountain, UT**	**Greer, SC**	**Murrieta, CA**	**Potomac River, VR**	**Pottsboro, TX**
Total Recoverable Calcium	ppm	0.91	4.9	0.14	52.4			62	81	67.3
Total Recoverable Magnesium	ppm	3.4	3.5	0.065	10.5			21	9.8	24
Total Recoverable Sodium	ppm	230	63	85	18	130		92	15.4	146
Potassium	ppm	2.4	1	0.12				3.7	2.9	
Bicarbonate	ppm	420	80	170	154				88	112
Carbonate	ppm	<2.5	<2.5	ND						
Hydroxide	ppm	<1.4	<1.4	ND						
Alkalinity as $CaCO_3$	ppm	350	65		126			132	0	112
Chloride	ppm	73	18	8.9	37			101	24.8	178
Fluoride	ppm	0.33	<0.050	0.11	0.34	1.55	0.68	0.6		0.45
Nitrate/nitrite as NO3	ppm	<0.44	1.5	14	0.11		0.16		1	0.13
Sulfate	ppm	45	53	10	24	157.5		168	28.9	189
Total Cations	meq/L	10	3.3							
Total Anions	meq/L	9.9	2.9							
Hardness as $CaCO_3$	ppm	16	27		174			242		267
pH	**-log(H+)**	**7.78**	**7.3**	**7.8**	**7**				**7.9**	**8**
Electrical Conductivity @ 25°C	umhos/cm	964	325	330				916	322	
Total Dissolved solids @ 180°C	ppm	775	225	260	234	320		544		688
Nitrate as N	ppb	<50	<50							
TDS w/o Hardness		**759**	**198**	**260**	**60**	**320**	**0**	**302**	**0**	**421**
Metals Analysis										
Total Recoverable	**Units**	**Corbett**	**Napa**	**Fresno**						
Aluminum	ppb	76	<50	ND					126	42
Antimony	ppb	<2.0	<2.0	ND						
Arsenic	ppb	<2.1	<2.0	1.4		11.2				
Barium	ppb	<10	11	ND	63	60		112	43.2	87
Beryllium	ppb	<1.0	<1.0	ND						
Cadmium	ppb	<1.0	<1.0	ND						
Chromium	ppb	<10	<10	3.2						6
Copper	ppb	520	180	46	1					
Iron	ppb	<50	<50	24					414	101
Lead	ppb	1.7	4	1						1
Manganese	ppb	50	<10	ND	2				31.2	5.8
Mercury	ppb	<.20	<0.20	ND						
Nickel	ppb	<10	<10	ND	2					3
Selenium	ppb	<2.0	<2.0	ND		5				3.2
Silver	ppb	<10	<10	ND						
Thallium	ppb	<1.0	<1.0	0.14						
Zinc	ppb	<50	<50	46	2					88

Appendix B

General Minerals Analysis							
Analyte	**Units**	**Richwood, TX**	**Rainbow,CA**	**Riverside, CA**	**Royse City, TX**	**Selbyville, DE**	**Troy, NY**
Total Recoverable Calcium	ppm	36.5	65	30	59.6		
Total Recoverable Magnesium	ppm	17.2	24	12	6		
Total Recoverable Sodium	ppm	143	93	70	49	99	8.9
Total Recoverable Potassium	ppm		4.7	2.9			
Bicarbonate	ppm	368			87		
Carbonate	ppm						
Hydroxide	ppm						
Alkalinity as $CaCO_3$	ppm	302	110	91	87	130	41.7
Chloride	ppm	116	97	80	48	24.4	18
Fluoride	ppm	0.56	0.9	0.7	0.74	1.07	0.96
Nitrate/nitrite as NO3	ppm	0.81			0.34		0.33
Sulfate	ppm	23	220	69	106		18
Total Cations	meq/L						
Total Anions	meq/L						
Hardness as $CaCO_3$	ppm	162	270	130	215	12	51
pH	**-log(H+)**	**7.3**			**8**	**7.38**	**8.78**
Electrical Conductivity @ 25°C	umhos/cm		960	593			
Total Dissolved solids @ 180°C	ppm	541	580	335	346	304	
Nitrate as N	ppb						
TDS w/o Hardness		**379**	**310**	**205**	**131**	**292**	
Metals Analysis							
Total Recoverable	**Units**						
Aluminum	ppb	14		96			
Antimony	ppb						
Arsenic	ppb	2		2.5			
Barium	ppb	197			41		25
Beryllium	ppb						
Cadmium	ppb						
Chromium	ppb					0.01	9
Copper	ppb	13			44	135	38
Iron	ppb	334			27	40	40
Lead	ppb						8
Manganese	ppb	44.6			1.7		20
Mercury	ppb						
Nickel	ppb	1			3		30
Selenium	ppb						
Silver	ppb						
Thallium	ppb						
Zinc	ppb	27			9		15

Appendix B

General Minerals Analysis									
Analyte	**Units**								
Total Recoverable Calcium	ppm	**Tampa Bay, FL**	**Chicago, IL**	**Rockmart Beach, GA**	**Ooltewah, TN**	**Columbia, SC**	**Greensboro, NC**	**Pawtucket, RI**	**Las Vegas, NV**
Total Recoverable Magnesium	ppm		35			85	4.2	0.21	77
Total Recoverable Sodium	ppm		11.5			67	2.3	0.069	26
Total Recoverable Potassium	ppm	52.7	7.3		4.8	41	5.4	0.676	98
Bicarbonate	ppm		1.6				2.7	39.6	6.1
Carbonate	ppm								
Hydroxide	ppm								
Alkalinity as $CaCO_3$	ppm								
Chloride	ppm		111		56	120	30		136
Fluoride	ppm		12		7.8	48	9	0.76	99
Nitrate/nitrite as NO3	ppm	0.75	0.08	0.89	0.97	1.01	0.12		0.8
Sulfate	ppm		0.29	0.48	0.2		0.26	5.16	
Total Cations	meq/L		22.9		38.4	80	8.4		243
Total Anions	meq/L								
Hardness as $CaCO_3$	ppm								
pH	**-log(H+)**	221	135	44	74	153	30		300
Electrical Conductivity @ 25°C	umhos/cm	**7.69**	**8.21**	**6.63**	**7**	**8.58**	**7.3**	**6.25**	**7.87**
Total Dissolved solids @ 180°C	ppm			140			95	521.4	1023
Nitrate as N	ppb		176.6	50	149	303	54		632
TDS w/o Hardness		160	<20	270		ND			700
Metals Analysis			**41.6**	**6**	**75**	**150**	**24**		**332**
Total Recoverable	**Units**								
Aluminum	ppb		47		15	ND	40		ND
Antimony	ppb	0.1	<1		<1	ND	<1		ND
Arsenic	ppb	0.5	<1	<2	<1	ND	<5		1.9
Barium	ppb	0.0181	16	0.011	27	104	<40.0		100
Beryllium	ppb		4		<.2	ND	<1		ND
Cadmium	ppb		<1		<0.1	ND	<1		ND
Chromium	ppb	0.5	1.1		<0.4	ND	<5		ND
Copper	ppb	583	3.8	0.063	380	53	<50		800
Iron	ppb		137	60	17	110	70		ND
Lead	ppb	1	<1	1.3	1	2	26		4
Manganese	ppb		5.2	<50	4	ND	50		ND
Mercury	ppb		<0.2		<0.1	ND	<.0.2		ND
Nickel	ppb	1.5	1		<0.7	ND	<5		ND
Selenium	ppb	1	<1		<0.6	ND	<5		2
Silver	ppb		<1		<0.4				ND
Thallium	ppb		<1		<0.6	ND	<1		ND
Zinc	ppb		<1		6	ND	<10		160