

Center for Food Safety and Applied Nutrition

To: Robin T. Johnson (HF-26)
Kennon Smith (HF-26)
LaJuana D. Caldwell (HF-27)

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171.1(c)(H) ENVIRONMENTAL ASSESSMENT

Section Contents

- 1 DATE:** November 15, 2002
- 2 PETITIONER:** Alcide Corporation
- 3 ADDRESS:** 8561 154th Avenue, NE
Redmond, WA 98052

4 DESCRIPTION OF THE PROPOSED ACTION

5 IDENTIFICATION OF CHEMICAL SUBSTANCES THAT ARE SUBJECT OF THE PROPOSED ACTION

6 INTRODUCTION OF SUBSTANCES INTO THE ENVIRONMENT

7 FATE OF EMITTED SUBSTANCES IN THE ENVIRONMENT

8 ENVIRONMENTAL EFFECTS OF RELEASED SUBSTANCES

001408

9 USE OF RESOURCES AND ENERGY

10 MITIGATION MEASURES

11 ALTERNATIVES TO PROPOSED ACTION

12 PREPARER

13 CERTIFICATION

14 APPENDICES

15 BIBLIOGRAPHY

001409

4 DESCRIPTION OF THE PROPOSED ACTION

4.1 REQUESTED APPROVAL

Approval is requested for the use of the system comprised of acidified sodium chlorite (ASC) solutions for use as an anti-microbial agent to reduce pathogenic and spoilage microorganisms on seafood or freshwater fish when used at a use concentration of 40 to 1,200 ppm within the pH range of 2.3 to 2.9.

The petitioned additive was originally approved as a Secondary Direct Food Additive (FAP 4A4433) on April 23, 1996 when new regulation 21CFR §173.325 was codified to reflect the acceptance of ASC for use as an anti-microbial agent in the processing of poultry meat as a component of a carcass spray or dip solution prior to immersion in pre-chiller or chiller waters, or for direct application in pre-chiller or chiller water solutions. Further approvals for the additive have been granted in the intervening period.

As of the date of submission of the current FAP, ASC is already approved for use on seafood or freshwater fish. This use was originally codified and/or listed on page 44122 of the Federal Register (Volume 64, No 156) on August 5, 1999 as follows:

§ 173.325 Acidified sodium chlorite solutions.

(d) The additive is used as an anti-microbial agent in water and ice that are used to rinse, wash, thaw, transport, or store seafood or freshwater fish in accordance with current industry standards of good manufacturing practice. The additive is produced by mixing an aqueous solution of sodium chlorite with any GRAS acid to achieve a pH in the range of 2.5 to 2.9 and diluting this solution with water to achieve an actual use concentration of 40 to 50 parts per million (ppm) sodium chlorite. Any seafood or freshwater fish that is intended to be consumed raw shall be subjected to a potable water rinse prior to consumption.

001410

- i) Alcide Corporation's present petition seeks to modify the current approval for the use of ASC solutions on seafood or freshwater fish to extend the dose and pH ranges as indicated earlier.

4.2 PROCESS DESCRIPTION

In ASC solutions, there are two components that are used to create the anti-microbial effect, the food-grade acid and the sodium chlorite. Both of these materials may initially be supplied at point of use as concentrates (typically for example 50% citric acid and 25% sodium chlorite), each of which is first separately diluted with water to form an intermediate liquid stream whose concentration is double the intended final use level. Alternatively, both materials may be formulated with stabilizers to create shelf-stable double strength solutions, which can then be shipped to the final use sites. In the final mixing step, sufficient acid is added to a 80 – 2,400 ppm solution of sodium chlorite to reduce its pH to the 2.3 - 2.9 range – typically pH 2.5 - and to create the desired final use concentration in the range 40 to 1,200 ppm. The resulting ASC solutions are then applied to the seafood or freshwater fish product surfaces by either spray or by immersion. In the case of a spray application, the liquid is dispensed from a spray apparatus in which either:

- ii) One stream each of the chlorite and the acid solutions are mixed at, or immediately before the spray nozzle, or;
- iii) A single stream of recently pre-mixed ASC solution is directed to the spray nozzle from a holding tank. The latter may be prepared prior to use, using ambient temperature or in cold temperature waters, so long as the chlorite and acid levels have been analytically determined to be within the acceptable range.

In the typical environment of a high-speed large volume seafood or freshwater fish processor, practical aspects of the process usually dictate that the product to be treated can only be exposed to the treatment solution for relatively short periods of time – usually measured in

001411

seconds. Thus where an ASC solution is applied by spray, this short exposure time will most likely dictate that the use concentrations will typically be at the upper end of the proposed use range i.e. between 500 to 1,200 ppm.

When an ASC solution is applied to seafood or freshwater fish by immersion in a high-speed processing environment, the actual period of immersion would typically also be relatively short thus the use concentrations would again tend to be in the upper use range. However in situations where seafood or freshwater fish is to be placed in iced storage or is to be contained for a period of time in a "wash tank" environment, then such immersion treatments could conceivably range anywhere from a few seconds up to several hours. In these situations, lower use concentrations and exposure times may be selected dependent upon the desired end point of the treatment process. Some of the factors, which may affect the choice of an immersion time and/or use concentration are listed as follows:

Rate of Kill

At the lowest use concentration of 40 ppm, the efficacy of an ASC solution, assuming constant maintenance of the treatment solution at the desired concentration, will be a direct function of the exposure time. Rate of kill as measured by C't values will increase with the period of time over which the treated surfaces are exposed to the ASC solution. Thus for a 40 ppm use concentration, exposure times measured in hours may not be uncommon as being necessary to achieve significant impacts on the microbial populations that are present on seafood or freshwater fish. Conversely, at the highest use concentration of 1,200 ppm, extremely short exposure times – 30 to 120 seconds – may be all that is required to achieve the same significant impacts on microbial populations.

001412

Desired Efficacy Outcome

Where pathogen reduction is the desired outcome and the lowest use concentration is proposed, exposure times may need to be extended in 15 to 30 minute increments to achieve the necessary efficacy end point. Where spoilage organism control is the desired outcome, these exposure times may be measured in hourly increments. Conversely, at the highest use concentrations, significant pathogen reduction outcomes may be achieved in 15 to 30 second exposures and dramatic impacts on spoilage organisms – with subsequent extension of product shelf-life – may be seen with as little as 2 minute exposure times.

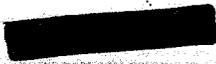
Seafood or freshwater fish Product to be Treated

Exposure times and use concentrations may also need to be modified dependent upon the seafood or freshwater fish product that is to be treated, simply to avoid any unnecessary or unacceptable impacts on the appearance or ultimate organoleptic qualities of the finished product.

4.3 NEED FOR THE ACTION

Millions of Americans become ill each year from something they eat. While diagnostic and surveillance methods for food-borne illness have improved dramatically in recent years, the exact number of cases can still only be approximated by government officials. As a result we must rely heavily on estimates when attempting to quantify the problem of food borne illness. As an example, the Centers for Disease Control and Prevention estimates that while deaths due to food poisoning have dropped from 9,000 to approximately 6,000 per year, the actual number of illnesses reported has risen to approximately 76 million per year. Much of this increase is attributed to better surveillance, more sensitive diagnostic techniques and more accurate diagnosis.

001413



Per capita, consumption of seafood or freshwater fish in the United States is rising.¹ As with other food processing systems where raw product is prepared for human consumption, seafood or freshwater fish – fish and shellfish – can be contaminated with both pathogenic and spoilage organisms during production (farming), harvesting, processing, distribution, handling and storage.

An estimated 11% of the food-borne outbreaks of illness in the United States are thought to involve seafood or freshwater fish, and 25% of these involve bacterial pathogens.² Such organisms include:

Salmonella spp.

Clostridium botulinum

Listeria monocytogenes

Vibrio cholerae

Vibrio parahaemolyticus

Vibrio vulnificus

One organism of particular importance in food borne illness is *Escherichia coli* O157:H7 which is reported to cause sickness in as many as 20,000 Americans each year through contaminated meats, seafood or freshwater fish and other sources. Of these infected people, up to 500 may die. This particular coliform organism, of animal fecal origin, is present in manure and animal droppings, which contaminate soil. Sewage sludge when allowed to flow into waterways or seaways untreated, contributes additional problems with respect to illness of seafood or freshwater fish origin. It is therefore easy to understand why it is that seafood or freshwater fish can readily enter the processing plant environment with significant levels of microbial contamination on their exterior surfaces, derived from organisms that were present in their environment during growth or from contamination that occurred during the harvesting or transporting processes.

Further, it is also evident that without careful attention to the implementation of

001414

appropriate practices to control these microbial contaminants during the preparation of the seafood or freshwater fish for processing, that these contaminants can easily be carried further along into the processing plant environment to ultimately contaminate the seafood or freshwater fish at the terminal handling stages.

Washing of seafood or freshwater fish with potable water after harvesting has most typically been the method used to render the product more acceptable from an overall appearance as well as possible contamination point of view. However, the primary purpose of washing is to remove excess or extraneous surface matter (e.g., soil, blood etc.) in order to gain an attractive appearance of the end product. While cleaning and washing processes do provide some limited reduction of the microbial load on most product surfaces, this method is not effective in rendering the final raw product sterile or even reducing the microbial load to a state of "disinfection."

Chlorinated water is often used in processing waters applied to seafood or freshwater fish during processing however its efficacy is readily dissipated by the presence of vegetable, soil and other organic matter. Thus at the typical use concentrations at which this material is applied the overall outcomes with respect to microbial reduction, tend to be relatively poor.

ASC was first approved by the US-Food and Drug Administration in 1999 for application to seafood or freshwater fish at a use concentration of 40 to 50 ppm and in a pH range of 2.5 to 2.9. At these use levels this anti-microbial intervention shows significant promise for the control of pathogen contamination and spoilage control. Despite this approval however, the need still exists to expand the use concentration and pH ranges of ASC in order to provide the seafood or freshwater fish industry with a more practical and more broadly useful anti-microbial intervention step that can safely be applied to all seafood or freshwater fish.

It is the position of Alcide Corporation that the proposed new ASC solution concentration and pH ranges which are the subject of this Food Additive Petition, and which have similarly already been approved by the US-FDA for use in poultry, red meat and produce processing (as

001415

well as for use, at the lowest concentrations, in seafood or freshwater fish processing), can play a major role in upgrading the overall microbial quality of seafood or freshwater fish in the United States.

4.4 LOCATIONS WHERE PRODUCTS WILL BE PRODUCED

There are two components to the ASC solutions being proposed for Secondary Direct Food Additive Status: the sodium chlorite or Base component, and the acidifier or Activator component needed to achieve the desired solution pH. The acidifier can be any one of a variety of US-FDA-approved GRAS acids, including but not limited to phosphoric, sulfuric, malic, acetic and citric. These are all materials of very high volume usage, and of many current and diverse applications in a wide variety of industries around the US today. These include:

- Liquid and powdered beverages
- Desserts
- Baked goods
- Meat pickling and fish preservation
- Jellies and preserves
- Candies
- Dairy products and cleaners
- Fats and oils (stabilizers)

The projected use volumes of any of these acids as an activator of sodium chlorite to generate an ASC solution are much below a fractional percentage of their other uses, thus the sites of production of these different acids, is not considered relevant to this environmental assessment.

001416

Sodium chlorite is currently being used as a chlorine dioxide (ClO₂) source in water treatment, as well as an industrial bleaching agent in a number of industries (primarily pulp and paper), in cleaning applications for the electronics industry, as a biocide in the food processing

industry, and in various applications in the oil industry. On April 23, 1996 the U.S. US-FDA first approved the use of sodium chlorite as a component of ASC solutions for microbial reduction pre-chill in poultry carcass sprays or dips and during the chill process as a component of the chill water. Thereafter, as a result of similar approval actions the US-FDA has also allowed for the use of ASC solutions for the following applications: i) pre- and post-chill in red meat carcass, carcass parts or organs sprays or dips; ii) pre-process on produce a.k.a. Raw Agricultural Commodities (RACs); iv) post-process on produce; and iv) in process waters on seafood or freshwater fish (the latter at use concentrations of 40 to 50 ppm and in the pH range 2.5 to 2.9).

The size of the worldwide sodium chlorite market is today estimated at 79.30×10^6 lb (36×10^6) Kg per year. Of this, the North American chlorite market is estimated to account for approximately 31% or 24.58×10^6 lbs (11.16×10^6 Kg) per year. European production of sodium chlorite accounts for an additional 42% of the worldwide production while Asia/Pacific production makes up the remaining 27%.^a Within North America, the largest producer of sodium chlorite is Vulcan Chemicals (Birmingham, Alabama) who produce approximately 23×10^6 lbs (10×10^6 Kg) per year at their facility in Wichita, Kansas. The balance of the North American production comes from Sterling Chemicals of Ontario, Canada. Major foreign production sites for sodium chlorite, which may be accessed if quality and economics are appropriate, include that of France's Atochem, S.A., Italy's Cafaro, and Spain's Energia Industrias Aragonesas in Madrid.

4.5 LOCATIONS WHERE THE PRODUCTS WILL BE USED

Once the pending FAP is accepted as a modification of the current regulation, the ASC anti-microbial solution will become available to all processors of seafood or freshwater fish as well as to a range of institutional facilities and home users. Geographically these solutions should find application in all areas of the country where seafood or freshwater fish are processed

^a Loic Le Dore. Welcoming address, Second European Symposium on Chlorine Dioxide and Disinfection. Paris, 24-25 June, 1999.

for final consumption. It is likely inevitable that there will be greater use of ASC solutions in those states which are recognized as being primary sources of seafood or freshwater fish including those where these products are harvested. For example, all of the coastal states, those states bordering the Great Lakes, the states of Mississippi and Louisiana - which are major suppliers of farmed catfish - and the state of Idaho which is a major supplier of farmed trout. Likewise, harvesting of crustaceans and farming of molluscs occurs around almost the entire coastline of the United States. Given the dominance of specific states in their respective seafood or freshwater fish production areas, relevant processing industries have naturally arisen to accommodate the further processing requirements of these various products. Overall therefore there is reason to believe that the potential for use of ASC solutions on seafood or freshwater fish covers the entire geographic area of the United States. But, it is this potential diversity of geographic and product use which also makes it extremely difficult to reach a reasonable estimate of the potential total annual usage for the ASC product.

IDENTIFICATION OF CHEMICAL SUBSTANCES THAT ARE THE SUBJECT OF THE PROPOSED ACTION

5.1 CHEMICAL NAMES AND PHYSICAL PROPERTIES

5.1.1 Sodium Chlorite (Appendix 1)

CAS Reg. No.:	7758-19-2
Color (31.25% Solution):	Colorless to light green
Specific Gravity:	1.21
Viscosity (@25°C):	1.62 cps
pH:	12.33

5.1.2 Acidifiers (GRAS)

Phosphoric Acid

CAS Reg. No.: 7664-38-2
Conforms with 21CFR §182.1073 as a Multiple Purpose GRAS Food Substance

Citric Acid

CAS Reg. No.: 77-92-9 (anhydrous)
5949-29-1 (monohydrate)
Conforms with 21CFR §182.1033 as a Multiple Purpose GRAS Food Substance

001419

Hydrochloric Acid

CAS Reg. No.: 7647-01-0

Conforms with 21CFR §182.1057 as Multiple Purpose GRAS Food
Substance

Malic Acid

CAS Reg. No.: 617-48-1 DL mixture
97-67-6 L isomer

Conforms with 21CFR §184.1069 as a Specific Substance Affirmed as
GRAS, with respect to the following ¶s,

- (a) description
- (b) specifications
- (c) use as pH control agent
- (d) maximum use level

Sulfuric Acid

CAS Reg. No.: 7664-93-9

Conforms with 21CFR §184.1095 as a Specific Substance Affirmed as
GRAS, with respect to the following ¶s,

- (a) description
- (b) specifications
- (c) use as pH control agent
- (d) maximum use level

001420

Acetic Acid

CAS Reg. No.: 64-19-7

Conforms with 21CFR §184.1005 as a Specific Substance Affirmed as GRAS, with respect to the following ¶s,

- (a) description
- (b) specifications
- (c) use as a pH control agent
- (d) maximum use level

5.2 MODE OF ACTION OF THE GERMICIDAL SYSTEM

ASC chemistry is principally the chemistry of chlorous acid (HClO_2), a metastable oxy-chlorine species which decomposes to form chlorate ion, chlorine dioxide, and chloride ion.³ To better understand chlorous acid chemistry, a brief overview of the chemistry of various oxy-chlorine species follows.

As illustrated in Table I, chlorine can exhibit oxidation states from -1 to $+7$. As a consequence, its chemistry is varied and complex.

Table1. Oxidation States of Chlorine

ClO_4^-	+7	Perchlorate ion
ClO_3^-	+5	Chlorate ion
ClO_2	+4	Chlorine dioxide
ClO_2^-	+3	Chlorite ion
ClO^- or OCl^-	+1	Hypochlorite ion
Cl_2	0	Chlorine (molecular)
Cl^-	-1	Chloride ion

Oxy-chlorine species are important as oxidants in a number of applications. The strength of an oxidant is measured by its oxidation strength, or oxidation potential. Table 2 lists some of the more common oxidants, their associated oxidation reactions, their oxidation strengths

001421

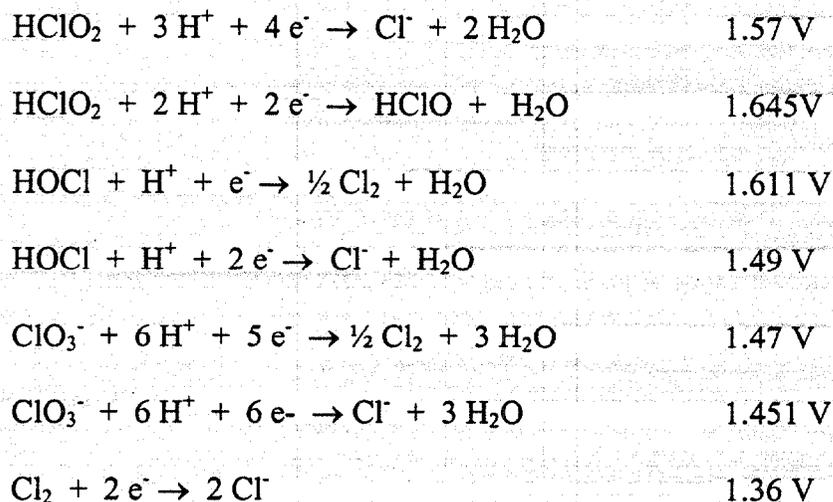
(measured in volts), and their oxidation capacities (the number of electrons accepted by the oxidant). The chlorous acid (HClO₂) reaction, with its 1.57 V oxidation strength and 4-electron oxidation capacity, ranks just below ozone and the hydroxyl-radical generation reaction of hydrogen peroxide.

Table 2. Common Oxidation Reactions

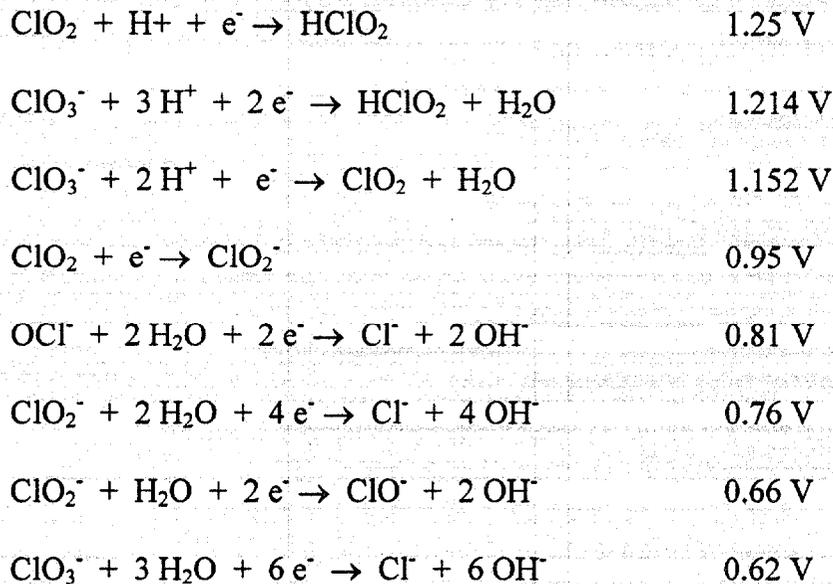
Oxidant Reaction	Oxidant	Oxidation Capacity	Oxidation Strength (V)
$O_3 + H_2O + 2 e^- \rightarrow O_2 + OH^-$	Ozone	2e ⁻	2.07
$H_2O_2 + 2e^- \rightarrow 2 OH^-$	Hydrogen Peroxide	2e ⁻	1.78
$HClO_2 + 3 H^+ + 4 e^- \rightarrow Cl^- + 2 H_2O$	Chlorous Acid (Acidified Sodium Chlorite)	4e ⁻	1.57
$ClO_2 (v) + e^- \rightarrow ClO_2^-$	Chlorine Dioxide (Vapor Phase)	1e ⁻	1.56
$HOCl + H^+ + 2 e^- \rightarrow Cl^- + H_2O$	Hypochlorous acid	2e ⁻	1.49
$HOBr + H^+ + 2 e^- \rightarrow Br^- + H_2O$	Hypobromous acid	2e ⁻	1.33
$ClO_2 + 4 H^+ + 5 e^- \rightarrow Cl^- + 2 H_2O$	Acidified Chlorine Dioxide	5e ⁻	1.51
$ClO_2 (aq) + e^- \rightarrow ClO_2^-$	Chlorine Dioxide (Aqueous Phase)	1e ⁻	0.95
$ClO_2^- + 2H_2O + 4e^- \rightarrow Cl^- + 4 OH^-$	Chlorite	4e ⁻	0.78

As mentioned before, oxy-chlorine chemistry is varied and complex. Listed below are oxidation half-cell reactions and their corresponding oxidation potentials for several additional reactions of oxy-chlorine species given by Gordon *et al.*,⁴ in the AWWA publication,

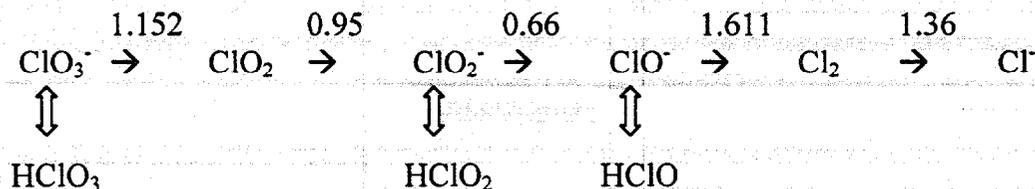
Disinfectant Residual Measurement Methods:



001422



The oxidation potential diagram given below shows that chlorous acid is unstable with respect to disproportionation, i.e. chlorous acid is a metastable species.



Numerous researchers have determined that the decomposition reaction of chlorous acid is approximately second order with respect to chlorous acid.^{5, 6, 7, 8} At pH values above 2.0 where $[\text{ClO}_2^-] > [\text{HClO}_2]$, the rate law can be written as follows:

$$\frac{-d[\text{HClO}_2]}{dt} = k [\text{HClO}_2]^2$$

(where $k = 0.023 \text{ M}^{-1} \text{ sec}^{-1}$ at 25°C)⁹

It is known that chloride ion accelerates the decomposition of chlorous acid and also alters the stoichiometry. Hong^{10, 11} developed the following empirical rate expression for the decomposition of chlorous acid, with the effect of chloride taken into account;

$$\frac{d[\text{ClO}_2]}{dt} = (m + nx) \left(1 - \frac{x}{\dots} \right)$$

001423

dt

p + qx

$$\text{where } m = 2\{k_1[\text{HClO}_2]^2 + k_2[\text{ClO}_2^-][\text{HClO}_2]\}$$

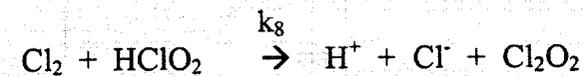
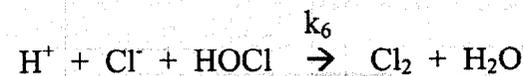
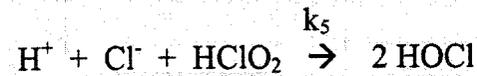
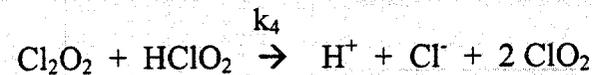
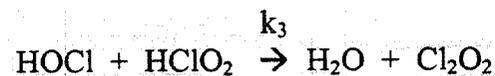
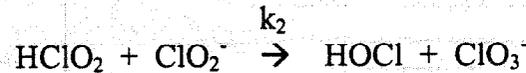
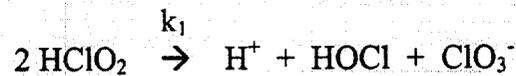
$$n = 4 k_5 [\text{H}^+][\text{HClO}_2]$$

$$p = \frac{k_3(k_7 + k_8)[\text{HClO}_2]}{k_6 k_7 [\text{H}^+]}$$

$$q = \frac{k_7 + k_8}{k_7}$$

$$x = [\text{Cl}^-]$$

Where the various rate constants refer to the following set of reactions:



In the absence of chloride, only the first four reactions need be considered. Doing this, Hong gives the following reaction equation, valid over the pH range of 0 to 3, for the initial rate

001424

law for the formation of chlorine dioxide:

$$\frac{d[\text{ClO}_2]}{dt} = k [\text{HClO}_2]^2 + k [\text{HClO}_2][\text{ClO}_2^-]$$

The rate of formation of chlorine dioxide given above, can be related approximately to the disappearance of chlorous acid by the following relation.⁸

$$-d[\text{HClO}_2]/4 = d[\text{ClO}_2]/2$$

In aqueous solution, chlorous acid, a relatively weak acid, dissociates as follows:

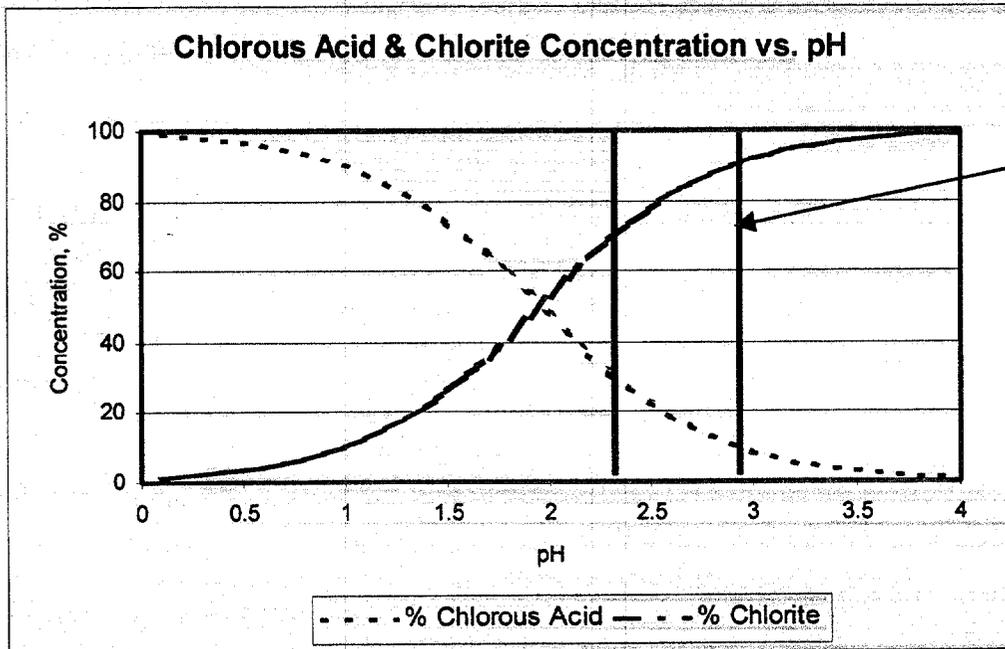


where K_a , the acid dissociation constant, is 1.01×10^{-2} at 23°C .¹² In terms of the acid dissociation constant (ionization constant) and the hydrogen ion concentration of the solution ($=10^{-\text{pH}}$), the chlorous acid concentration can be found from the total titratable chlorite concentration as follows:

$$\% \text{HClO}_2 = \frac{1}{1 + (1.1 \times 10^{-2})/[\text{H}^+]} \times 100\%$$

The following is a graph of this relationship.

001425



Typical ASC solution operational range from pH 2.3 to 2.9

From this basic understanding of the chemistry and, combined with the results of microbiological testing, the optimal parameters for application of the ASC process as a short-term anti-microbial intervention on seafood or freshwater fish have therefore been determined to be

- i) A pH range of approximately 2.3 to 2.9;
- ii) A sodium chlorite concentration ranging from 40 ppm to 1200 ppm.

001426

6 INTRODUCTION OF SUBSTANCES INTO THE ENVIRONMENT

6.1 PRODUCTION RELEASES

As noted in Section 4, the ASC solution will be produced on site some time prior to application in the processing facility, be it a major operation, a contract operation for a specific chain, a supermarket facility, or ultimately even in the home. The solution mixing will take place through the confluence of the separate acid activator and sodium chlorite base solutions at some point prior to the final applicator nozzles. The acid and sodium chlorite solutions will typically be prepared in ambient temperature tap water although circumstances may arise where the solutions are prepared with chilled water down to temperatures as low as 4°C. Note that there may also even be circumstances where ASC solutions are frozen after initial constitution then ultimately allowed to, thaw gradually while in contact with the seafood or freshwater fish.

For freshly mixed solution application circumstances, the time that normally elapses between the creation/activation of the ASC solution and its final delivery to the surface to be treated is typically brief (no greater than 2 – 3 minutes). Thus, the levels of dissolved chlorine dioxide that might typically generate within the ASC solution over time will not exceed *ca.* 2 – 3 mg/liter (2 – 3 ppm).

In larger operations, it is anticipated that a spray treatment will be the primary mode of application to products which are the subject of this petition, in essentially the same manner as is currently commercially utilized for the pre-chill ASC treatment of various meat products and produce; i.e., the seafood or freshwater fish will pass through a semi-enclosed and baffled spray enclosure. The spray will be applied via pressurized spray nozzles, for varying exposure times up to about 30 seconds before the product exits the enclosure. In order to minimize the potential for possible off-gassing into the immediate worker environment, the semi-enclosed spray enclosure will be negatively pressurized via an aspirating air hose venting to the outside of the building. This will

ensure the removal of excess gaseous materials, while a dedicated drainpipe will route excess fluids to an enclosed drain for removal with other plant wastes. Short-term exposure, "immersion dip" processes may also be developed for some of the products that are the subject of this petition to conform with current industry practices vis-à-vis the inclusion of an anti-microbial into processing waters to reduce the spoilage-related microbial load of seafood or freshwater fish. As for the spray treatments, such systems would also be semi-enclosed and negatively pressurized via an aspirating air hose venting to the outside of the building to accommodate any potential worker safety issues.

In smaller operations where the application of product is expected to typically be limited to infrequent and/or small batch application using either hand-held "on/off-type" applicators or purpose-designed "dual-cylinder" hand-held spray bottles, the volume of product use and therefore the potential for off-gassing and worker environment exposure is significantly reduced compared to the larger commercial systems. As a result, no special precautions other than the inclusion of label precautionary statements regarding handling, adequate venting of the work area and use of the material are therefore anticipated.

001428

6.1.a. THEORETICAL WORSE CASE PRODUCTION RELEASES

While chlorine dioxide has a minimum tendency to form in ASC solutions when the chlorite and acid are initially combined immediately prior to spraying (typically measured as $< 2 - 3$ mg/liter dissolved in solution), it may exhibit an increasing tendency to form as the applied solution concentrates during the evaporative process or as a mixed but unused solution is allowed to "age." Thus, in a typical situation, the potential for chlorine dioxide entry into the air of the workplace would be expected to derive primarily from this evaporative source, more so than from that which is retained in solution. Chlorine dioxide also has a significant tendency to react with, and be degraded by soluble organic matter (such as soil) to form chlorite, chlorate and ultimately chloride. It is therefore expected that a major portion of both the initially projected chlorine dioxide maximum of $2 - 3$ mg/liter in solution and any quantity formed upon subsequent solution evaporation will be reduced to a non-volatile, chlorine-containing ion that will ultimately be removed in the organic matter laden waste waters of the processing plant.

Finally, it is further expected that the degree of chlorine dioxide evolution out of the ASC solution within the application enclosure during the treatment's maximum 30-second residence time on the seafood or freshwater fish will be low. This is particularly true because the high humidity conditions prevailing in the application cabinet will tend to suppress evaporation and therefore out-gassing of chlorine dioxide from the ASC solution. Thus the $2 - 3$ mg/liter level of chlorine dioxide that can typically be measured in an ASC solution within $2 - 3$ minutes of activation of sodium chlorite can be assumed to correspond to the most likely "maximum" amount of this substance that will arise from both initial and evaporative sources.

To put this into perspective from present day experiences with the application of ASC solutions in commercial poultry processing plants, a typical ASC spray operation applies 111 mL/kg of solution (1.67 fl. ozs. per 1.0 lb; average carcass is 3 lb) inside of a 2.45 m³ spray enclosure over the course of 15.9 seconds^b. Therefore, in a "worst case" scenario where all of the

^b For a standard 90 bird per minute evisceration line a typical SANOVA spray cabinet enclosure measures $3 \times (0.67 \text{ m} \times 1 \text{ m} \times 1.22 \text{ m})$. Therefore internal volume = 2.451 m^3 . Average carcass exposure time to ASC chemistry while transiting the spray cabinet = cabinet length (3.66 m)/Line Speed. Line Speed = No. birds per second \times shackle

dissolved chlorine dioxide were to be released into the environment, 450 kg (1,000 lb) of meat treated (333 carcasses), corresponding to 50 L of ASC solution applied^c, would theoretically release 150 mg of chlorine dioxide in 3.70 minutes (at the 3 mg/L concentration). Assuming a static air environment inside the application enclosure, with no venting or circulation of the air in the vicinity of the treated poultry meat, the dispersal of up to 40.54 mg of chlorine dioxide into 2.45 m³ of air in one minute would immediately raise its concentration above the OSHA 8-hour TLV of 0.3 mg/m³ and therefore lead to unsafe conditions both within the enclosure and in the immediate external environs.

For typical applications of ASC solutions to seafood or freshwater fish, it has already been established that the application volumes necessary for the achievement of significant pathogen reduction or for significant impacts on shelf-life have been established – based on depletion studies – to be approximately 84% of those used on poultry carcasses i.e. 93 mL/kg (1.24 fl. oz./lb) of seafood or freshwater fish, therefore the “worst case” concentrations of chlorine dioxide in the theoretical case described above would also be approximately 84% or up to 34.05 mg of chlorine dioxide into 2.45 m³ of air.

6.1.b. ACTUAL PRODUCTION RELEASES

Drawing on the current experiences with the application of ASC solutions in commercial poultry processing plants, air quality testing in the immediate area around commercial spray enclosures installed into poultry plants in the US shows that chlorine dioxide is generally undetectable (Appendix 2). Additionally, air quality testing of the air exhaust from these same commercial systems shows extremely low levels of chlorine dioxide present. These data clearly support the fact that the majority of the chlorine dioxide material that is in solution, remains so, and is ultimately disposed of in the liquid waste stream.

In an immersion or dipping operation there is not expected to be any change, certainly no

001430

width = (90/60) x 0.15 m. Therefore transit time = 3.66/0.23 = 15.9 second ds

^c 450 kg meat = 333 carcasses. At 90 birds per minute line speed 333 carcasses = 3.72 minutes of kill time. 450 kg meat x 111 mL/kg x 1 L/1000 mL = 50 L.

increase to the potential for air dispersal of either the ASC solution or of any dissolved chlorine dioxide, when compared to that of a spray operation. In fact, due to the likely accumulation of organic matter over time within the dip solution, plus the known interaction (reduction) of chlorine dioxide with organic matter it is anticipated that actual levels of this material in immersion or dipping operations will be lower than are typically seen in spray systems. However, as with the commercial spray systems that are currently being utilized in US poultry processing facilities, the environs surrounding an immersion or dipping operation will be controlled with appropriate enclosures, containment of liquid wastes and positive pressure air venting to the exterior of the building.

Based on the above estimates, it is Alcide Corporation's belief that chlorine dioxide is unlikely to be a production release of any significance as a result of the proposed use of ASC in seafood or freshwater fish processing facilities.

001431

6.2 USE RELEASES

6.2.1 ESTIMATES OF RAW MATERIAL VOLUME

6.2.1.a INTRODUCTION

As previously mentioned in Section 4.4 of the Environmental Assessment, there is reason to believe that the potential for use of ASC solutions on seafood or freshwater fish covers the entire geographic area of the United States. But, it is this potential diversity of geographic and specific-product use which makes it extremely difficult to reach a reasonable estimate of the potential total annual usage for the product.

6.2.1.b SODIUM CHLORITE ESTIMATES

While the overall scale of the seafood or freshwater fish industry in the United States alone is enormous, surveys of industry need and evaluations of projected interest that have been conducted so far, suggest that the majority of "use interest" for ASC solutions is likely to be seen and expressed primarily by the highly controlled, value-added aquaculture industry. Finfish industries such as those of the deep sea trawling operations etc. appear to be less likely to be interested in utilizing an anti-microbial in the storage, processing or handling of their products. Thus best case "guestimates" of market penetration and market share would suggest that a realistic value for market uptake would be in the order of 25% of the aquaculture industry. Within North America, this market produced a total of 382×10^6 Kg (842×10^6 lbs) of product in 2000. The following table shows the major production species and quantities for the year 2000.

001432

US Aquaculture Market Production by Key Species (2000) and the Estimated Market Uptake for Acidified Sodium Chlorite

	Seafood or freshwater fish Type	Production (million lbs)	25% Market Uptake
Finfish	Baitfish	16.4	NA
	Catfish	596.6	149.2
	Salmon	39.1	9.8
	Striped Bass	9.7	2.4
	Tilapia	17.8	4.5
	Trout	60.3	15.1
Shellfish	Clams	10.7	2.7
	Mussels	0.5	0.1
	Oysters	18.7	4.7
Crustacea	Shrimp	4.6	1.2
	Crawfish	42.9	10.7
Other spp.		24.7	6.2
	Totals	842.0	206.4

As mentioned in the previous section, the projected application rate of ASC solutions onto seafood or freshwater fish has been evaluated in depletion studies and calculated to be in the order of 0.09 mgs/cm² of treated surface (approximately 93 mL/kg, 1.24 Fl. Oz. Per lb). Using this rate of application, the estimated use rate for ASC on seafood or freshwater fish can be recalculated as shown in the following table.

001433

**The Potential Annual Consumption of Sodium Chlorite from use as a
Processing Aid on US Seafood or freshwater fish Derived from
Aquaculture**

	Seafood or freshwater fish Type	25% Market Uptake (million lbs)	Use Volume (million gallons)	Sodium Chlorite (million lbs)
Finfish	Baitfish	NA	NA	NA
	Catfish	149.2	11.563	0.1157
	Salmon	9.8	0.756	0.0076
	Striped Bass	2.4	0.186	0.0019
	Tilapia	4.5	0.349	0.0035
	Trout	15.1	1.170	0.0117
Shellfish	Clams	2.7	0.209	0.0021
	Mussels	0.1	0.008	0.0001
	Oysters	4.7	0.364	0.0036
Crustacea	Shrimp	1.2	0.093	0.0009
	Crawfish	10.7	0.829	0.0083
Other spp.		6.2	0.481	0.0048
	Totals	206.4	16.008	0.1602

The total estimated ASC use volume of 60.60×10^6 L (16.01×10^6 gallons) on aquaculture product equates to a total sodium chlorite use – at the highest application rate of 1200 ppm – of 0.35×10^6 Kg (0.16×10^6 lbs) or 1.4% of the annual production of sodium chlorite in the United States.

001434

6.2.2 WATER AND AIR RELEASES

6.2.2.a INTRODUCTION

The components of the ASC solutions are the GRAS acid, of high purity, and the sodium chlorite (of a technical grade), which has sodium chloride and sodium chlorate as impurities. Upon acidification the chlorite, through chlorous acid, can be expected to minimally transform to chlorine dioxide and to chlorate. At the level of use of these components, and the minimum standing time for the mixed ASC solution, the amount of chlorine dioxide that is dissolved in solution will not exceed *ca.* 2 – 3 mg/liter. Being a highly reactive compound, this chlorine dioxide will quickly be reduced (by reaction with organic matter and with microorganisms on the seafood or freshwater fish surfaces) to even smaller quantities of chlorite and chloride ions. An even lower amount of chlorate will also be formed in this process by a separate pathway involving dis-proportionation of the chlorine dioxide.

As shown from the poultry plant data in previous Section 6.1, the air releases of chlorine dioxide are *de minimis*. Of greater possible interest are the relatively higher levels of sodium chlorite, i.e. 1,200 ppm as a maximum, of which the chlorite ion represents 895 ppm that might be reasonably expected to be disposed of into a processing plant's waste stream. The following projection puts this quantity into relative perspective, with respect to estimates of the total water volume throughput in seafood or freshwater fish processing plants.

Although no specific published data can be found on the quantities of water utilized in the diversity of water-washing operations where seafood or freshwater fish are processed, a projected level of chlorite release into processing plant effluent water can be derived from specific information made available from a current processor of farm raised salmon. In this processing plant, a single day's run of 77,180 Kg (170,000 lb) of salmon required 454,200 L (120,000 gallons) of water and/or ice for processing, in addition to other plant requirements for water such as transport of removed solids and overall plant sanitation. Calculations are confined, for the moment, to processing waters alone, and make use of the ASC application-rate estimate of 93

001435

mL/Kg (1.24 Fl. Oz/lb) of product treated. On that basis, 77,180 Kg of salmon would consume^d 7,177 L (1,896 gal) of ASC solution. This amount of solution would be diluted by the 454,200 L of daily processing water thereby effecting an approximate 63-fold reduction, in the concentration of chlorite in the waste stream. At a maximum use level of 1,200 ppm (1,200 mg/L, 1.25 oz/gal,) of sodium chlorite, the worse-case total amount of this material used per day would be approximately 8.61 Kg^e (18.96 lb), of which 6.42 Kg (14.14 lb) is the chlorite ion. Depletion studies have shown that approximately 10% of the chlorite ion is degraded as a result of the treatment or from reduction through contact with organic matter thus again the worse-case remaining amount of chlorite ion that might ultimately be available for dilution into the 454,200 L of processing water would be approximately 5.78 Kg (12.73 lb), reducing the final chlorite concentration to a theoretical final level of 13 ppm.^f

Since the plant waste-waters from all of the sanitary and house-keeping operations will contain additional organic matter, a major fraction of the available chlorite ion not already consumed, will further degrade on contact with this organic material. Additional factors which would be expected to result in a low to negligible chlorite ion load in the waste-waters of the plant include:

- i) The known instability of chlorite in the ASC system and its ultimate reduction predominantly to chloride.
- ii) The high reactivity of the oxychlorine species (chlorite, chlorate, chlorine dioxide) with soil and organic matter in general. (Refer to Section 7:0 – Fate of Emitted Substances in the Environment).
- iii) The zero chlorite ion profiles that naturally exist in the waste-waters of processing facilities utilizing an ASC system. (Refer to Section 7:0 – Fate of Emitted Substances in the Environment).

The fraction of chlorite that might therefore be expected to survive or remain in the

^d $(77,180 \text{ Kg} \times 93 \text{ ml/Kg})/1000 = 7,177 \text{ L}$

^e $7,177 \text{ L} \times 1200 \text{ mg/L} = 8.61 \text{ Kg}$

^f $5.78 \text{ Kg}/454,200 \text{ L} = 12.73 \text{ mg/L} = 13 \text{ ppm}$

001436

processing plant waste stream to ultimately be transported into an external treatment process such as a POTW is highly likely to be less than the LOD for chlorite i.e. <0.1 ppm.

For chlorate ion, the relative amount present in the waste stream, of a seafood or freshwater fish processing plant, assuming the above worse case scenario would be considerably less than the value calculated for chlorite. While this number can probably be estimated as a fraction of the chlorite that has been calculated, both compounds are expected to be present in such low amounts as to have a *de minimus* effect on local POTWs. For the purposes of this discussion therefore, chlorate levels will also be considered to be present at concentrations < 0.1 ppm.

The levels of acid used to achieve the requisite initial pHs of 2.3 to 2.9 for the ASC solutions are as follows (for a few representative GRAS acids):

- Sulfuric acid, <0.04% (<400 ppm)
- Phosphoric acid, 0.02 to 0.04% (200 to 400 ppm)
- Malic acid, 0.04 to 0.08% (400 to 800 ppm)
- Acetic acid, 0.50 to 1.0% (5,000 to 10,000 ppm)
- Citric acid, 0.50 to 1.2% (5,000 to 12,000 ppm)

These levels are reduced by their subsequent dilution in the same quantities of water used for seafood or freshwater fish washing, transport and plant sanitation and are therefore of little environmental concern.

With respect to institutional or home use of ASC solutions vis-à-vis water discharges, the much greater ratio of organic matter to the small quantity of oxy-chlorine species in the ASC should result in virtually full degradation of these materials upon contact with the facilities' or home's waste systems.

In summary, worse case estimates of the oxy-chlorine species that might be expected to be

001437

present in the waste streams of processing plants that utilize ASC as an anti-microbial intervention on seafood or freshwater fish are:

Chlorine dioxide	<i>de minimis</i>
Chlorite	<0.1 ppm
Chlorate	<0.1 ppm

6.2.2.b IMPACT OF WATER RELEASES

Alcide Corporation does not believe that the above-indicated concentrations of oxychlorine species or food acids will have a negative impact on the operation of POTWs, for the following reasons:

- 1) Neither chlorite, chlorate nor chlorine dioxide is listed as an Interfering Substance in POTWs, as provided in Page 125 of the Wetzel document¹¹. These interfering substances, as contained in certain industrial discharges, can cause "a POTW's noncompliance with its permit or inability to lawfully use or dispose of its sludge." Chloride was listed as a potentially interfering substance, but at a level significantly higher (180 ppm) than its presence either as an impurity in the technical grade chlorite or if all the oxychlorines were converted to chloride. Acidity is also listed as a potential interference in POTW operation, but the levels contributed by this application would not have a measurable impact on pH.
- 2) None of the species present at the levels indicated can interfere with the microbiological treatment systems. Chlorine dioxide, a recognized anti-microbial, will have no effect at the *de minimis* levels estimated; neither can the chlorite, a much weaker source of activity, at the <0.1 ppm level estimated.
- 3) "(M)ost interference problems at POTWs are related to intermittent discharges of high-strength conventional wastes which overload a POTW's

001438

organic capacity, causing plant upset," according to an EPA reporter¹². The organic contribution of these systems is minimal, and the other common causes of plant interference are not a factor here:

- low pH[corrosion]
- solids or viscous pollutants.....[flow obstruction]
- high volatiles[explosion or fire hazard]
- heated discharges[altered biological activity]
- toxic discharges [inhibited biological activity]

6.2.2.c WATER RELEASES – SMALLER FACILITIES

It is anticipated that some ASC usage in the processing of seafood or freshwater fish will be distributed over a wide range of local facilities of low volume production, thereby reducing the "per site" ASC volume.

Because of the diversity of such small-use operations the prediction of specific ASC quantities with respect to other waters in the effluent of a particular type of facility is not feasible.

However it can be readily concluded that the much smaller chlorite and acid quantities in the facility's effluent would be at least as likely to react with and be degraded by the organic matter in its effluent water as in the larger facilities. Once again, the maximum level of oxychlorines (mostly chlorite) that might be expected in the plant effluent of a seafood or freshwater fish processing operation is not expected to be greater than 0.1 ppm. The same basic calculations with respect to impact on POTWs apply.

6.2.2.d AIR RELEASES – LARGER AND SMALLER FACILITIES

As seen earlier, based on the commercial plant data that is available from ASC application in the poultry industry, the spray application of an ASC solution to seafood or freshwater fish is expected to create negligible air levels of chlorine dioxide, in an environment

001439

of normal air turnover, assuming the use of an appropriately designed spray cabinet enclosure to confine its dispersal and to control the gaseous and liquid effluents.

In ASC immersion dip operations, where seafood or freshwater fish will generally have some soil or other organic material on their surfaces this organic matter is also expected to destroy any small levels of chlorine dioxide that may have formed in the solution upon its activation. However, as with the SANOVA commercial spray systems currently used in commercial poultry and beef slaughter facilities, the environs surrounding an immersion or dipping operation in a seafood or freshwater fish processing plant will also be controlled with appropriate enclosures, containment of liquid wastes and positive pressure air venting to the exterior of the building.

6.2.3. RELATION OF PLANT WATER RELEASES TO TOTAL PUBLICLY OWNED TREATMENT WORKS QUANTITIES

The industrial discharges to local Publicly Owned Treatment Works (POTWs), such as might be expected to occur from seafood or freshwater fish processing facilities, are further diluted by discharges from other industrial and non-industrial sources. The previous section of this petition discussed the relationship of such plant discharges to total POTW intakes. Reference was made to an EPA-sponsored study,¹⁵ that provided guidance in minimizing the discharge effects on these POTWs. In this report it was shown that the average influent wastewater from industrial sources was 26.3% of the total intake. That information was used to estimate the projected impact of the seafood or freshwater fish processing facilities using ASC treatments.

Using Alcide Corporation's estimates of market share, the application of ASC on processed seafood or freshwater fish would result in an overall increase in the POTW discharges attributable to sodium chlorite. However, as calculated in Section 6.2.2.a, the contribution from such a processor to its handling POTW is probably no more than the "worse case" estimates of <0.1 ppm.

001440

A similar analogy holds for the food-grade acids used for ASC activation, where the acid contribution to POTW facilities would be *de minimis*.

On the basis of these discussions, Alcide corporation does not believe that the above-indicated concentrations of oxy-chlorine species or food acids will have a negative impact on the operation of POTWs, for the following reasons:

- a) The levels of oxy-chlorines, *i.e.*, chlorite, chlorate, and chlorine dioxide, that would reach the POTWs, is at the parts per billion level, at most. Neither chlorite, chlorate, nor chlorine dioxide is listed as an Interfering Substance in POTWs, as provided in a document listing Interferences at POTWs¹⁵. These interfering substances, as contained in certain industrial discharges, can cause "a POTW's noncompliance with its permit or inability to lawfully use or dispose of its sludge." Acidity is also listed as a potential interference in POTW operation, but the levels contributed by this application would not have a measurable impact on pH.
- b) None of the species present at the levels indicated can interfere with the microbiological treatment systems. Chlorine dioxide, a recognized anti-microbial, will have no effect at the calculated parts per billion level; neither will the chlorite, a much weaker source of activity, at the minuscule levels possibly present.

6.2.4 COMPLIANCE WITH EMISSION REQUIREMENTS

Alcide Corporation fully anticipates that any seafood or freshwater fish processing operation that intends to use the ASC solutions, if deemed appropriate, will obtain the necessary permits and approvals for discharging process waters containing chlorite, chlorate and chlorine dioxide to POTWs. It should be noted that sodium chlorite, used in preparation of these ASC solutions, is an EPA-registered product. It is Alcide Corporation's current intention to use one of three EPA registered sodium chlorite products for the proposed application (or the equivalent):

001441

Vulcan Chemicals 79% Technical Sodium Chlorite, Technical Sodium Chlorite Solution 31.25, or 31% Active Sodium Chlorite Solution. Copies of the Technical Data Sheets and Material Safety Data Sheets for these products are provided in Appendix 2 of this section. Alcide Corporation intends to request that Vulcan Chemicals include label copy, which mandates that users of the sodium chlorite must discharge the solutions in accordance with the requirements of the facility's National Pollution Discharge Elimination System permit. Any warning statements on the labels concerning the hazard of the products to organisms that may be exposed to it in the environment will also be on the labels of the FDA-regulated use.

6.2.5. COMPLIANCE STATUS

Sodium chlorite has a number of commercial uses, primarily as a source of chlorine dioxide, *e.g.*, pulp and paper bleaching, drinking water treatment, as a slimicide in cooling towers, as a food disinfectant, and as a cleaning agent in the electronics industry. The current U.S. production of sodium chlorite is close to 11.16×10^6 Kg.

As shown in Section 6.2.1 of this petition, in the estimates of "worse case" usage that Alcide Corporation has made, the total maximum projected use of sodium chlorite for seafood or freshwater fish, was estimated at 0.35×10^6 Kg (0.16×10^6 lbs) or 1.4% of the total sodium chlorite market in the US. Accordingly Alcide does not believe that approval for the proposed use will affect current compliance by sodium chlorite producers with environmental regulations.

Use of the food grade acid activators is significantly less, of a larger total commercial utilization, and a similar conclusion is drawn for these materials as well.

7 FATE OF EMITTED SUBSTANCES IN THE ENVIRONMENT

7.1. Introduction

Chlorine dioxide (produced from sodium chlorite) is used widely in drinking water treatment in the U.S. When chlorine dioxide reacts in drinking water, approximately 50 - 70% is converted back into chlorite and the remainder into chloride and chlorate. The MCL (Maximum Contaminant Level) for chlorite in drinking water is 1.0 ppm, corresponding to 1.34 ppm sodium chlorite. The Rfd (reference dose) for the chlorate ion is much higher than that for chlorite, and therefore the US EPA (Environmental Protection Agency) has not set a MCL for the chlorate ion. Under The Emergency Planning and Community Right-to-Know Act statute (40 CFR Sect. 313 TRI), the US EPA considers chlorine dioxide releases to the environment at levels below 1.0 ppm to be *de minimis*. Because chlorine dioxide decays rapidly into chlorite, chloride and chlorate, this limit is reflective of the low environmental toxicity of those ions as well.

The chlorite ion is thermodynamically unstable with respect to other chlorine species, e.g., hypochlorite and chloride. It reacts rapidly with Fe(II) and Mn(II) as well as with reduced sulfur species and organic compounds. It is also rapidly degraded photochemically. Consequently, it does not persist in the environment.

In the following, some of the aqueous reactions of the chlorite ion are examined along with its photochemical degradation.

7.2. Chemical Degradation of Chlorite

In acid media, the chlorite ion is in equilibrium with chlorous acid



Below a pH of ~3.5 the following mechanisms predominate



The positive oxidation potentials indicate that the reactions proceed spontaneously as written. The hypochlorous acid, HClO, produced from the second reaction rapidly reacts to produce chloride ion as shown in the following pathway:



This reaction is much faster than that of hypochlorous acid with organics. Consequently, very few chlorinated organics are formed.

At higher pH values, chlorite can degrade by one or both of the following pathways:



Chlorite can also undergo disproportionation reactions (reactions in which two or more molecules of one species react to seafood or freshwater fish one species with a higher oxidation state along with one of lower oxidation state). This is illustrated in the following reaction in which chlorite/chlorous acid (oxidation state +3) decays into hypochlorous acid (oxidation state +1) and chlorate (oxidation state +5):



Fabian ¹⁷ demonstrated that iron(III) catalyzes the decomposition of chlorite. Iatrou *et al.* ¹⁸ investigated the feasibility of using ferrous iron (Fe(II)) to reduce chlorite concentrations.

Laboratory tests indicated a required reaction stoichiometry of 3.0 - 3.1 mg Fe(II)/mg ClO₂⁻. The reaction rate was rapid for pH values of 5 and greater. Interference from dissolved oxygen was minimal. The ferric hydroxide solids produced as a by-product for the Fe(II)-ClO₂⁻ reaction had no adverse effect on alum coagulation for the removal of turbidity and dissolved organic carbon. Iron catalysis of chlorite is an important degradation pathway in both soils and wastewater streams.

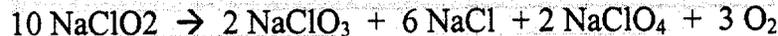
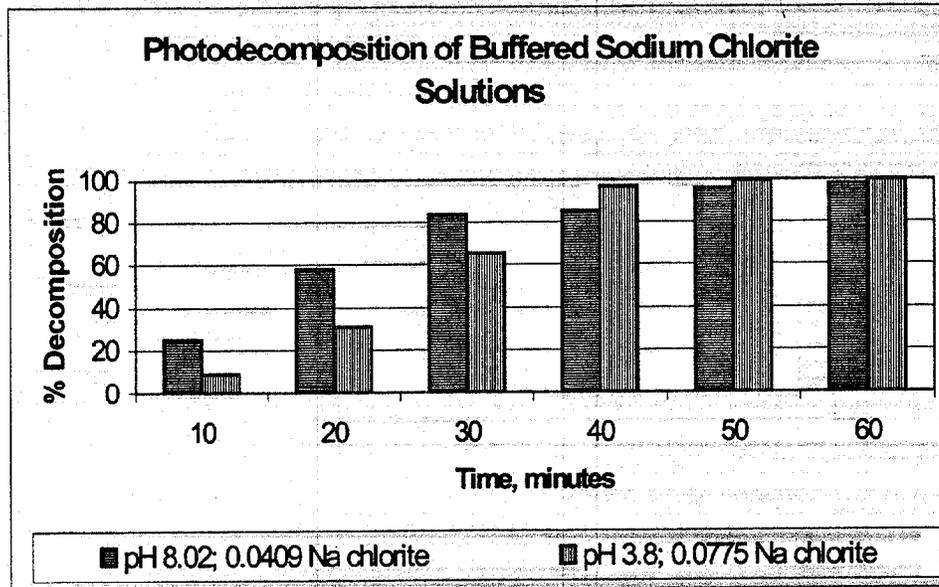
7.3. Photochemical Degradation of the Chlorite Ion

Buxton and Subhani¹⁹ indicated that the chlorite ion undergoes photolytic decomposition to form chlorate, hypochlorite, chlorine dioxide and oxygen. The results of work by Cosson *et al.*¹⁹ suggest that chlorate is not formed by direct photodecomposition of chlorite, but rather by decomposition of chlorine dioxide. Their results are consistent with the stoichiometry



Unless the chlorine dioxide formed from the photolysis of sodium chlorite solutions is removed from solution as soon as it is formed (e.g., via an air sparge) it is rapidly degraded into chlorate and chloride.

In 1964, Nabar *et al.*²⁰ published the results of their work on the photodecomposition of chlorite. The following figure shows their results for the fadeometer decomposition of a 0.0409 N NaClO₂ solution (3699 ppm) buffered at pH 8.2 and a 0.0775 N NaClO₂ solution (7009 ppm) buffered at pH 3.8. The half-life of the higher pH solution was less than 20 minutes; that of the pH 3.8 solution was less than 30 minutes. Decomposition of chlorite solutions by sunlight was reported to be significantly faster. Nabar *et al.* suggested the following photochemical reaction pathways for the degradation of chlorite under alkaline and acidic conditions, respectively:



In other work, Zika *et al.*²¹ found that chlorite has a half-life of less than 10 minutes in direct sunlight. More recently, Wang²² determined that chlorite solutions degraded rapidly (half-life ~ hours) under laboratory fluorescent lighting and even more rapidly in direct sunlight (half-life ~ minutes). This was verified in a field trial at the Los Angeles Country Reservoir²³ in which chlorine dioxide was applied to control algal blooms. Chlorine dioxide was applied at night to give adequate reaction time with the algae present. Within four hours after sunrise, levels of, both chlorine dioxide and its primary degradation byproduct, chlorite, were below detection limits.

7.4. Chlorite Degradation in Soil

In 1999, Certified Laboratories (Plainview, NY) conducted a study (Appendix 3) to simulate the rate of degradation of a spilled chlorite-containing product (Alcide 4XLA Teat Dip, 2400 ppm chlorite acidified with lactic acid to a pH of 3.0). Three different soil samples differing in moisture

and organic content were used. The results are shown in the following table. It was assumed that in a spill the product would be diluted 1:10. The last column gives the time at which the chlorite level was below the analytical detection limit (~20 ppm in the soils studied).

The rate of degradation was clearly a function of organic loading and also of soil moisture. From these samples, chlorite is not expected to be persistent in soils, and consequently will not have an adverse impact on the environment.

Chlorite Degradation in Soil				
Characteristics of Soil Samples				
Sample	Moisture, %	Organics Dry Basis	Organics Soil Basis	Chlorite to "0.0"
A	30.0	13.34	9.34	4 hours
C	3.2	0.72	0.9	8 days
E	44.2	53.07	29.6	8 hours

7.5. Chlorite Degradation in Manure

In another study (Appendix 4), ASC was added to cow manure at an initial level of 229 ppm. Aliquots were analyzed over a two-day period. The results, in the table below, show that the chlorite levels had declined approximately 91% (to the 20 ppm detection limit of the method) within 24 hours.

Chlorite Degradation in Manure	
Exposure time (hours)	[Sodium Chlorite] ppm
0	229
0.33	217
0.75	213
1.25	45
4.0	45
5.0	49
15	45
24	20
48	20

Note: Method detection limit was ~20 ppm.

7.6. Chlorite Degradation in Poultry Processing Waste Waters

A study was conducted to evaluate the persistence of sodium chlorite in typical poultry processing wastewaters (Appendix 5). Samples of wastewater containing spent ASC (ASC) treatment solution were collected from four poultry processing plants immediately prior to discharge to the local POTW (publicly owned treatment works), cooled, and shipped to a third-party laboratory for chlorite analysis. Samples were protected from UV exposure during the analytical process.

The following table gives specifics for the four plants where these samples were taken, as well as the calculated chlorite levels in the wastewater. The ASC solution as applied is 1,000 ppm sodium chlorite. Typically, 90% of the applied solution goes to drain. The sodium chlorite in this spent solution typically measures 900 ppm.

NaClO ₂ Concentrations in 4 Poultry Processing Facilities Using ASC					
Plant	Processing Rate Birds/Day	ASC Usage oz/bird	ASC Usage GPD	Total Plant Wastewater MGD	Calculated [†] [NaClO ₂] ppm
1	232,050	6 oz	10,877	1.5	5.9
2	156,500	6 oz	7,336	1.5	3.96
3	154,833	6 oz	7,258	1.3	7.64
4	170,260	6 oz	7,981	1.2	5.39

[†]Calculated chlorite in plant effluent = ASC Usage 90% (900 ppm/Total Plant Wastewater)

When the samples were analyzed (Ion Chromatography, EPA Method 300.1), both chlorite and chlorate were not detected, indicating that chlorite is not persistent in the environment.

Furthermore, before discharge into the environment these wastewaters are commingled with other industrial wastewater discharges and domestic wastewaters. Assuming a typical POTW processes 25 MGD, any chlorite from the plants is diluted by a factor of 15-20 (25/1.5 to 25/1.2) using the examples above. The resulting calculated concentration of chlorite contribution to the total effluent entering POTW waters would be well below the 1.0 ppm MCL for drinking water, albeit no degradation occurs.

7.7. Conclusion

Theory predicts, and lab studies and analyses of actual samples (soil, manure, wastewater) confirm, that chlorite decays rapidly in the environment and is not expected to exert any adverse impact.

8 ENVIRONMENTAL EFFECTS OF RELEASED SUBSTANCES

8.1 EFFECTS ON AQUATIC ORGANISMS

Summaries of the aquatic-toxicity of relevant oxy-chlorines that might enter the environment as a result of processed seafood or freshwater fish treatment are provided in the next paragraphs. Following the discussion of each specific oxychlorine is a projection of the effects from each of these materials as a result of the treatment of seafood or freshwater fish.

Sodium Chlorite: The LC₅₀ aquatic toxicity to fish and oyster species ranges from 41 to 149 ppm, and from 0.151 to 0.650 ppm for *Daphnia magna* and Mysid shrimp, resp. The US-EPA has determined that sodium chlorite is toxic to fish, on the basis of the *Daphnia magna* figure. It was shown in Section 6.2.2.b. that a theoretical worse case maximum level of about <0.1 ppm of sodium chlorite would reach the typical POTW.

During subsequent waste-water treatment or at the POTW, chlorite will mix with other organic laden waters and be rapidly reduced. For effluents that might not be directed to POTWs, but are directed to catch ponds and leaching beds, the high levels of organic matter in the earth environment would rapidly reduce the chlorite to safe levels before the entraining water reached habitable waters for aquatic species.

Sodium Chlorate: The LC₅₀ for freshwater and marine fish is consistently >1000 ppm.

Sodium chlorate, being a small fraction of the impurities in technical grade sodium chlorite, and forming to a *de minimis* extent during the degradation of ASC solutions, is therefore of no concern from their use in product treatments. This conclusion is also directly applicable to the lower volume use of ASCs for treatment of processed seafood or freshwater fish.

Chlorine Dioxide: The rapidity of degradation of chlorine dioxide in organic

environments, coupled with its *de minimis* production in ASC solutions eliminates any aquatic toxicity concerns from product treatments. This conclusion is also appropriate for effluents resulting from ASC use on processed seafood or freshwater fish.

8.2. EFFECTS ON TERRESTRIAL ORGANISMS

A broad variety of toxicological studies have been carried out on the oxychlorine species chlorite, chlorate and chlorine dioxide, in connection with the worldwide use of chlorine dioxide in the disinfection of potable water. The ClO_2 has been found to seafood or freshwater fish virtually no chlorinated hydrocarbons as potential mutagens, as does chlorine. On a concentrated basis, the oxychlorines have been found to cause oxidative changes to erythrocytes, both in loss of structural integrity and formation of methemoglobin. However at the parts per billion levels that it is expected that these materials will be found in seafood or freshwater fish processing plant effluents, the data obtained in connection with drinking water levels of the oxychlorines are more relevant.

On an acute basis, the toxicity of sodium chlorite is in the range of 300 - 350 mg/kg, based on the LD_{50} values for mice, rats, and guinea pigs. For sodium chlorate, the LD_{50} range from ~600 to 8000 mg/kg for mice, rats, dogs, cats and rabbits. With respect to the acute toxicity of chlorine dioxide, an LD_{LO} of 500 ppm was found for 15 minutes air exposure by rats. In man, a 5 ppm level in the air was found to be an irritant to the respiratory and gastrointestinal tracts. Such levels would not be found in seafood or freshwater fish processing plants.

A variety of sub-acute studies have been conducted on animals and human volunteers, who ingested waters containing up to 40 ppm of chlorine dioxide in a single episode, or 5 ppm solutions of chlorine dioxide or sodium chlorite for a 12 week period. In the latter case there were some effects on blood chemistry, but little other effects. In the former case there was headache, nausea and abdominal discomfort which passed in 5 minutes.

U.S. EPA's recently completed re-assessment of chlorite and chlorine dioxide safety has

established a Reference Dose (RfD) for both of these materials of 0.03/mg/kg/day in drinking water, based on an NOAEL (No Observable Adverse Effect Level) of 3 mg/kg/day and a 100-fold safety factor²⁴. This corresponds to 2.1 mg/kg/day intake of chlorite or chlorine dioxide for a 70 kg individual. The report of the American Water Works Association's evaluation of chlorite and chlorate residues established a NOEL for chlorate of 78 mg/kg/day, which, translates to a maximum intake of 54.6 mg of chlorate per day for a 70 kg person, including the 100-fold safety factor²⁵.

On the basis of the oxidative tendency of these oxychlorine species to be chemically reduced by organic matter in seafood or freshwater fish processing plant waters, and subsequent municipal water treatment facilities, the levels of the three oxychlorine species are anticipated to be significantly lower in waste waters than are the actual levels calculated to be of minimal risk to individuals.

8.3 ENVIRONMENTAL BENEFITS

The use of ASC acid systems for treatment of seafood or freshwater fish offers the possibility of several environmental benefits:

8.3.1 NON-FORMATION OF MUTAGENS AND CARCINOGENS

In those instances where ASC solutions might be used, or are used in place of chlorinated water for disinfecting seafood or freshwater fish surfaces, the potential for the formation of chlorinated organic materials in the environment would be significantly reduced.

8.3.2. REDUCTION IN AQUATIC TOXICITY

Similar considerations would apply to the reduction of hypochlorite in aquatic environments, which has the following toxicity:²⁶

- Cold water fish 0.132 – 135 ppm (LC₅₀-96 hr)
- Warm water fish 0.28 - 2.1 ppm (LC₅₀-96 hr)
- *Daphnia magna* 0.037 - 2.1 ppm (LC₅₀-48 hr)

These data indicate that chlorine/hypochlorite is much more toxic to both cold and warm freshwater fish than is chlorite or chlorate, and generally slightly more toxic to the *Daphnia magna* invertebrate.

001453

9 USE OF RESOURCES AND ENERGY

As estimated earlier in Section 6, in the worse case scenario, if the total seafood or freshwater fish uses of ASC were to follow the market penetration assumptions made, the amount of additional sodium chlorite consumed would be 1.4% of the total present consumption of sodium chlorite. Therefore, the impact on national resources and energy by such incremental use will be of minimal significance. Also no minerals will be used in the preparation or production of the subject additive. Environmental releases of chlorite, chlorate, chlorine dioxide and any of the GRAS acid activators are not expected to adversely affect threatened or endangered species nor impact historic structures.

10 MITIGATION MEASURES

No adverse environmental effects are anticipated from residual "worst-case" levels of chlorine dioxide as a result of any aspect of use of the subject additive, if this petition is approved. Therefore, no mitigation measures are required.

11 ALTERNATIVES TO PROPOSED ACTION

Inasmuch as no potential adverse environmental effects are expected to occur, no mitigation alternative actions are necessary.

12 PREPARER

This Environmental Assessment was prepared by G. Kere Kemp, Chief Scientific Officer of Alcide Corporation. Dr. Kemp has an educational background in Veterinary Science. His 28 years of work experience have been primarily directed toward the fields of microbiology, pharmacology and pharmacotherapeutics with specific focus on the development and registration of novel and unique anti-microbial substances for potential uses in animal, human and industrial applications.

001457

13 CERTIFICATION

The undersigned official certifies that the information presented is true, accurate and complete to the best knowledge of the firm.

Date: November 15th, 2002

Signature: _____

Name: G. Kere Kemp

Title: Executive Vice President

Chief Scientific Officer

001458



14 APPENDICES

Appendix 1. Sodium Chlorite Technical Data Sheets and Materials Safety Data Sheets.

Appendix 2. Carlisle Consulting, Inc. *Air Sampling Survey for Chlorine & Chlorine Dioxide:*
1999, Harrison, Arkansas

Appendix 3. Certified Laboratories, Inc. *Degradation of Chlorite in Soil – Final Report on
Performance of Protocol of 3/24/1999.* 1999, Plainview, NY.

Appendix 4. Certified Laboratories, Inc. *Degradation of Chlorite in Cow Manure.* 1999,
Plainview, NY.

Appendix 5. ABC Research Corporation. *Determination of Chlorite, Chloride and Chlorate in
Waste Stream Waters.* 2000, Gainesville, FL.

001459

PRODUCT SPECIFICATION

Sodium Chlorite (NaClO₂)

Technical Sodium Chlorite Solution 31.25 (25% Active Sodium Chlorite)

COMPONENT

SPECIFICATIONS

Sodium Chlorite, wt% as NaClO ₂	24.25 - 25.75
Sodium Chlorate, wt% as NaClO ₃	0.7 max.
Sodium Chloride, wt% as NaCl	3.0 max.
Total Alkalinity, wt% as NaOH @ pH4	0.5 max.
Hydrogen Peroxide, wt% as H ₂ O ₂	0.01 max.
Water (by difference), wt%	70 - 75

TYPICAL PROPERTIES

Appearance	Clear, slightly yellow liquid
Turbidity, NTU	10 max
Density, lb/gal @ 25°C	10.1 (typical)

Typical properties are listed for information only, and are not to be considered as specification requirements. These items are not analyzed on a routine basis. Product meeting the specification test items will exhibit the listed typical properties.

CONTAINERS:

- Tank Trucks (stainless steel) - 3400 gallon
- Drums - 55 Gallon Plastic Drums, 565 lbs net
- VMC non-returnable 275 gallon tote with steel box and plastic bottle
- Customer provided returnable totes

NSF Listed, ANSI/NSF Standard 60 (Wichita, KS)
Meets requirements of AWWA B303a(2)-97
EPA Reg. No: 5382-43

001461

Form No.: 6-4-0

Sterling Pulp Chemicals

Sodium Chlorite Solution

Product Specifications

Sodium Chlorite Solution 37

Chemical Properties	Units	Typical Analysis	Specification Minimum	Specification Maximum
NaClO ₂	% w/w	38.2	37.0	39.5
NaOH	% w/w	0.38	0.10	0.80
NaCl	% w/w	0.20		0.60
Na ₂ CO ₃	% w/w	0.18		0.50
NaClO ₃	% w/w	0.07		0.35
Turbidity	NTU	0.2		1.0
Specific Gravity	@ 25°C	1.34	1.33	1.36

EPA Registration Number 53345-12

Sodium Chlorite Solution 31 (ERCOPURE 31)

Chemical Properties	Units	Typical Analysis	Specification Minimum	Specification Maximum
NaClO ₂	% w/w	31.2	31.0	31.4
NaOH	% w/w	0.31	0.10	0.68
NaCl	% w/w	0.18		0.51
Na ₂ CO ₃	% w/w	0.15		0.42
NaClO ₃	% w/w	0.06		0.30
Turbidity	NTU	0.2		1.0
Specific Gravity	@ 25°C	1.26		

EPA Registration Number 53345-21

Sodium Chlorite Solution 25 (ERCOPURE 25)

Chemical Properties	Units	Typical Analysis	Specification Minimum	Specification Maximum
NaClO ₂	% w/w	25.2	25.0	25.4
NaOH	% w/w	0.25	0.10	0.55
NaCl	% w/w	0.14		0.41
Na ₂ CO ₃	% w/w	0.12		0.34
NaClO ₃	% w/w	0.06		0.25
Turbidity	NTU	0.2		1.0
Specific Gravity	@ 25°C	1.20	001462	

EPA Registration Number 53345-14

Note: Analytical methods per Sterling Pulp Chemicals' standard methods

EN



APPENDIX 2

001463

CARLISLE CONSULTING, INC.

AIR SAMPLING SURVEY

for

**CHLORINE
&
CHLORINE DIOXIDE**

FOR

Alcide Corporation

At

Alcide Sanova Site 1

on

September 28-29, 1999

October 22, 1999

001464

I. Executive Summary

Carlisle Consulting, Inc. was contracted to perform air sampling services in the evisceration/chiller room of the facility, for the purpose of determining if chlorine or chlorine dioxide was present, and if so, to establish whether the air concentrations found were less than established OSHA permissible exposure limits (PELs) or ACGIH Threshold Limit Values (TLVs).

Samples were collected on September 28th and 29th, 1999 and submitted to DataChem Laboratories, in Salt Lake City, Utah, an AIHA (American Industrial Hygiene Association) accredited laboratory, for analysis. The sampling strategy for this survey was to collect two 15-minute samples and two 4-hour samples at two workplace sample locations, for chlorine dioxide analysis. Also, five 75-90 minute samples and two 15-minute samples were collected for chlorine analysis at these locations.

The Occupational Safety and Health Administration (OSHA) enforces compliance with permissible exposure limits (PELs) for many air contaminants. The American Conference of Governmental Industrial Hygienists (ACGIH) recommends allowable air concentrations for many chemicals, which are called threshold limit values (TLVs). The air concentrations of concern for chlorine dioxide are:

OSHA PEL - .1 ppm (as an 8-hour time-weighted average air concentration, or TWA),
ACGIH TLV - .1 ppm (as an 8-hour time-weighted average air concentration, or TWA), and
ACGIH TLV - .3 ppm (as a 15 minute short term exposure limit, or STEL).

Air concentrations of concern for chlorine are:

OSHA PEL - 1 ppm (as an ceiling concentration),
ACGIH TLV - .5 ppm (as an 8-hour time-weighted average air concentration, or TWA), and
ACGIH TLV - 1 ppm (as a 15 minute short-term exposure limit, or STEL).

Air concentrations calculated from the analytical results were combined in a formula, resulting in an 8-hour time-weighted average air concentration for each sample location, which was then compared to applicable 8-hour employee exposure limits (OSHA PELs and ACGIH TLVs). The 15-minute sample results were used to calculate air concentrations which were compared directly with short-term (15-minute) PELs and TLVs.

The locations sampled were: at the USDA inspection station, and by the entrance end of the chiller. Chlorine dioxide was not detected at these locations. The detection limit was 2 μ g, which resulted in

001465

[REDACTED]

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detection limit air concentrations ranging from 0.097 ppm, for the short-term samples and from 0.0064-0.0066 ppm, for the four-hour samples. Detection limit concentrations vary inversely with air sample volumes, i.e. - the short-term air sample (lower air sample volume) detection limits are greater than the longer term air sample detection limits.

Chlorine was detected in most of the samples analyzed (at low concentrations). The results ranged from undetected to 0.170 ppm, well below applicable occupational exposure limits.

II. Air Sampling and Analytical Methods

Air samples were collected for chlorine dioxide analysis by bubbling air at a known flow rate through approximately 15 ml of an impinger solution (0.02% potassium iodide in a sodium carbonate/sodium bicarbonate buffer) in a standard glass midget impinger. The analytical method (OSHA ID-202) specified the use of special "fritted" impinger nozzles. Sintered glass "frits" allow greater contact between the sampled air and the solution in the impinger. Personal air sampling pumps were calibrated to sample the air at a flow rate of approximately .5 liters per minute. This air sampling pump calibration was performed before and after each sample was collected by using a Gilian Instruments "Giliblator", a primary (NIST-traceable) standard air flow measurement device, with the impinger to be used for sampling in-line. The flow rates measured before and after sampling were averaged. The resulting average flow rate was multiplied by the duration of the sampling period in order to get an air sample volume. The analytical result (reported by the laboratory in micrograms) was divided by the air sample volume (in cubic meters) in order to calculate the air concentration.

Samples were collected for chlorine analysis in a similar manner, using a filter cassette (loaded with a silver membrane filter and teflon prefilter), as specified in the NIOSH (National Institute for Occupational Safety and Health) Analytical Method #6011, at a flow rate of approximately 1 liter per minute.

001466

Samples were collected for comparison with the OSHA and ACGIH 8-hour time-weighted average exposure limits (for chlorine dioxide - two 4 hour samples at two locations, for chlorine - five 75-90 minute samples at two locations) as well as the short-term/ceiling exposure limits (2- 15 minute samples at each of those locations, for chlorine and chlorine dioxide). The two sample locations were chosen based on proximity to the source and potentially exposed workers. The inlet to the sampling device was placed as closely as possible to breathing zone height. The sampling pump, tubing, and impinger (or filter cassette) were placed in a plastic container, before carrying into the processing area and during sampling, in order to alleviate concern about potential breakage.

The analytical method used for the analysis of the chlorine dioxide samples was the OSHA ID-202 method; the liquid impinger solution is analyzed with an ion chromatograph equipped with a conductivity detector and gradient pump. The chlorine analytical method (NIOSH 6011) also uses ion chromatography with a conductivity detector.

III. Discussion of Results

Chlorine dioxide was not detected in the samples collected during this survey (from the entry end of the chiller and at the USDA inspection station).

Chlorine was detected in all but four of the fourteen samples collected on September 28, and all but three of the fourteen samples collected on September 29. The short-term (15-minute) sample results ranged from <0.023 ppm - 0.075 ppm. The time-weighted average chlorine concentrations found were all well below the occupational exposure limits, as shown in the following table:

Location	September 28	September 29
Chiller	0.016 ppm	0.022 ppm
FSIS inspection station	0.014 ppm	0.010 ppm

It should be noted that the OSHA PELs and ACGIH TLVs are personal exposure limits, and are based on the air concentrations in any given worker's breathing zone. Personal exposure to an air contaminant is best estimated by placing the inlet to the sampling device (in this case, the impinger inlet) in the worker's breathing zone, and attaching the air sampling pump (which draws air through the impinger) to the worker's belt or pocket. Because of the possibility for breakage of the glass impingers or sample collection solution spilling in the vicinity of the product, area air monitoring (with the entire sampling apparatus contained) was chosen as the most feasible alternative.

IV. Conclusions

The 8-hr. time weighted average chlorine and chlorine dioxide air concentrations detected on September 28th and 29th at the chiller and drip pan sample locations were low (undetectable amounts of chlorine dioxide and 2-4.4% of the chlorine eight hour ACGIH threshold limit value (.5 ppm TWA).

001467

The short-term (15 minute) samples also resulted in undetectable amounts of chlorine dioxide. The highest chlorine concentration found in the short-term samples collected at these locations was only .075 ppm (7.5% of the OSHA ceiling and ACGIH STEL of 1 ppm).

001468

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**Table 1
Alcide Sanova site 1
Area Air Monitoring
Chlorine Dioxide Results**

OSHA PEL - .1 ppm (8 hr. TWA)
ACGIH TLV - .1 ppm (8 hr. TWA)
- .3 ppm (15 min. STEL)

Samples collected: 9/28/99 (am shift) & 9/29/99 (pm shift)

Sample Number	Area	Total Time (min.)	Average Flow Rate (Lpm)	Sample Volume (m ³)	Mass Found/ Sample ClO ₂ (µg)	Air Concentration ClO ₂ (mg/m ³)	Air Concentration ClO ₂ (ppm)
92802	Chiller, entrance end	226	.50	.11	<	<0.018	<0.0066
92803	USDA station	228	.50	.11	<	<0.018	<0.0065
92808	Chiller, entrance end	15	.50	.0075	<	<0.27	<0.097
92809	USDA station	15	.50	.0075	<	<0.27	<0.097
92820	Chiller, entrance end	225	.50	.11	<	<0.018	<0.0064
92821	USDA station	222	.50	.11	<	<0.018	<0.0065
92832	Chiller, entrance end	15	.50	.0075	<	<0.27	<0.097
92833	USDA station	15	.50	.0075	<	<0.27	<0.097
92834	Blank	-	-	-	<	-	-
92902	Chiller, entrance end	225	.50	.11	<	<0.018	<0.0064
92903	USDA station	225	.50	.11	<	<0.018	<0.0064
92908	Chiller, entrance end	15	.50	.0075	<	<0.27	<0.097
92909	USDA station	15	.50	.0075	<	<0.27	<0.097
92920	Chiller, entrance end	225	.50	.11	<	<0.018	<0.0064
92921	USDA station	225	.50	.11	<	<0.018	<0.0064
92932	Chiller, entrance end	15	.50	.0075	<	<0.27	<0.097
92933	USDA station	15	.50	.0075	<	<0.27	<0.097
92934	Blank	-	-	-	<	-	-

001469

**Table 2
Alcide Sanova site 1
Area Air Monitoring
Chlorine Results**

OSHA PEL - 1 ppm (ceiling)
ACGIH TLV - .5 ppm (8 hr. TWA)
- 1 ppm (15 min. STEL)

Samples collected: 9/28/99 (am shift)

Sample Number	Area	Total Time (min.)	Average Flow Rate (Lpm)	Sample Volume (m ³)	Mass Found/ Sample Cl ₂ (µg)	Air Concentration Cl ₂ (mg/m ³)	Air Concentration Cl ₂ (ppm)
92805	Chiller, entrance end	82	1.0	.082	4.2	0.051	0.018
92806	USDA station	82	1.0	.082	3.4	0.041	0.014
92811	Chiller, entrance end	15	1.0	.015	2.6	0.173	0.059
92812	USDA station	15	1.0	.015	2.2	0.147	0.050
92814	Chiller, entrance end	90	1.0	.090	10	0.111	0.039
92815	USDA station	90	1.0	.090	9.1	0.101	0.035
92817	Chiller, entrance end	98	1.0	.098	1.4	0.014	0.0051
92818	USDA station	98	1.0	.098	<1	<0.010	<0.0035
92823	Chiller, entrance end	90	1.0	.090	1.2	0.013	0.0047
92824	USDA station	90	1.0	.090	<1	<0.011	<0.0044
92826	Chiller, entrance end	90	1.0	.090	<1	0.60	<0.0038
92827	USDA station	90	1.0	.090	1.5	<0.011	0.0059
92829	Chiller, entrance end	15	1.0	.015	1.1	0.073	0.025
92830	USDA station	15	1.0	.015	<1	<0.067	<0.023
92835	Blank	-	-	-	2.3	-	-

8 Hr. TWAs - conservatively calculated (results of "non-detect" included at the detection limit)

Chiller - (Sample numbers - 92805, 11, 14, 17, 23, 26, & 29)

$$[(82 \text{ min.} \times 0.018 \text{ ppm}) + (15 \times 0.059) + (90 \times 0.039) + (98 \times 0.0051) + (90 \times 0.0047) + (90 \times 0.0038) + (15 \times 0.025)] / 480 \text{ min.} = 0.016 \text{ ppm}$$

USDA station - (Sample numbers - 92806, 12, 15, 18, 24, 27, & 30)

$$[(82 \text{ min.} \times 0.014 \text{ ppm}) + (15 \times 0.050) + (90 \times 0.035) + (98 \times 0.0035) + (90 \times 0.0044) + (90 \times 0.0059) + (15 \times 0.023)] / 480 \text{ min.} = 0.014 \text{ ppm}$$

001470

**Table 2
Alcide Sanova site 1
Area Air Monitoring
Chlorine Results**

OSHA PEL - 1 ppm (ceiling)
ACGIH TLV - .5 ppm (8 hr. TWA)
- 1 ppm (15 min. STEL)

Samples collected: 9/29/99 (pm shift)

Sample Number	Area	Total Time (min.)	Average Flow Rate (Lpm)	Sample Volume (m ³)	Mass Found/ Sample Cl ₂ (ug)	Air Concentration Cl ₂ (mg/m ³)	Air Concentration Cl ₂ (ppm)
92905	Chiller, entrance end	75	1.0	.1125	8.9	0.079	0.041
92906	USDA station	75	1.0	.1125	1.2	0.011	0.0054
92911	Chiller, entrance end	15	1.0	.015	<1	<0.067	<0.023
92912	USDA station	15	1.0	.015	3.3	0.22	0.075
92914	Chiller, entrance end	90	1.0	.090	9.6	0.11	0.037
92915	USDA station	90	1.0	.090	2.8	0.031	0.011
92917	Chiller, entrance end	90	1.0	.090	5.3	0.059	0.020
92918	USDA station	90	1.0	.090	2.7	0.03	0.010
92923	Chiller, entrance end	75	1.0	.075	3.9	0.052	0.018
92924	USDA station	75	1.0	.075	1.5	0.020	0.0069
92926	Chiller, entrance end	15	1.0	.015	1.1	0.073	0.024
92927	USDA station	15	1.0	.015	<1	<0.067	<0.023
92929	Chiller, entrance end	90	1.0	.090	<1	<0.011	<0.0038
92930	USDA station	90	1.0	.090	1.4	0.016	0.0053
92935	Blank	-	-	-	<1	-	-

8 Hr. TWAs - conservatively calculated (results of "non-detect" included at the detection limit)

Chiller - (Sample numbers - 92905, 11, 14, 17, 23, 26, & 29)

$$[(75 \text{ min.} \times 0.041 \text{ ppm}) + (15 \times 0.023) + (90 \times 0.037) + (90 \times 0.02) + (75 \times 0.018) + (15 \times 0.024) + (90 \times 0.0038)] / 480 \text{ min.} = 0.022 \text{ ppm}$$

USDA station - (Sample numbers - 92906, 12, 15, 18, 24, 27, & 30)

$$[(75 \text{ min.} \times 0.0054 \text{ ppm}) + (15 \times 0.075) + (90 \times 0.011) + (90 \times 0.01) + (75 \times 0.0069) + (15 \times 0.023) + (90 \times 0.0053)] / 480 \text{ min.} = 0.010 \text{ ppm}$$

001471

CARLISLE CONSULTING, INC.

AIR SAMPLING SURVEY

for

**CHLORINE
&
CHLORINE DIOXIDE**

FOR

Alcide Corporation

at

Alcide Sanova Site 2

on

October 5, 1999

October 22, 1999

001472

I. Executive Summary

Carlisle Consulting, Inc. was contracted to perform air sampling services in the evisceration/chiller room of the facility, for the purpose of determining if chlorine or chlorine dioxide was present, and if so, to establish whether the air concentrations found were less than established OSHA permissible exposure limits (PELs) or ACGIH Threshold Limit Values (TLVs).

Samples were collected on October 5, 1999 and submitted to DataChem Laboratories, in Salt Lake City, Utah, an AIHA (American Industrial Hygiene Association) accredited laboratory, for analysis. The sampling strategy for this survey was to collect two 15-minute samples and two 4-hour samples at each of three sample locations, for chlorine dioxide analysis. Also, five 75-90 minute samples and two 15-minute samples were collected for chlorine analysis at these locations.

The Occupational Safety and Health Administration (OSHA) enforces compliance with permissible exposure limits (PELs) for many air contaminants. The American Conference of Governmental Industrial Hygienists (ACGIH) recommends allowable air concentrations for many chemicals, which are called threshold limit values (TLVs). The air concentrations of concern for chlorine dioxide are:

OSHA PEL - .1 ppm (as an 8-hour time-weighted average air concentration, or TWA),

ACGIH TLV - .1 ppm (as an 8-hour time-weighted average air concentration, or TWA), and

ACGIH TLV - .3 ppm (as a 15 minute short term exposure limit, or STEL).

Air concentrations of concern for chlorine are:

OSHA PEL - 1 ppm (as an ceiling concentration),

ACGIH TLV - .5 ppm (as an 8-hour time-weighted average air concentration, or TWA), and

ACGIH TLV - 1 ppm (as a 15 minute short-term exposure limit, or STEL).

Air concentrations calculated from the analytical results were combined in a formula, resulting in an 8-hour time-weighted average air concentration for each sample location, which was then compared to applicable 8-hour employee exposure limits (OSHA PELs and ACGIH TLVs). The 15-minute sample results were used to calculate air concentrations which were compared directly with short-term (15-minute) PELs and TLVs.

001473

The locations sampled were: near the spray cabinet entrance, at the USDA inspection station, and by the entrance end of the chiller. Chlorine dioxide was not detected in any of the samples. The detection limit was 2 µg, which resulted in a detection limit air concentration of 0.097 ppm, for the short-term samples and from 0.0064 ppm, for the four-hour samples.

Detection limit concentrations vary inversely with air sample volumes, i.e. - the short-term air sample (lower air sample volume) detection limits are greater than the longer term air sample detection limits.

Chlorine was detected in most of the samples analyzed (at low concentrations). The results ranged from undetected to 0.093 ppm, well below applicable occupational exposure limits.

II. Air Sampling and Analytical Methods

Air samples were collected for chlorine dioxide analysis by bubbling air at a known flow rate through approximately 15 ml of an impinger solution (0.02% potassium iodide in a sodium carbonate/sodium bicarbonate buffer) in a standard glass midjet impinger. The analytical method (OSHA ID-202) specified the use of special "fritted" impinger nozzles. Sintered glass "frits" allow greater contact between the sampled air and the solution in the impinger. Personal air sampling pumps were calibrated to sample the air at a flow rate of approximately .5 liters per minute. This air sampling pump calibration was performed before and after each sample was collected by using a Gilian Instruments "Giliberator", a primary (NIST-traceable) standard air flow measurement device, with the impinger to be used for sampling in-line. The flow rates measured before and after sampling were averaged. The resulting average flow rate was multiplied by the duration of the sampling period in order to get an air sample volume. The analytical result (reported by the laboratory in micrograms) was divided by the air sample volume (in cubic meters) in order to calculate the air concentration.

Samples were collected for chlorine analysis in a similar manner, using a filter cassette (loaded with a silver membrane filter and teflon prefilter), as specified in the NIOSH (National Institute for Occupational Safety and Health) Analytical Method #6011, at a flow rate of approximately 1 liter per minute.

Samples were collected for comparison with the OSHA and ACGIH 8-hour time-weighted average exposure limits (for chlorine dioxide - two 4-hour samples at three locations, for chlorine - five 75-90 minute samples at three locations) as well as the short-term/ceiling exposure limits (2 - 15 minute samples at each of those locations, for chlorine and chlorine dioxide). The three sample locations were chosen based on proximity to the source and potentially exposed workers. The inlet to the sampling device was placed as closely as possible to breathing zone height. The sampling pump, tubing, and impinger (or filter cassette) were placed in a plastic container, before carrying into the processing area and during sampling, in order to alleviate concern about potential breakage.

The analytical method used for the analysis of the chlorine dioxide samples was the OSHA ID-202 method; the liquid impinger solution is analyzed with an ion chromatograph equipped with a conductivity detector and gradient pump. The chlorine analytical method (NIOSH 6011) also uses ion chromatography with a conductivity detector.

001474

001485

III. Discussion of Results

Chlorine dioxide was not detected in any of the samples.

Chlorine was detected in all but two of the twenty-one samples collected. The initial sample collected at the chiller location could not be analyzed, because the filter cassette seal opened as the sample was retrieved. The time-weighted average calculated for this sample location assumed that the air concentration during this period was the same as during the second sample period (0.039 ppm). The short-term (15-minute) sample results ranged from <0.067 ppm- 0.093 ppm. The time-weighted average chlorine concentrations found were all well below the occupational exposure limits, as shown in the following table:

Location	
Spray cabinet	0.021 ppm
Chiller	0.023 ppm
FSIS inspection station	0.022 ppm

It should be noted that the OSHA PELs and ACGIH TLVs are personal exposure limits, and are based on the air concentrations in any given worker's breathing zone. Personal exposure to an air contaminant is best estimated by placing the inlet to the sampling device (in this case, the impinger inlet) in the worker's breathing zone, and attaching the air sampling pump (which draws air through the impinger) to the worker's belt or pocket. Because of the possibility for breakage of the glass impingers or sample collection solution spilling in the vicinity of the product, area air monitoring (with the entire sampling apparatus contained) was chosen as the most feasible alternative.

IV. Conclusions

Chlorine dioxide was not detected in any of the samples. The sample results for chlorine were well below applicable occupational exposure limits.

The highest chlorine concentration found in the short-term samples collected was only 0.093 ppm (9.3% of the OSHA ceiling and ACGIH STEL of 1 ppm. Time-weighted average chlorine concentrations were also very low (0.021 ppm- 0.023 ppm).

001475 [REDACTED]
[REDACTED]
[REDACTED]

**Table 1
Alcide Sanova site 2
Area Air Monitoring
Chlorine Dioxide Results**

OSHA PEL - .1 ppm (8 hr. TWA)
ACGIH TLV - .1 ppm (8 hr. TWA)
- .3 ppm (15 min. STEL)

Samples collected: 10/5/99 (am shift)

Sample Number	Area	Total Time (min.)	Average Flow Rate (Lpm)	Sample Volume (m ³)	Mass Found/ Sample ClO ₂ (ug)	Air Concentration ClO ₂ (mg/m ³)	Air Concentration ClO ₂ (ppm)
10501	by spray cabinet	225	.5	.1125	<2	<0.018	<0.0064
10502	Chiller, entrance end	225	.5	.1125	<2	<0.018	<0.0064
10503	USDA station	225	.5	.1125	<2	<0.018	<0.0064
10507	by spray cabinet	15	.5	.0075	<2	<0.27	<0.097
10508	Chiller, entrance end	15	.5	.0075	<2	<0.27	<0.097
10509	USDA station	15	.5	.0075	<2	<0.27	<0.097
10519	By spray cabinet	225	.5	.1125	<2	<0.018	<0.0064
10520	Chiller, entrance end	225	.5	.1125	<2	<0.018	<0.0064
10521	USDA	225	.5	.1125	<2	<0.018	<0.0064
10531	By spray cabinet	15	.5	.0075	<2	<0.27	<0.097
10532	Chiller, entrance end	15	.5	.0075	<2	<0.27	<0.097
10533	USDA	15	.5	.0075	<2	<0.27	<0.097
10534	Blank	-	-	-	<2	-	-

001476

**Table 2
Alcide Sanova Site 2
Area Air Monitoring
Chlorine Results**

OSHA PEL - 1 ppm (ceiling)
ACGIH TLV - .5 ppm (8 hr. TWA)
- 1 ppm (15 min. STEL)

Samples collected: 10/5/99 (am shift)

Sample Number	Area	Total Time (min.)	Average Flow Rate (Lpm)	Sample Volume (m ³)	Mass Found/ Sample Cl ₂ (µg)	Air Concentration Cl ₂ (mg/m ³)	Air Concentration Cl ₂ (ppm)
10504	by spray cabinet	75	1.0	75	7.0	0.093	0.032
10505	Chiller, entrance end		VOID		-	-	-
10506	USDA station	75	1.0	75	9.8	0.13	0.045
10510	by spray cabinet	15	1.0	15	3.4	0.22	0.077
10511	Chiller, entrance end	15	1.0	15	1.8	0.12	0.041
10512	USDA station	15	1.0	15	4.1	0.27	0.093
10513	by spray cabinet	90	1.0	90	12	0.13	0.046
10514	Chiller, entrance end	90	1.0	90	10	0.11	0.039
10515	USDA station	90	1.0	90	7.4	0.081	0.028
10516	by spray cabinet	90	1.0	90	1.5	0.016	0.0056
10517	Chiller, entrance end	90	1.0	90	3.7	0.041	0.014
10518	USDA station	90	1.0	90	2.6	0.028	0.0098
10522	by spray cabinet	75	1.0	75	2.1	0.027	0.0094
10523	Chiller, entrance end	75	1.0	75	2.1	0.027	0.0094
10524	USDA station	75	1.0	75	1.9	0.025	0.0087
10525	by spray cabinet	15	1.0	15	<1	<0.067	<0.023
10526	Chiller, entrance end	15	1.0	15	1.4	0.096	0.033
10527	USDA station	15	1.0	15	<1	<0.067	<0.023
10528	By spray cabinet	90	1.0	90	1.8	0.020	0.0068
10529	Chiller, entrance end	90	1.0	90	3.7	0.041	0.014
10530	USDA station	90	1.0	90	2.5	0.028	0.0096
10535	Blank	-	-	-	<1	-	-

8 Hr. TWAs - conservatively calculated (results of "non-detect" included at the detection limit)

Spray cabinet - (Sample numbers - 10504, 10, 13, 16, 22, 25 & 28), unsampled 30 min. period assumed equal to last sampled period)
[75 min. (.032ppm) + 15(.077) + 90(.046) + 90(.0056) + 75(.0094) + 15(<0.023) + 90(.0068) + 30(.0068)] / 480 min. = 0.021 ppm

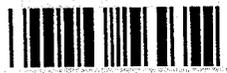
Chiller - (Sample numbers - 10511, 14, 17, 23, 26, & 29) [75 min. (.039 ppm) + 15(.041ppm) + 90(.039) + 90(.014) + 75(.0094) + 15(.033) + 90(.014) + 30(.014)] / 480 min. = 0.023 ppm

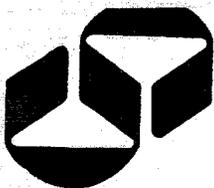
USDA station - (Sample numbers - 10506, 12, 15, 18, 24, 27, & 30) [75 min.(.045 ppm) + 15(.093) + 90(.028) + 90(.0098) + 75(.0098) + 15(<.023) + 90(.0096) + 30(.0096)] / 480 min. = 0.022 ppm

001477

[REDACTED]

[REDACTED]





Certified Laboratories, Inc.

**Degradation
of
Chlorite in Soil
Final Report
on
Performance of Protocol
of
3/24/1999**

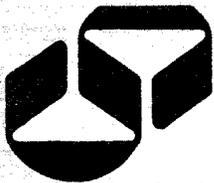
001479

For: Alcide Corporation
May 21, 1999

**Copy
of
Proposed Protocol**

001480





DEGRADATION OF CHLORITE IN SOIL: PROTOCOL OF 3/24/1999

This document reflects changes and refinement in experimental design relative to the protocol dated 2/9/1999. These changes are based on the results of that study.

Significant new text is italicized for clarity.

I. OBJECTIVE

To estimate the rate of degradation of the chlorite ion in soil, simulating conditions applicable to use of 4XLA Teat Dip.

II. BACKGROUND

The study is being undertaken at the request of Alcide Corporation, to satisfy regulatory requirements in the Netherlands. Some parameters of the study are therefore specified by the test protocols in use under the regulatory regime. For example, this study is done at a temperature of 10°C to typify outdoor ambient temperature.

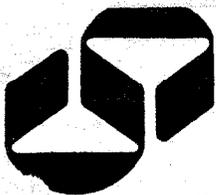
Three soil samples have been provided by Alcide's representative Dr. Robert Kross, that vary in organic content and microbiological load.

III. TECHNICAL ISSUES

The total rate of degradation of chlorite ion is determined by the sum of the rate of reduction of chlorite by materials in the soil and that of any auto-degradation of the chlorite. In a matrix with a high organic load, reduction is likely to be dominant. Under these conditions we believe that the kinetics are likely to be simple as long as the reducing capacity of the matrix is large compared to the amount of analyte added to the matrix. In effect the process will then behave as if it were zero order in terms of constituents of the matrix.

Further, the spiking level chosen for the experiment should be at least as high as any levels likely in the real-life application.

001481



DEGRADATION OF CHLORITE IN SOIL: PROTOCOL OF 3/24/1999

The teat dip contains about 2400 ppm of chlorite ion. If we assume that any spillage of the teat dip is likely to be diluted by a factor of at least 10 by dispersion in soil we expect an initial concentration of chlorite ion equal to no more than 240 ppm in the soil. This would appear to be a reasonable a priori assumption.

Prior experience with chlorite determinations leads us to expect detection limits in the 5-20ppm range in a matrix with high levels of co-extractable. We believe, therefore, that a spiking level of 240 ppm chlorite will meet both of the above requirements. The concentration is high enough to represent a reasonable simulation of the actual conditions and makes for relatively straightforward quantitation, yet low enough that it is unlikely to affect the substrates in the matrix to any great extent.

This study will attempt to determine whether, under these conditions, the concentration of chlorite ion in soil falls below detectable levels within a month.

In order to guard against unexpectedly high reaction rates the chlorite level will be monitored over relatively short intervals in the early stages of the study.

A preliminary evaluation of the protocol has been performed. This protocol reflects the experience of that evaluation.

The study will be run as follows:

A number of sub-samples of soil, sufficient for the number of data points desired, will be treated with a 4XLA solution containing about 2400 ppm chlorite ion, in combination with lactic acid at a pH of ca. 3.0. This will provide about 240 μ g chlorite ion per gram of soil and require only about 0.1ml of solution per gram of soil. Sufficient water will then be added to moisten the soil without leaving any supernatant. This matrix will be mixed and set aside for the appropriate time period.

001482

Sub-samples will be set up in separate centrifuge tubes, one per data point.

Tubes will be taken at appropriate intervals. A known amount of water will be added to facilitate extraction, and a portion of the liquid will be removed after appropriate mixing. This portion will be analyzed by HPLC and the chlorite level will be calculated to reflect the level in the reaction mixture.

**DEGRADATION OF CHLORITE IN SOIL:
PROTOCOL OF 3/24/1999**

IV. EQUIPMENT/MATERIALS

1. HPLC system, isocratic, with autosampler, UV detector at 214nm and Waters Associates IC-PAK Anion HC column, 4.6mm id X 150mm, guard column, borate-gluconate mobile phase specified by Waters Associates.
2. Sodium tetraborate, gluconic acid and acetonitrile (for mobile phase)
3. Sodium chlorite stock solution (supplied by Dr. Kross)
4. Syringe filters, syringes and other consumables as needed
5. Miscellaneous laboratory glassware as needed
6. Circulating water bath or other suitable equipment for maintenance of temperature at 10° C

V. METHODOLOGY

Soil samples have been provided by Alcide Corporation. Bacterial load has been characterized. Samples are being stored under refrigeration.

1. *Prepare a solution containing 2400 ppm chlorite ion (1:1 Aqueous dilution of 4XLA base), at a pH of 10. Call this solution A.*
2. *Take a known weight of soil (3-4 g) in a centrifuge tube.*
3. *Add a quantity of solution A. such that there is 240 ppm chlorite ion on original soil basis. Mix well. Dilute with known amount of water to ensure appropriate mechanical handling.*
4. *Immediately remove an aliquot and filter for HPLC.*
5. *Determine level of chlorite in the extract, expressed as ppm relative to original weight of soil. This provides a time zero level.*
6. *Prepare a 4XLA solution containing 2400 ppm chlorite ion and 1.32% lactic acid at pH 3. Call this solution B.*
7. *In additional centrifuge tubes take similar weighed portions of soil. Add solution B, so as to have 240ppm chlorite on original soil basis. Add enough water to allow for the soil to be moist but not waterlogged. Record the amount of water required and keep consistent for all data points for any given sample throughout the experiment. Mix well and maintain at 10°C.*
8. *At appropriate intervals remove the tubes. Add known amounts of water to dilute the sample and to enable removal of a liquid aliquot from the supernatant. Measure the weight, dilute with a known amount of water and remove an aliquot for HPLC examination.*

001483

**DEGRADATION OF CHLORITE IN SOIL:
 PROTOCOL OF 3/24/1999**

9. Filter through an appropriate membrane filter and measure the chlorite level. Relate back to soil basis.
10. In additional centrifuge tubes take similar weighed portions of soil. Add deionized water. Mix well and maintain at 10° C. Use these as blanks. Ensure that the soil to water ratio is the same as for the samples in the degradation portion of the study. Set up enough blanks to cover the duration of the experiment.
11. Examine the data to obtain an understanding of the rate of degradation.

VI. SCHEDULING

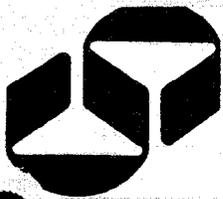
The schedule for the study has been designed to provide 8 days worth of data on day 8 of the study and final data on day 28. Sub-samples will be set up in reverse order, so that all will be ready for analysis, in two batches, one to provide data at day 8, the other to provide data at day 28.

The schedule is as follows:

Day 0 is the day on which the samples will be set up. The blanks will be set up in parallel. The time zero experiment with alkaline chlorite will be set up and performed on day 8.

Reaction time	Day on which set up	Day on which analyzed
8 days	0	8
4 days	4	8
2 days	6	8
1 day	7	8
8 hours	8	8
4 hours	8	8
28 days	0	28
24 days	4	28
20 days	8	28
16 days	12	28
12 days	16	28

001484



**DEGRADATION OF CHLORITE IN SOIL:
PROTOCOL OF 3/24/1999**

VII. FINAL REPORT

The final report will provide documentation of any change in conditions relative to the protocol. Results will be presented graphically, as a plot of the chlorite concentration against time.

The blank data will be used to determine if any baseline problems develop as the experiment proceeds.

VIII. COST

The cost for executing this final protocol will be \$4500.

001485

Final Report

001486



DEGRADATION OF CHLORITE IN SOIL
FINAL REPORT ON PERFORMANCE OF PROTOCOL DATED 3/24/1999
REPORT DATED 5/21/1999

CHARACTERIZATION OF SOIL SAMPLES

Three samples of soil were received from Alcide Corporation. These were characterized as follows:

Sample id	Moisture (%)	Organics (%)	
		Dry basis	Soil basis
A	30.0	13.34	9.34
C	3.2	0.71	0.69
E	44.2	53.07	29.6

The moisture content was determined again at the beginning of the study to allow for an accurate estimate of the effective volume of the final aqueous phase. Results were as follows:

Sample Identification	Moisture content (%)
A	26.55
C	1.81
E	53.12

PREPARATION OF CHLORITE SOLUTIONS

Materials for the preparation of 4XLA Teat Dip were provided by Alcide Corporation. This product consists of a solution of sodium chlorite labeled "4XLA Base", Alcide lot #AC071-014B and one of lactic acid labeled "4XLA Activator", Alcide lot #AC071-014A. Mixing equal volumes of the two solutions produces 4XLA Teat Dip, with a concentration of 2400 ppm of chlorite ion.

All experiments were set up to deliver a nominal 240µg of chlorite ion per gram of soil. Slightly different treatment of the samples permitted the production of more homogeneous reaction mixtures for each sample. Actual levels of added chlorite are documented for each sample.

001487

**DEGRADATION OF CHLORITE IN SOIL
FINAL REPORT ON PERFORMANCE OF PROTOCOL DATED 3/24/1999
REPORT DATED 5/21/1999**

4XLA Teat Dip solutions:

The components for the teat dip were mixed as per the instructions to produce 4XLA Teat Dip at a concentration of 2400 ppm of chlorite ion.

A further 5 times dilution of the 4XLA Teat Dip was made with water, to obtain a solution with a concentration of 480ppm of chlorite ion.

The 2400ppm solution was used for samples A and C. The 480ppm solution was used for sample E. The solutions were prepared immediately prior to use.

Spiking solutions for the time zero experiment

A spiking solution for the time zero experiments was prepared by dilution of the 4XLA Base, as provided by Alcide for preparation of the teat dip, with an equal volume of water instead of the lactic acid solution. This yielded a solution containing 2400 ppm of chlorite ion, but without the acid.

A further 5 times dilution was made with water, to obtain a solution with a concentration of 480ppm of chlorite ion.

The 2400ppm solution was used for samples A and C. The 480ppm solution was used for sample E.

The difference in handling for samples A and C on the one hand and sample E on the other was made necessary by the much higher water-holding capacity of sample E. This is presumably attributable to the much higher organic content. This makes it difficult to distribute a small amount of liquid uniformly through the matrix. Further, the bulk density of sample E appears to be much lower than for the other samples. This also required some adjustment in sample size to keep the volume of sample manageable.

Analytical standards

Analytical standards were prepared by dilution of a 30.7% solution of sodium chlorite provided by Alcide Corporation. These standards provided quite stable response at the HPLC over the duration of the chromatographic work.

**DEGRADATION OF CHLORITE IN SOIL
FINAL REPORT ON PERFORMANCE OF PROTOCOL DATED 3/24/1999
REPORT DATED 5/21/1999**

ADDITION OF CHLORITE TO SOIL

The nominal target level for addition of chlorite ion was 240µg per gram of soil. Each sample was handled in such a way that subsamples, representing different exposure times, were very close in weight. The actual levels were therefore very consistent during this study, thus making the kinetics of the process more obvious.

Actual amounts and spike levels are tabulated below.

Preparation of samples for time zero experiment

A weighed portion of soil was taken in a 50 ml centrifuge tube. Spiking solution was added as tabulated below.

Sample	Sample weight (g)	Spiking solution used	Volume used	Spike level (µg/g soil)
A	8.5	2400 ppm	1 ml	282
C	8.1	2400 ppm	1 ml	282
E	5.2	480 ppm	3.6 ml	332

The solution was mixed into the soil. Water (20 ml) was added. The tube was shaken for 2 minutes to homogenize the aqueous phase and immediately centrifuged for 5min. A portion of the supernatant was removed and filtered through a PTFE membrane filter. The filtrate was used immediately for HPLC analysis.

Preparation of samples for degradation experiments

A weighed portion of soil was taken in a 50 ml centrifuge tube. 4XLA Teat Dip (or the 5X dilution) was added to the soil as tabulated below.

Sample	Sample weight (g)	Teat dip solution used	Volume used	Spike level (µg/g soil)
A	8.5	2400 ppm	1 ml	282
C	8.1	2400 ppm	1 ml	282
E	5.2	480 ppm	3.6 ml	332

**DEGRADATION OF CHLORITE IN SOIL
FINAL REPORT ON PERFORMANCE OF PROTOCOL DATED 3/24/1999
REPORT DATED 5/21/1999**

The solution was mixed into the soil. The sample was set aside for the appropriate degradation period.

At the end of the appropriate period water (20 ml) was added. The tube was shaken for 2 min. to homogenize the aqueous phase and immediately centrifuged for 5min. A portion of the supernatant was removed and filtered through a PTFE membrane. The filtrate was used for HPLC analysis.

Preparation of blanks

A weighed portion of soil was taken in a 50 ml centrifuge tube. Water was added and mixed in to produce a wet sample corresponding to the samples as prepared above. The tube was then set aside for the appropriate storage period.

At the end of the appropriate period water (20 ml) was added. The tube was shaken for 2min to homogenize the aqueous phase and immediately centrifuged for 5 min. A portion of the supernatant was removed and filtered through a PTFE membrane. The filtrate was used for HPLC analysis.

A separate blank was prepared for each sample, for each degradation period.

CHROMATOGRAPHIC CONDITIONS

Mobile phase for HPLC:

Sodium gluconate (16 g), boric acid (18 g) and sodium tetraborate decahydrate (25 g) were dissolved in about 500 ml deionized water. Glycerin (250 ml) was added and the mixture was made up to 1 L with deionized water. This concentrate was kept in the refrigerator and used as needed for production of mobile phase.

The actual mobile phase was made by taking 20 ml of the above concentrate and 120 ml of acetonitrile and making up to 1 L with deionized water.

A flow rate of 2 ml/min provided retention time of about 4 min for chlorite.

The size of the chlorite peak was estimated as the height of the peak above the nominal baseline.

001490



**DEGRADATION OF CHLORITE IN SOIL
FINAL REPORT ON PERFORMANCE OF PROTOCOL DATED 3/24/1999
REPORT DATED 5/21/1999**

Using this height as the estimate of response, chlorite ion concentration was calculated as μg chlorite ion per gram of original soil.

The analytical standards were of concentration 91.6, 45.8 and 18.3 $\mu\text{g}/\text{ml}$, expressed as chlorite ion.

OBSERVATIONS AND CONCLUSIONS

Time zero experiment

Exposure time	Final chlorite concentration (ppm, soil basis)		
	Sample A	Sample C	Sample E
Minimum possible	149	228	204

It may be noted that the time zero experiment is a "best effort" at establishing the level of chlorite detectable at the start of the experiment and is not precisely a measurement at time = 0 seconds. It does represent the absolute minimum time consistent with the handling and extraction operations. Further, for this experiment the chlorite solutions were not acidified with lactic acid. Since the rate of reduction of chlorite ion is higher in acidic media, this experiment provides a worst-case estimate of the level of chlorite recoverable from the matrix at the start of the experiment. In all cases where the actual teat dip (with the acidified solutions) were applied, the corresponding levels would be expected to be lower, given the likely lower reaction rates.

Degradation experiments

Exposure time	Final chlorite concentration (ppm, soil basis)		
	Sample A	Sample C	Sample E
4 hrs	0	109	38
8 hrs	0	85	0
1 day	0	66	0
2 days	0	24	0
4 days	0	7	0
8 days	0	0	0

We include copies of the relevant chromatograms for blanks, the time zero experiment and the extracts for the degradation experiment.

001491

DEGRADATION OF CHLORITE IN SOIL
FINAL REPORT ON PERFORMANCE OF PROTOCOL DATED 3/24/1999
REPORT DATED 5/21/1999

Our conclusions are as follows:

- The chlorite is completely consumed in less than eight days, even for the sample with lowest organic content.
- In sample E, which has the highest organic content (29.6% on as-is soil basis), a starting chlorite concentration of 332 μ g chlorite ion per gram of soil falls below the limit of detection in less than 8 hours.
- In sample A, which has intermediate organic content (9.34% on as-is soil basis), a starting chlorite concentration of 282 μ g chlorite ion per gram of soil falls below the limit of detection in less than 4 hours.
- In sample C, which has the lowest organic content (0.69% on as-is soil basis), a starting chlorite concentration of 282 μ g chlorite ion per gram of soil falls below the limit of detection in between 4 days and 8 days.
- The time zero experiment, which provides the most conservative, worst-case estimate of the starting concentration as actually measured, shows that even under those conditions there is significant degradation at essentially zero exposure time.

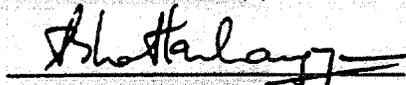
It may be noted that the disappearance of chlorite occurs earlier in sample A than in sample E, even though sample E has the higher organic content. It is reasonable to attribute this to the higher initial level of chlorite in sample E as also to the lower effective concentration in the aqueous phase, given the need to use a larger volume of solution to administer that chlorite level to the bulkier sample E.

Signed:


Yevana Soria
(Analyst)

Date: 05/24/99

Reviewed and approved


Shankar Bhattacharyya
(Manager, Instrumentation,
& Science Officer)

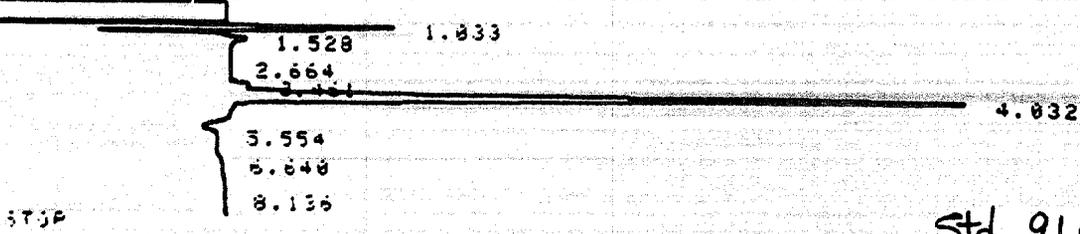
Date: 5/24/99

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* ID STO 91.6/H20

BEST AVAILABLE COPY

RUN # 4492 APR 15, 1999 09:10:48
START



Closing signal file MISIGNAL .BNC

RUN# 4492 APR 15, 1999 09:10:48

SAMPLE NAME: SOIL
METHOD NAME: M*CHLORITE.NET
G/IC-PORT: 2101A

IDENTIFIER: STO 91.6/H20
SIGNAL FILE: MISIGNAL.BNC

CHLORITE

ESTO-MREW

RT	PE	AREA	WIDTH	HEIGHT	CALC	PPM	NAME
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1.528	P	1967569	.546	50090		.000	
2.664	P	3233	.203	265		.000	
3.461	P	116166	.211	9158		.000	
4.032	B	5065213	.261	322635	IR	71.157	CHLORITE
5.554	B	255360	.554	7582		.000	
6.648	B	460364	.793	3676		.000	
8.136	B	228610	1.327	11663		.000	

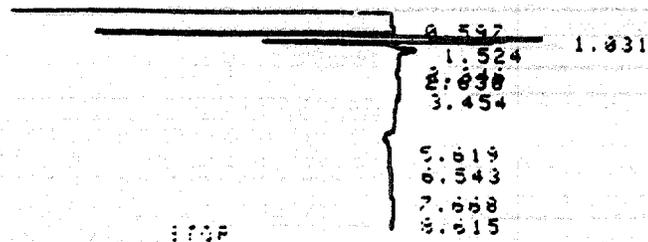
TOTAL AREA=1.0942E+07

MUL FACTOR=1.0000E+00

001493

*10 MWTO BLANK

* RUN # 4496 APR 15, 1999 09:57:13
START



Sample A-Blank
start Exp.

STOP

Closing signal file MSIGNAL .BNC

RUN# 446 APR 15, 1999 09:57:19

SAMPLE NAME: SOIL
METHOD NAME: CHLORITE.MET
G/IC-94732:014

IDENTIFIED MWTO BLANK
SIGNAL FILE: MSIGNAL.BNC

CHLORITE

NO CHLORITE PEAKS FOUND
AREA:

RET	AREA	TYPE	WIDTH	AREA%
1.031	3352341	BP	.542	7.96682
1.524	3312766	PV	.247	7.80294
1.524	581263	VV	.618	13.68799
2.146	4895950	VV	.614	11.53176
2.146	7363650	VV	.706	12.68120
3.474	3884544	VV	1.611	25.51985
3.474	1332456	VV	.319	3.55594
6.543	3445613	VV	1.002	6.53814
7.468	134568	VV	.843	1.14346
8.019	412103	I VH	1.737	1.17194

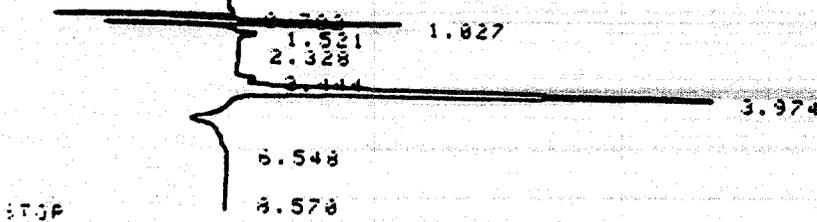
TOTAL AREA=3.1455E+07
MUL FACTOR=1.3866E+00

001494

*10 #M/TOSAMPLE

* RUN # 4497 APR 15. 1999 10:13:43
START

Sample A
Start Exp.



Closing signal file M:SIGNAL .BNC

RUN# 4497 APR 15. 1999 10:13:43

SAMPLE NAME: SOIL
METHOD NAME: M*CHLORITE.MET
G/IC-PART 921014

IDENTIFIER: #M/TOSAMPLE
SIGNAL FILE: M:SIGNAL.BNC

CHLORITE

ESTD-WREA

RT	TYPE	WREA	WIDTH	HEIGHT	CHL#	PPM	NAME
1.027	PP	202274	.127	37155		.000	
1.521	PP	1896309	.209	150950		.000	
2.328	PV	3056629	.552	78107		.000	
3.444	VV	1651900	.523	52660		.000	
3.974	VV	1088755	.550	33014		.000	
6.548	IR	3638358	.371	323762	IR	51.112	CHLORITE
8.578	IR	1359386	1.319	17183		.000	
8.578	M	2126939	1.057	17250		.000	

TOTAL WREA=1.5103E+07

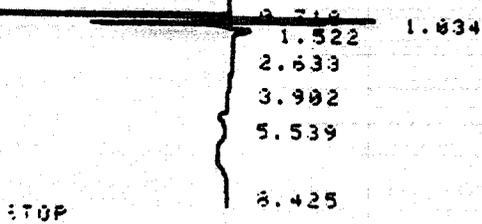
MUL FACTOR=1.0000E+00

001495

NO #C/TO BLANK

RUN # 4498 APR 15, 1999 10:28:43
START

Sample C - Blank
Start Exp.



STOP

Closing signal file M:SIGNAL .BNC

RUN# 4498 APR 15, 1999 10:28:43

SAMPLE NAME: SOIL
METHOD NAME: M*CHLORITE.NET
G:\IC-PORT\32101A

IDENTIFIER : #C/TO BLANK
SIGNAL FILE: M:SIGNAL.BNC

CHLORITE

ESTD-AREA

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	PPM	NAME
0.718	SP	3251862	.386	140495		.000	
1.034	SV	3171010	.239	221486		.000	
1.522	VB	3195765	.582	91478		.000	
2.633	IV	15500	.248	1041		.000	
3.902	IV	125755	.718	2919	IR	1.767	CHLORITE
5.539	FP	311251	.331	4236		.000	
8.425	SV	265472	2.073	2134		.000	

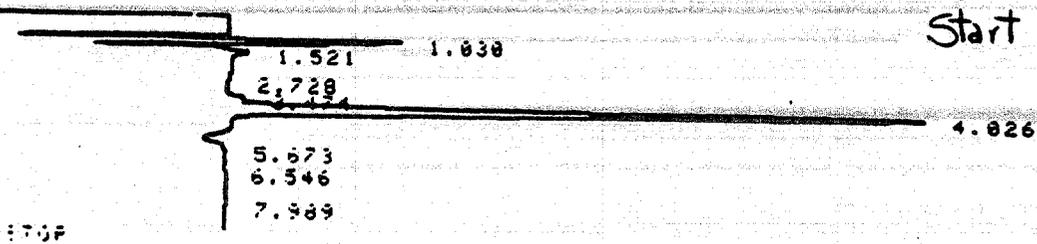
TOTAL AREA=1.0297E+07
MUL FACTOR=1.0000E+00

001496

*10 00/10

* RUN # 4499 APR 15. 1999 10:40:22
START

Sample C
Start Exp.



STOP

Closing signal file SIGNAL.BNC

RUN# 4499 APR 15. 1999 10:40:22

SAMPLE NAME: SOIL
METHOD NAME: CHLORITE.MET
GC (C-PORT) 11914

IDENTIFIED: CHLORITE
SIGNAL FILE: SIGNAL.BNC

CHLORITE

ESTD-NAME

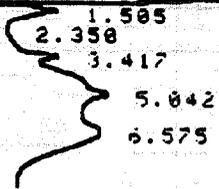
RT	AREA	WIDTH	HEIGHT	CALC	PPM	NAME
1.030	1964066	.210	163922		.000	
1.521	3080208	.615	33471		.000	
2.728	921664	.343	44724		.000	
3.470	1604288	.808	33089		.000	
4.026	5383363	.201	319418	1R	75.626	CHLORITE
5.673	517787	.972	10598		.000	
6.546	234710	.470	10093		.000	
7.989	736603	1.177	11282		.000	

TOTAL AREA=1.4753E+07
MUL FACTOR=1.5000E+00

001497

*10 WE TO BLANK

RUN # 9500 APR 15, 1999 10:59:11
START



STOP

Closing signal file MISIGNAL .BNC

Sample E - Blank
Start Exp.

RUN# 9500 APR 15, 1999 10:59:11

SAMPLE NAME: SOIL
METHOD NAME: M*CHLORITE.MET
G: IC-PM-732101A

IDENTIFIER: WE TO BLANK
SIGNAL FILE: MISIGNAL.BNC

CHLORITE

NO CALIB PEAKS FOUND
WREN%

RT	WREN	TYPE	WIDTH	WREN%
0.900	4750170	SHB	.149	11.36394
1.505	3931714	UV	.756	9.18670
2.350	1144184	UV	.302	2.73726
3.417	5127242	UV	1.000	12.26602
5.042	12592848	UV	1.977	30.12616
6.575	14354224	UV	2.310	34.33994

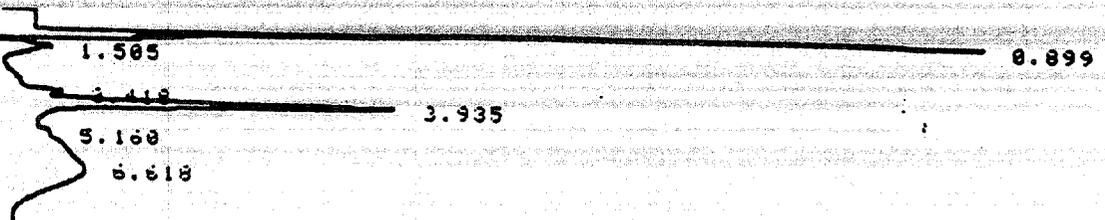
TOTAL AREA=4.1300E+07
MUL FACTOR=1.0000E+00

001498



*10 WE-73

* RUN # 9501 APR 15, 1999 11:15:57
START



STOP

Closing signal file MISIGNAL .BNC

Sample E
Start Exp.

RUN# 9501 APR 15, 1999 11:15:57

SAMPLE NAME: SOIL
METHOD NAME: CHLORITE.MET
G/IC-PRM: 1.0000

IDENTIFIER: 95-70
SIGNAL FILE: SIGNAL.BNC

CHLORITE

ESTD-WPE-

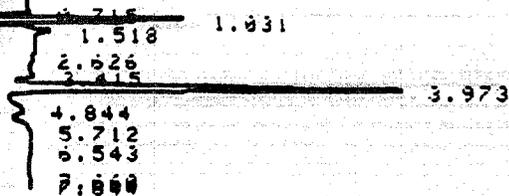
RT	WPE	AREA	WIDTH	HEIGHT	CALC	PPM	NAME
0.899	0.00	4137093	.136	506196		.000	
1.505	0.00	3042218	.657	77213		.000	
3.418	0.00	2931046	1.414	34549		.000	
3.935	0.00	2975654	.296	167327	IR	41.802	CHLORITE
5.160	0.00	134602	.281	7974		.000	
6.618	0.00	2847608	1.806	26286		.000	

TOTAL WPE=1.0000E+00
MUL FACTOR=1.0000E+00

001499

* RUN # 3503 APR 15, 1999 11:33:50
START

STOP



Closing signal file M:SIGNAL .BNC

RUN# 3503 APR 15, 1999 11:33:50

SAMPLE NAME: SOIL
METHOD NAME: M*CHLORITE.MET
G/IC-PORT32101H

IDENTIFIER : STD 45.8 PPM
SIGNAL FILE: M:SIGNAL.BNC

CHLORITE

ESTD-WREN

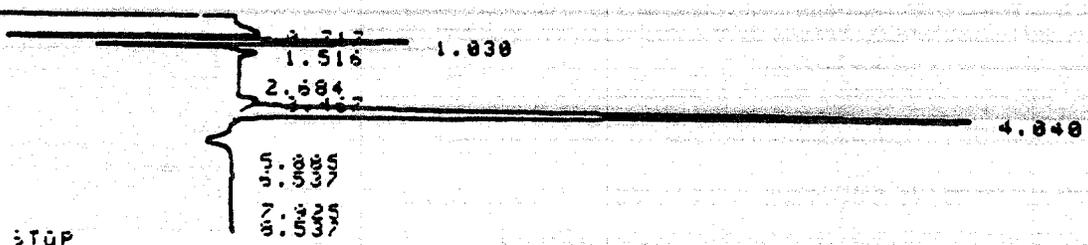
RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	PPM	NAME
0.715	SP	3574302	.463	128704		.000	
1.031	PV	3278085	.243	324487		.000	
1.518	VV	5238432	.566	154256		.000	
2.626	VV	3768722	.516	121494		.000	
3.415	VV	3972282	.625	105988		.000	
3.973	VV	5545421	.358	257876	IR	77.983	CHLORITE
4.844	VV	3783798	.874	78648		.000	
5.712	VV	3534882	1.078	54629		.000	
6.543	VV	1289476	.583	36894		.000	
7.060	VV	1059340	1.415	12475		.000	
7.844	VV	156669	.301	8667		.000	

TOTAL WREN=3.5113E+07
MUL FACTOR=1.0000E+00

001500

*ID STD 91.6 PPM/H2O

* RUN # 9504 APR 15. 1999 11:43:39
START



Closing signal file M:SIGNAL .BNC

RUN# 9504 APR 15. 1999 11:43:39

SAMPLE NAME: SOIL
METHOD NAME: M:CHLORITE.NET
G/IC-PART321014

IDENTIFIER : STD 91.6 PPM
SIGNAL FILE: M:SIGNAL.BNC

CHLORITE

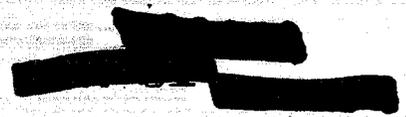
ESTD-MREW

RT	TYPE	MREW	WIDTH	HEIGHT	CAL#	PPM	NAME
0.717	BP	2370206	.446	58552		.000	
1.030	PP	2059223	.208	165100		.000	
1.516	PB	1806140	.527	57135		.000	
2.584	BV	17504	.537	543		.000	
3.467	VV	140730	.232	10112		.000	
4.040	VB	5126291	.262	325550	IR	72.015	CHLORITE
5.335	BV	593010	.370	11901		.000	
6.537	VV	300663	.435	11059		.000	
7.925	VV	378732	1.176	12454		.000	
8.537	VV	646307	.350	12676		.000	

TOTAL MREW=1.4032E+07

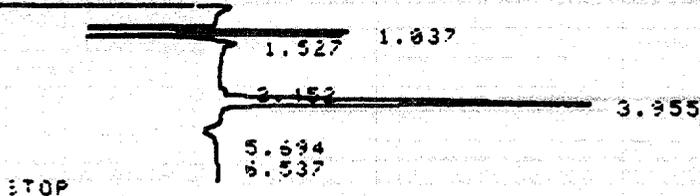
MUL FACTOR=1.0000E+00

001501



*10 45.8/H20

* RUN # 8638 APR 20, 1999 12:40:56
START



Closing signal file M:SIGNAL .BNC

RUN# 8638 APR 20, 1999 12:40:56

Std 45.8 ppm

SAMPLE NAME: SOIL
METHOD NAME: M*CHLORITE.MET
GIC-F-4/T32101A

IDENTIFIER : 45.8/H20
SIGNAL FILE: M:SIGNAL.BNC

CHLORITE

ESTD-HEIGHT

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	PPM	NAME
1.037	BP	2532101	.184	229145		.000	
1.527	BP	1484725	.192	34087		.000	
3.453	BP	30433	.134	6917		.000	
3.955	BP	4502765	.235	326952	1R	50.295	CHLORITE
5.694	BP	713345	.961	12377		.000	
5.537	BP	276818	.397	11627		.000	

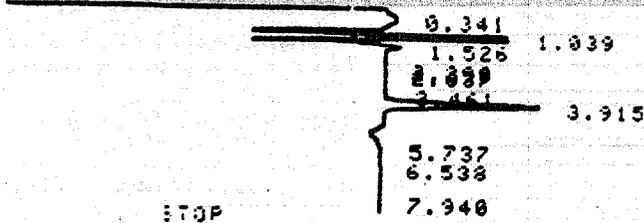
TOTAL HEIGHT= 37:105
MUL FACTOR=1.3000E+00

001502

[REDACTED]
[REDACTED]

*ID TO 18.32 PPM

* RUN # 9634 APR 20, 1999 12:51:05
START



STOP

Closing signal file M:SIGNAL .BNC

RUN# 9634 APR 20, 1999 12:51:05

SAMPLE NAME: SOIL
METHOD NAME: 1*CHLORITE.MET
G/IC-PA-111111

IDENTIFIER: STD 18.32 PPM
SIGNAL FILE: M:SIGNAL.BNC

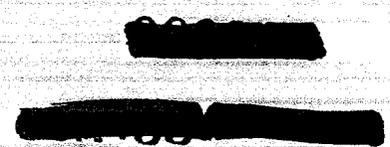
CHLORITE

ESTD-HEIGHT

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	PPM	NAME
0.341	SP	2556437	.848	50229		.000	
1.039	SP	3659370	.193	223776		.000	
1.526	SP	5052675	.715	117795		.000	
2.039	SP	1714515	.392	72863		.000	
3.461	SP	1353977	.430	54413		.000	
3.915	SP	1415150	.612	38552		.000	
5.737	SP	2672178	.285	156432	1R	24.064	CHLORITE
6.538	SP	925771	.923	9446		.000	
7.940	SP	117213	.808	8700		.000	
7.940	SP	686363	1.095	10445		.000	

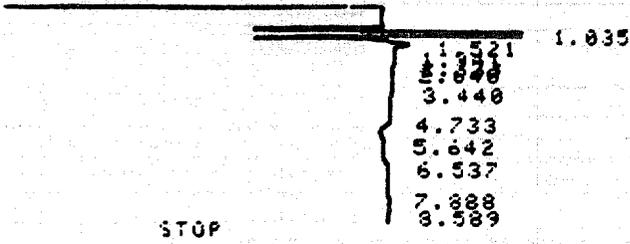
TOTAL HEIGHT= 751646
MUL FACTOR=1.0000E+00

001503



*ID #A/BLANK.4H

* RUN # 9640 APR 20, 1999 13:02:05
START



Closing signal file M:SIGNAL .BNC

RUN# 9640 APR 20, 1999 13:02:05

Sample A - Blank
4 hours

SAMPLE NAME: SOIL
METHOD NAME: M*CHLORITE.MET
G/IC-PAK/T32101A

IDENTIFIED : #A/BLANK.4H
SIGNAL FILE: M:SIGNAL.BNC

CHLORITE

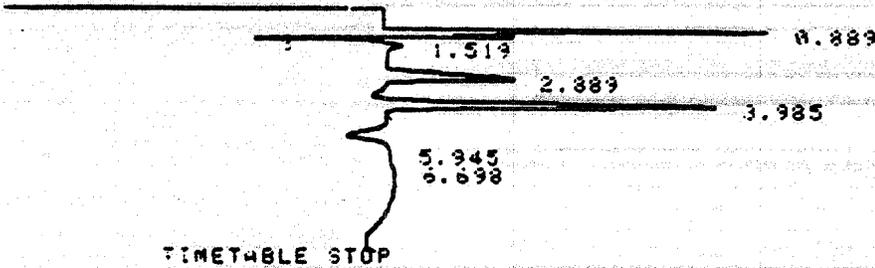
NO CALIB PEAKS FOUND
AREAS:

RT	AREA	TYPE	WIDTH	AREA%
1.035	3140450	< BP	.245	11.39150
1.521	1872574	< PV	.501	14.04716
1.941	1274294	UV	.195	4.62230
2.033	1956493	UV	.475	10.72422
2.640	1759221	UV	.466	10.00864
3.440	4943837	UV	.999	17.93300
4.733	1623607	UV	.461	4.61435
5.642	1279246	UV	.717	3.26761
6.537	1344502	UV	.396	3.52245
7.469	1132640	"	.360	3.33395
8.589	106525	"	.144	0.33436

TOTAL AREA=1.7543E+07
MUL FACTOR=1.0000E+00

001504

* RUN # 9643 APR 20, 1999 13:40:23
START



Closing signal file M:SIGNAL .BNC

RUN# 9643 APR 20, 1999 13:40:23

SAMPLE NAME: SOIL
METHOD NAME: M=CHLORITE.MET
G/IC-P4K/TS21014

Sample C
4 hours

IDENTIFIER : * C/4h
SIGNAL FILE: M:SIGNAL.BNC

CHLORITE

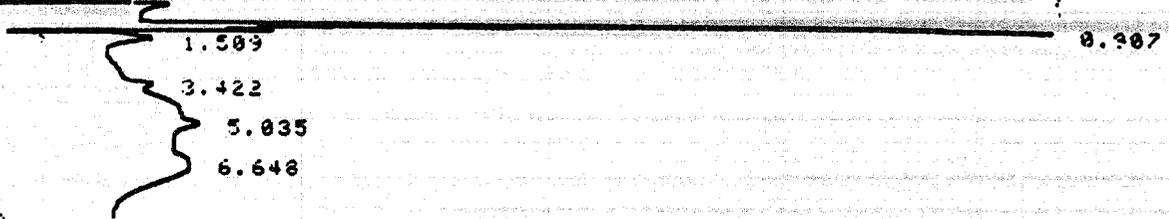
ESTD-WEIGHT

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	PPM	NAME
0.889	SB	4221722	.195	361026		.000	
1.519	SB	2385638	.471	34485		.000	
2.889	SB	2109877	.507	114546		.000	
3.985	SB	4074906	.227	199257	IR	46.835	CHLORITE
5.945	SB	1368985	.576	39394		.000	
6.698	SB	1864677	.729	42645		.000	

TOTAL HEIGHT= 941353
MUL FACTOR=1.0000E+00

001505

* RUN # 4644 APR 20, 1999 13:52:15
START



STOP

Closing signal file M:SIGNAL .BNC

RUN# 4644 APR 20, 1999 13:52:15

SAMPLE NAME: -SIL
METHOD NAME: CHLORITE.MET
G/IC-PCX 1111314

Sample E - blank
4 hours

IDENTIFIED: e blank / 4h
SIGNAL FILE: M:SIGNAL.BNC

CHLORITE

NO CALIB PEAKS FOUND
AREA:

RT	AREA	TYPE	WIDTH	AREAX
8.987	7101859	<SBB	.140	10.88825
1.509	4768099	<BV	.623	7.31024
3.422	4763563	VV	1.269	14.97672
5.035	14553373	VV	1.953	29.87667
6.648	14034176	I VV	2.499	36.84913

TOTAL AREA=6.5335E+07
MUL FACTOR=1.0000E+00

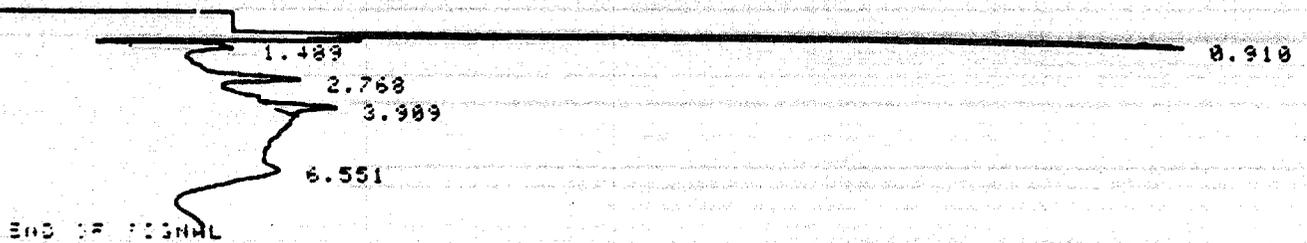
001506

* ZERO 20 2

*RM

RUN # 9646 -PP 20. 1999 14:16:12

STWPT



Closing signal. file M:SIGNAL .BNA

RUN# 9646 APR 20. 1999 14:16:12

SAMPLE NAME: CHL

METHOD NAME: CHLORITE.MET

Q/IC-PAN 11111-

Sample E
4 hours

IDENTIFIED: 1 = e/4h
SIGNAL FILE: M:SIGNAL.BNA

CHLORITE

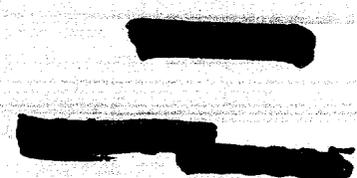
ESTD-HEIGHT

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	PPM	NAME
1.410	BB	8388720	.121	1154675		.000	
1.489	EV	3167362	.445	118497		.000	
2.768		7948589	.755	175522		.000	
3.989		17812736	2.155	288958	1R	32.144	CHLORITE
6.551	W	14125912	1.487	158275		.000	

TOTAL HEIGHT=1115927

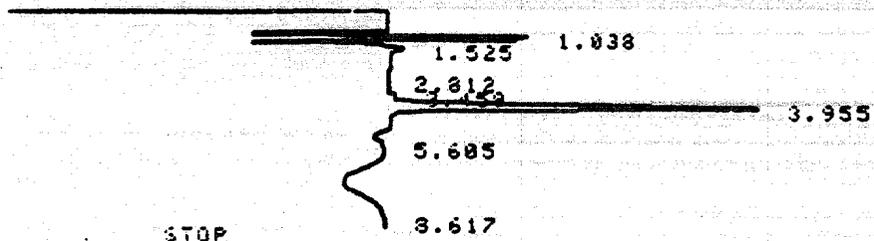
MUL FACTOR=1.0000E+00

001507



IO STD

* RUN # 9647 APR 20, 1999 14:30:36
START



Closing signal file M:SIGNAL .BNC

RUN# 9647 APR 20, 1999 14:30:36

SAMPLE NAME: SOIL
METHOD NAME: M=CHLORITE.MET
G/IC-PAK.T32101A

IDENTIFIER : STD# 45.8 ppm
SIGNAL FILE: M:SIGNAL.BNC

CHLORITE

ESTO-HEIGHT

RT	TYPE	AREA	WIDTH	HEIGHT	CAL#	PPM	NAME
1.038	SP	2654062	.184	240820		.000	
1.525	SP	4499709	.622	120552		.000	
2.812	SP	1933516	.563	57246		.000	
3.459	SP	1350067	.548	41052		.000	
3.955	IR	5327453	.258	344450	IR	52.987	CHLORITE
5.605	SP	1293483	1.187	18156		.000	
8.617	SP	1381065	1.314	17511		.000	

TOTAL HEIGHT= 39787
MUL FACTOR=1.2000E+00

001508