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# THE PRESENT STATE OF DEVELOPMENT OF ANALYTICAL METHODS FOR DETERMINING LOW CONCENTRATIONS OF CHLORIDE ION IN REACTOR WATERS

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# THE PRESENT STATE OF DEVELOPMENT OF ANALYTICAL METHODS FOR DETERMINING LOW CONCENTRATIONS OF CHLORIDE ION IN REACTOR WATERS

## Introduction

The determination of chloride ion at a concentration level of 0.5 ppm ($1.4 \times 10^{-6}$ molar) and under would necessitate reducing the working range of any of our present day methods by at least a factor of ten. Increasing the sensitivity of many of the present day methods would not in any degree be an insurmountable task on a regular laboratory basis; however, extending the range of the methods and simultaneously precluding the possibility of contamination by chloride (which undoubtedly exists aboard ship) will in all probability demand a considerable amount of ingenuity both in instrumentation and in chemical application. In almost any conceivable chemical analysis reagents will have to be added to the sample specimen, and they must be added in such a manner as to avoid any possible chloride contamination. If it were a safe assumption that the chloride concentration in the reactor water was arising only from contamination of sea water it would be far easier to analyze for calcium, for example, by some very sensitive method such as flame photometry. The most desirable method of analysis would be a direct reading instrumental method which circumvents the addition of reagents and minimizes the possibility of contamination.

## Proposed Areas of Investigation

The following areas of investigation appear to be the only alternatives at the present.

1) Emission Spectroscopy
2) Coulometric
3) Colorimetric
4) Radioactive Exchange
5) Potentiometric
6) Catalytic

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Some of these were discussed with Professor John A. Dean of the University of Tennessee and are considered together, some are the result of a brief literature search and others result from the thinking of Dr. Goward and are described in some detail elsewhere. Except for the discussion with Professor Dean, no attempt is made to separate the various contributions.

## Emission Spectroscopy

The possibility of using the emission spectrograph to detect chlorine or chlorates in the concentration range of parts per million or less presents a number of problems. Little or no work has been done on the halogens spectroscopically in comparison to other elements. McNally and workers(1) and Gatterer and Frodl(2) made preliminary investigations within the past 15 years. McNally et al were able to detect Cl in concentrations as low as 10 ppm and their results seem good enough to warrant investigating their technique. The line used was 8375.97A.

One of the investigators used the electrodeless discharge source (Gatterer and Frodl) and the other the hollow cathode source. Their ability to get good results in the above-mentioned concentration range makes either system look attractive. When it is taken into account that they were not using the most sensitive lines of the elements under investigation, but much less sensitive lines, it would leave one to believe that by proper refinement of either technique and the use of more sensitive lines, perhaps concentrations of Cl, F, etc., could be detected in the parts per ten million range or slightly lower on a quantitative basis. The detection of Cl would not be influenced to any great extent by the presence of remains of other elements.

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(1) McNally, et al., J.O.S.A. Vol. 37, No. 2, Feb. 1947.

(2) Gatterer and Frodl. Richerche Specttroscopiche, Vol. 1, No. 7.

Unfortunately, the use of more sensitive lines presents a very difficult experimental problem. The most sensitive lines of Cl (and several other of the halogens) is in the vacuum ultra-violet region of the spectrum. This means that any work carried out, such as photographic spectroscopic, photo-electric detection, etc., must be under vacuum conditions. With the high speed vacuum pumps available at present, this phase of the work would not be as time consuming as in the past. One of the most troublesome aspects of this type of analysis is the source. It must also be operated under vacuum conditions. Window materials to enclose the discharges are of some concern; not many practical optical materials are available. (It might be mentioned that the sensitive lines, i.e., R.U's of Cl are at approximately 1347A). Calcium fluorite is probably the most satisfactory of the commercially available ultra-violet transmitting materials.

If this approach to the detection of chlorine and its complexes could be proven to be satisfactory in regard to sensitivity, very small monitoring instruments could undoubtedly be constructed. At the present time two manufacturers are in a position to supply larger laboratory vacuum spectrographs that could be used in the initial investigation.

## Consultation with Professor Dean

The problem of determining chloride ion in reactor water below the 0.5 ppm level was discussed with Professor J. A. Dean of the University of Tennessee. Professor Dean is a consultant to Oak Ridge and was therefore familiar with the problem since Oak Ridge has also been concerned with the chloride determination as related to stress corrosion.

The possible methods of attack which were discussed include:

(1) Coulometric, or anodic stripping.
(2) Colorimetric.
(3) Radioactive exchange.

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## I. Coulometric

The coulometric method as proposed consists of electrolytically depositing the chloride in the form of mercurous chloride $Hg_2Cl_2$ onto a small mercury electrode or an amalgamated platinum electrode and then reversing the potential in such a manner as to produce a coulometric dissolution of the deposit. This is essentially the course of attack taken by Oak Ridge, however, they have not as yet developed a reliable method. They have apparently been having considerable difficulty in obtaining reproducibility. A similar method was employed by Lord et al(3) in determining silver down to $2.5 \times 10^{-12}$ mole of silver in 20 µ l. of solution. In general the method appears to be capable of handling very low concentrations.

The advantages of this method are:

(1) Small sample size required.

(2) Possible applicability to very low concentrations by increasing sample size and plating time.

The disadvantages are:

(1) An acidic solution must be used (this limitation will very probably apply to any chemical method of analysis, particularly so if mercury is used as one of the constituents).

(2) The method is sensitive to temperature changes, motion of the solution and aging of electrodes.

(3) The data presents itself in the form of a current-time curve, with the area under the curve being proportional to the concentration of chloride. From this must be subtracted a blank correction because of residual current and this blank varies in magnitude with the size of the electrode.

(4) The electrodeposition of chloride will never be 100%. Lord et al, obtained only 80% deposition over extended deposition time with silver. In the case of mercurous chloride the molar solubility in water at room temperature is

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(3) Lord, S.S. and Roger, L.B., Anal. Chem. 24, 209 (1952).

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$0.65 \times 10^{-6}$ molar which produces a $1.3 \times 10^{-6}$ molar chloride solution, whereas 0.1 ppm chloride is approximately $2.8 \times 10^{-6}$ molar and 0.5 ppm is approximately $14.1 \times 10^{-6}$ molar. Hence it is seen that the chloride concentration established by the solubility of the mercurous chloride is only a factor of 10 below the highest limit permissable for the chloride itself. This means that there would be some loss due to the solubility of the deposit. This may not be a serious limitation since comparison against standards would be necessary in any event.

(5) The effect of the phosphate and sulfite on the method is unknown. Sulfate would probably not interfere. Unless the deposition was made in a strongly acidic solution, phosphate would in all probability interfere.

## II. Colorimetric

The colorimetric method developed by Swain(4) and others(5) involves the reaction of the chloride ion with mercuric thiocyanate to liberate the thiocyanate ion which subsequently reacts with an excess of ferric ion to produce a color. The method as developed is applicable to the 1 to 10 ppm concentration range using 4 cm cells.

The disadvantages in applying this are:

(1) It would require the addition of several reagents, hence working in open systems and would therefore run the risk of contamination.

(2) It would be necessary to extend the lower limit of the method by a factor of ten which would probably increase the susceptibility to interference and would probably involve large blank corrections.

(3) Phosphate interferes with the method giving a positive error.

(4) The method would probably be pH and temperature sensitive.

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(4) Swain, J.S., Chemistry and Industry, 418 (1956).

(5) Iwasaki, I., et al, Bull. Chem. Soc. Japan 25, 226 (1952).

The method's only apparent advantage is its simplicity in operation and instrumentation. The complexity of instrumentation would be increased considerably in attempting to adapt the method to a closed system.

## III. Radioactive Exchange

An exchange of radioactive chloride in an insoluble material (fixed phase) with the non-radioactive chloride in the water and the subsequent monitoring of the radioactivity as an indication of the chloride concentration would provide a means of analysis essentially in a closed system and would circumvent the addition of reagents.

The main disadvantages are:

(1) Salts (normally considered insoluble) such as silver chloride or mercurous chloride are probably not usable because their solubility becomes appreciable when considering a chloride concentration of 0.5 ppm or $14.1 \times 10^{-6}$ molar. The molar solubility of silver chloride is $1 \times 10^{-5}$ molar and mercurous chloride is $0.65 \times 10^{-6}$ molar which produces a chloride concentration of $1.3 \times 10^{-6}$ molar. It is evident that the fixed phase or insoluble salt might contribute substantially to the radioactive chloride going into solution not only because of exchange but also because of solubility.

(2) The rate of radioactive exchange in all probability depends to a great extent on the nature of the surface of the fixed phase. The nature of the surface of the fixed phase would be continually changing not only because of exchange with non-radioactive chloride, but also because of the various other materials present in the water which might be absorbed or mechanically attached to the surface. This presents a rather dangerous situation in that a large negative error might result.

(3) The possibility of using an ion exchange type material for the exchange is precluded because the relative large concentration of phosphate, sulfate, sulfite, and sodium hydroxide which would also be exchanged thus liberating radioactive chloride.

The main advantages are:

(1) Assuming that a suitable fixed phase could be found, which had a rapid rate of exchange with the chloride in the water and which was unaffected by pH and the other constituents present, an instrumental method might be developed which would avoid the addition of reagents.

## IV. Additional Comments

Assuming the contamination of chloride ion is from sea water, an analysis for some of the other constituents of sea water, such as sodium, (assuming sodium hydroxide was not used to adjust the pH of the solution) or calcium might give an indirect indication of the level of chloride concentration. A very low concentration of sodium or calcium, for example, is readily detected by flame photometry.

## Potentiometric or Concentration Cell

Electrolytic cells, which consist of a solid material such as mercurous chloride or silver chloride deposited on an inert electrode which is placed in contact with a soluble component such as chloride ion in water, develops a potential proportional to the log of the concentration of the soluble constituent. Cells of this type are generally used in such work as potentiometric titrations and generally respond to concentrations as low as 0.35 ppm. When two such cells are coupled together in which case one is a known standard and the other the unknown; a potential is developed depending on the difference in chloride concentration in the two cells. This is then a direct method of determining the chloride concentration. Such a method has been applied by Gunther, et al(6). Watanabe(7) has developed electrodes or cells usable continuously down to about 3 ppm.

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(6) Gunther, Agriculture and Food Chemistry, 2, No. 16 (Aug. 8, 1954).

(7) Watanabe, Hideo, Beckman Instrument Co., Fullerton, Calif. (Private Communication with Westinghouse APD).

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feasible. The theoretical limitations should be examined in each case in order to establish which, if any, of these approaches offers a fruitful field of endeavor. The exploratory work should then be followed up with a development program aimed at reducing the most feasible approach to the desired limits of concentration.

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