Survey of Chlorine Analytical Methods Suitable for the Power Industry

EPRI

EPRI EA-929
Project 879-1
Interim Report
October 1978

ywords:
Chlorine
Amperometric Titration
DPD
Cooling Water
Iodimetry
Syringaldazine

MASTER

Prepared by
Public Service Electric and Gas Company
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College Park, Maryland

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Prepared by

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ABSTRACT

This report contains the results of a study of four instrumental-electrochemical and two colorimetric methods for chlorine analysis to determine which ones would be most suitable for power plant applications. The methods were: an automated amperometric titration, amperometry (using the NBS chlorine flux monitor), membrane probe amperometry (using the Delta Scientific Multi-Range Analyzer for Chlorine), potentiometry (using the Orion chlorine electrode), as well as methods based on the use of DPD and syringaldazine colorimetric reagents. At this time, we recommend the automated amperometric titration when concentrations below 0.1 mg/L Cl must be determined. A precision of ± 0.0015 mg/L has been obtained with standard solutions using this method for total halogen residual. However, in the future if an improved version of the NBS flux monitor becomes available, it will be an attractive alternative. For situations in which quantification below the 0.1 mg/L level is not needed, the Orion electrode is a comparatively inexpensive alternative, although it should be field tested before being adopted by a power company. The colorimetric methods appear to have inadequate sensitivity for low-level analysis. The claimed specificity of the syringaldazine method for free chlorine disappeared when the method was used in bromide-containing solutions similar to seawater.

EPRI PERSPECTIVE

PROJECT DESCRIPTION

This report describes the laboratory phase of RP879, an effort to evaluate the performance of selected methodologies for determination of chlorine residuals in water. The laboratory phase will be followed by a field evaluation of selected instruments. The work discussed in this report is one aspect of EPRI-sponsored research on biofouling control and the ecological effects of residual chlorine from biofouling control. Research in these areas is being carried out both in the Water Quality Control and Heat Rejection Program of the Fossil Fuel and Advanced Systems Division and in the Ecological Effects Program of the Energy Analysis and Environment Division.

PROJECT OBJECTIVES

The principal objective was to evaluate the ability of selected methods to determine chlorine residuals at levels approaching 0.001 mg/ℓ in both fresh and marine waters. Both instrumental electrochemical and colorimetric methods were studied. The methods selected for study fairly represent most of the principles that have been used for chlorine analysis, but do not include all the procedural and instrumental variations that have been used.

CONCLUSIONS AND RECOMMENDATIONS

Colorimetric procedures based on diethyl-p-phenylenediamine and syringaldazine were found to have inadequate sensitivity in comparison with electrochemical procedures. The automated amperometric titration procedure described in this report was the only procedure evaluated with adequate sensitivity for analysis of chlorine residuals below 0.1 mg/ℓ. At this time, the instrumentation is not portable and requires a skilled operator. Further research on the ability of

iodide to react quantitatively and to be converted to iodine stoichiometrically is recommended, since the accuracy with which a chlorine-produced oxidant can be measured is limited by this factor. This report should be useful to analytical chemists faced with regulatory needs to determine chlorine in power plant effluents, which often presents problems at low levels and saline conditions.

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Section 1

SUMMARY

The requirements for determining chlorine in power plant effluents differ from the requirements in drinking waters for municipal wastewaters in that lower levels frequently must be quantified. Furthermore, in coastal states many power plants depend upon brackish or marine waters for cooling, and the chemistry of chlorine in these waters is different from that in non-saline waters. This report contains the results of a study of four instrumental-electrochemical and two colorimetric methods for chlorine analysis to determine which ones would be most suitable for power plant applications.

The methods were: an automated amperometric titration, amperometry (using the NBS chlorine flux monitor), membrane probe amperometry (using the Delta Scientific Multi-Range Analyzer for Chlorine), potentiometry (using the Orion chlorine electrode), as well as methods based on the use of DPD and syringaldazine colorimetric reagents. At this time, we recommend the automated amperometric titration when concentrations below 0.1 mg/L Cl must be determined. A precision of ± 0.0015 mg/L has been obtained with standard solutions using this method for total halogen residual. However, in the future if an improved version of the NBS flux monitor becomes available, it will be an attractive alternative. For situations in which quantification below the 0.1 mg/L level is not needed, the Orion electrode is a comparatively inexpensive alternative, although it should be field tested before being adopted by a power company. We would not favor any of the colorimetric methods because of poor sensitivity. Extensive tests with DPD revealed a number of potential problems, many of which would not be solved even by the titrimetric variation of this method. One of the main reasons that some people recommend the syringaldazine method is that it detects only free chlorine. However, this selectivity is lost in seawater or in synthetic solutions containing Br^-.

Since all of the methods for determining total chlorine depend upon the use of KI as a catalyst or activator, we have examined potential problems inherent in iodine chemistry. Although we can show that instrumental methods produce very precise and sensitive measurements, the accuracy with which the amount of chlorine produced oxidants can be measured, particularly in seawater, may be limited by the ability of iodide to react quantitatively and to be converted to iodine stoichiometrically. More research on this question is needed.

Section 2

INTRODUCTION

STATEMENT OF THE PROBLEM

Chlorine has been used in water disinfection for almost a century. In recent decades, it has also been used to control biofouling in cooling waters of electric power plants and similar industrial installations which must discharge waste heat. In the past few years considerable concern has arisen among environmental scientists over the possibility of adverse effects of chlorinated discharges on aquatic organisms. This has led to pressure on utility companies to reduce and to monitor closely their chlorine discharges.

Historically, virtually all of the research which has been conducted on methods for chlorine analysis has been done with applications to drinking waters or wastewaters in mind. For a number of reasons, the analytical requirements for monitoring power plant discharges are quite different from the requirements for monitoring drinking waters and wastewaters. For example, regulations governing discharges from power plants normally specify a maximum allowable level in the discharge effluent, the intent being to protect organisms in the receiving water. On the other hand, regulations governing drinking waters and wastewaters usually specify a minimum allowable level, the intent being to insure adequate disinfection. The practical consequence of this difference in philosophy is that analysts who monitor power plants must work accurately at much lower levels. Indeed, the newly approved Water Quality Control Plan for Ocean Waters of California specifies a 6 month median limitation of 0.002 mg/L Cl, at least two orders of magnitude below levels commonly measured in the disinfection applications. Another important difference is

that many power plants employ estuarine or marine waters for cooling. The chemistry of chlorine in seawater is appreciably different from that in freshwaters and wastewaters, and the need to determine chlorine in seawater adds new complexities to the analyst's task.

The number of analytical methods available for monitoring chlorinated discharges is overwhelming. Standard Methods for the Examination of Water and Wastewater (1), an influential reference work in the disinfection field, lists 8 alternate methods. Not included are methods based on several newer devices and instruments. The principal aim of the present 12 month study has been to examine some of these methods in the light of the need to determine chlorine residuals at very low levels (i.e. approaching 0.001 mg/L) in both non-marine and marine waters.

The methods selected for evaluation were the amperometric titration, amperometry itself (using the National Bureau of Standards chlorine flux monitor), the membrane probe (Delta Scientific), the Orion chlorine electrode, several variations on the DPD method, and the syringaldazine (FACTS) method. This selection gives fair representation to most of the analytical principles which have been exploited for chlorine analysis, but does not include testing of all procedural and instrumental variations that have been used in the application of these principles. Such testing would be far beyond the scope of a 12 month study. Our principal aim is not to recommend a specific instrument or a specific procedure for use by utility companies, but rather to identify the one or two general methods which offer the best prospect of fulfilling the chlorine analysis requirements at power plants.

NOMENCLATURE

It is well known that when chlorine is used in disinfection, a variety of by-products form. It is often possible to classify these products according to analytical behavior into free chlorine ($HOCl$, OCl^-, Cl_2) and combined chlorine (inorganic and organic chloramines). When chlorine is added to estuarine or marine waters, however, reactions with Br^- in seasalt give rise to many additional bromine containing oxidants ($HOBr$, OBr^-, Br_2, inorganic and organic bromamines, etc.). In the course of this work we have shown that at least some analytical methods which are intended to distinguish free chlorine may, in marine waters, detect certain other species, such as NH_2Br. Thus a clean, operational segregation of "free" species from "combined" species is not always achievable and the terms become meaningless. Elsewhere (2,3), we have suggested that the by-products of chlorine in water of unspecified salinity might best be described as Chlorine Produced Oxidants, rather than as chlorine, and that these by-products should be reported on a μN basis. However, since this procedure might confuse some readers, we will continue to use here the more familiar mg/L Cl (ppm) unit. The use of this unit does not imply that the oxidant residual necessarily consists of chlorine species. To convert these numbers into μN units, simply multiply by 28.2.

Section 3

IODINE CHEMISTRY

All methods which claim to measure total chlorine produced oxidants employ iodide salts (normally KI) at some stage. The main purpose in most instances is to catalyze what would otherwise be a sluggish or negligible response to certain oxidant fractions. In some cases these salts are additionally used to control ionic strength, to retard volatilization, or to serve other functions. Thus if errors are introduced into an analysis by imperfect behavior of iodine, all methods will be adversely affected. For this reason we will discuss iodine chemistry at the outset of this report, rather than discussing it repeatedly later.

A generalized reaction between a chlorine produced oxidant and iodide can be written as follows:

$$R\text{-}X + 2I^- + H^+ \rightarrow I_2 + R\text{-}H + X^- \qquad (1)$$

where X represents a halogen atom. For relatively strong, labile oxidants, such as HOCl, HOBr or NH_2Cl, this reaction goes spontaneously to the right even at neutral pH ($H^+ = 10^{-6}$-10^{-8}) and relatively low I^- concentrations. For more inert oxidants, e.g. $NHCl_2$, the reaction must be encouraged by increasing I^- and H^+. By controlling I^- and H^+, one can in principle selectively determine the concentrations of different oxidant fractions. The iodine generated can be measured volumetrically by titration with a standard reducing agent, voltammetrically by cathodic reduction, potentiometrically with an inert electrode, or spectrophotometrically by its reaction with an indicator or by its absorbance in the ultraviolet region. Several excellent reviews of iodometry and its applications exist (4-9).

OXIDANT SPECIES

To understand what takes place during analysis of chlorine produced oxidants with iodine, it is helpful to know what chemical species are likely to be present and what reactions must take place. During the course of this work we modified a previously developed thermodynamic model for oxidant speciation in marine waters (2-3) to include systems either containing natural iodine or to which iodide had been added. The computer calculations based on this model provide a somewhat idealized picture of the actual speciation, because it is assumed that the oxidant species achieve metastable equilibrium with respect to one another and because oxidative organic compounds such as organic halamines are neglected. There is evidence that the metastable equilibrium assumption may be reasonable for estuarine waters where bromine species are dominant, but it may not be reliable for freshwaters where kinetically sluggish chloramines are important.

The calculation of the oxidant species distribution is based on the use of the 5 conservation equations:

$$\text{Total } m_{Cl} = m_{Cl^-} + 2\, m_{Cl_2} + 3\, m_{Cl_3^-} + m_{OCl^-} + m_{HOCl} + m_{BrCl} + 2\, m_{BrCl_2^-} + m_{Br_2Cl^-} + 6\, m_{BrCl_6^{5-}} + m_{NH_2Cl} + 2\, m_{NHCl_2} + 3\, m_{NCl_3} \quad (2)$$

$$\text{Total } m_{Br} = m_{Br^-} + 2\, m_{Br_2} + 3\, m_{Br_3^-} + 5\, m_{Br_5^-} + m_{OBr^-} + m_{HOBr} + m_{BrCl} + m_{BrCl_2^-} + 2\, m_{Br_2Cl^-} + m_{BrCl_6^{5-}} + m_{NH_2Br} + 2\, m_{NHBr_2} + 3\, m_{NBr_3} \quad (3)$$

$$\text{Total } m_N = m_{NH_2Cl} + m_{NHCl_2} + m_{NCl_3} + m_{NH_2Br} + m_{NHBr_2} + m_{NBr_3} + m_{NH_3} + m_{NH_4^+} \quad (4)$$

$$\text{Total } m_I = m_{I^-} + 2\, m_{I_2} + 3\, m_{I_3^-} + m_{OI^-} + m_{IO_3^-} + m_{HOI} \quad (5)$$

$$\text{Total } m_{oxidant} = m_{Cl_2} + m_{Cl_3^-} + m_{OCl^-} + m_{HOCl} + m_{BrCl}$$
$$+ m_{BrCl_2^-} + m_{Br_2Cl^-} + m_{BrCl_6^{5-}} + m_{NH_2Cl}$$
$$+ 2\, m_{NHCl_2} + 3\, m_{NCl_3} + m_{Br_3} + m_{Br_3^-}$$
$$+ 2\, m_{Br_5^-} + m_{OBr^-} + m_{HOBr} + m_{NH_2Br}$$
$$+ 2\, m_{NHBr_2} + 3\, m_{NBr_3} + m_{I_2} + m_{I_3^-}$$
$$+ m_{OI^-} + 3\, m_{IO_3^-} + m_{HOI} \qquad (6)$$

These equations are solved simultaneously through the use of equilibrium expressions to reduce them to 5 equations containing the activities of only 5 components as variables. The components chosen are a_{Cl^-}, a_{Br^-}, a_{NH_3}, a_{I^-} and a_{e^-}. (For a detailed account of these computational procedures see (3)).

The results of this oxidant species calculation are shown in Figures 3-1 and 3-2, which represent seawater (34 g/kg salinity) and estuarine water (3.5 g/kg salinity), respectively. Figures 3-1a and 3-2a show the equilibrium distribution of oxidant species as a function of pH for a water containing 1 mg/L chlorine and 0.10 mg/L NH_3-N in the absence of any added iodide; 0.10 mg/L NH_3 is higher than free ammonia itself would normally be in coastal waters but is in the range of typical total amino nitrogen values. Organic amines and amino acid should behave qualitatively similar to NH_3. Lower NH_3 values result in the bromamines, shown in Figures 3-1a and 3-2a, being replaced by HOBr and OBr^-. Figures 3-1b,c,d and 3-2b,c,d, illustrate the oxidant species distribution when 25 mg/L, 250 mg/L and 2500 mg/L KI are added to these same waters.

The most important point to be made is that all the bromine oxidant species present in seawater are unstable with respect to the iodine species. They are all capable of reacting quantitatively with I^- to form I_2, I_3^- and IO_3^-. Although the rates for the conversions of many of these species to iodine

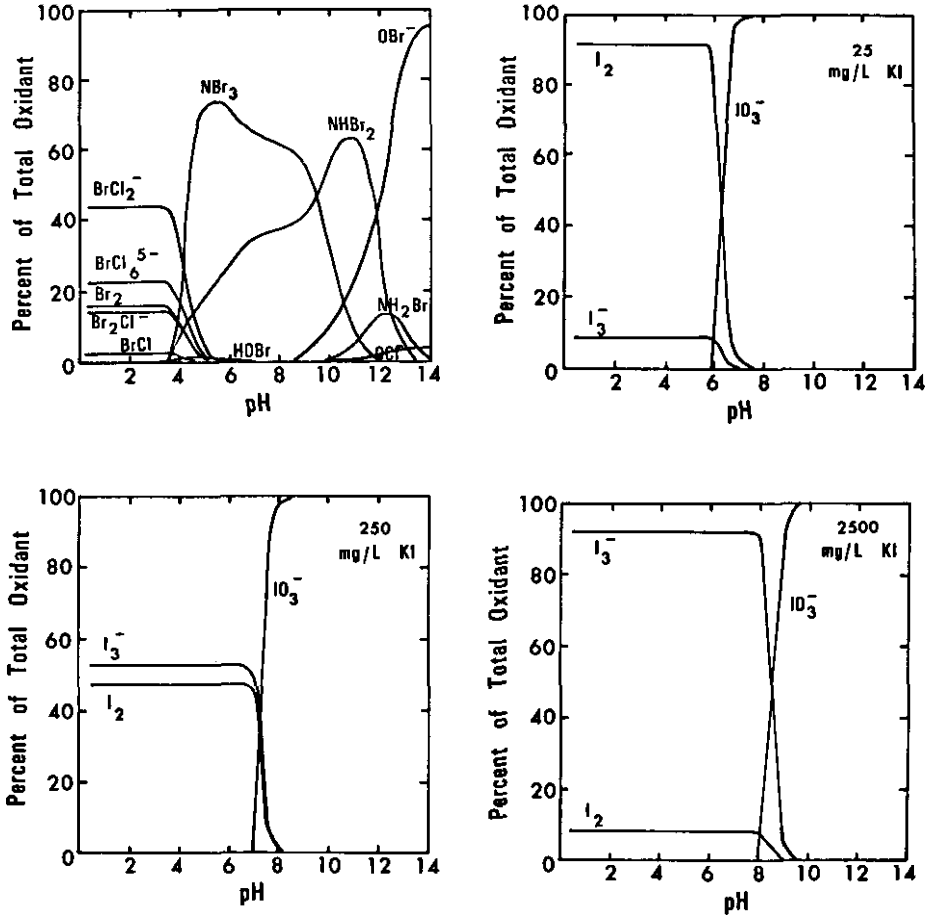


Figure 3-1. Oxidant speciation in seawater (35 g/kg salinity) and in seawater with varying amounts of added KI. Total amino nitrogen is 0.1 mg/L and total oxidant is 1 mg/L as chlorine. Temperature is 25°C.

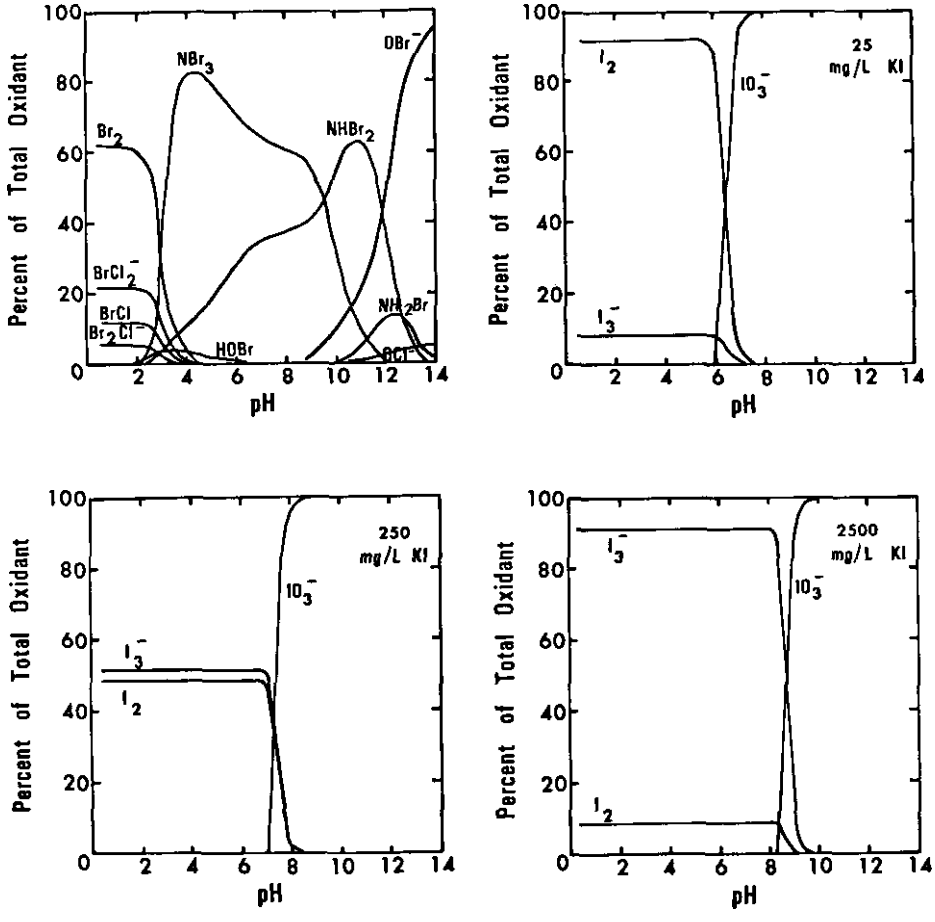


Figure 3-2. Oxidant speciation in estuarine water (3.5 g/kg salinity) with 0-2500 mg/L KI added. Total amino nitrogen, total oxidant, and temperature are the same as in Figure 3-1.

species are not known, our laboratory experience suggests that except for formation of IO_3^- they probably occur very rapidly. The results show that there is little difference in the iodine species present at equilibrium as a result of decreasing salinity. Both the seawater and estuarine water exhibit the same characteristics. The proportion of I_2 to I_3^- is controlled by the concentration of I^- added as expressed by reaction 7:

$$I_2 + I^- \rightleftarrows I_3^- \qquad (7)$$

This is an important consideration for systems which employ an amperometric response because the electrode is most sensitive to I_2 (8).

The stability of IO_3^- depends upon the pH and the I^- concentration. At low KI concentrations (25 mg/L KI), IO_3^- is stable above pH 6.5. As the I^- concentration increases, the IO_3^- stability field moves to higher pH levels as seen in the figures. Therefore, based upon thermodynamic considerations, one can destroy IO_3^- by increasing KI and reducing pH.

SOURCES OF ANALYTICAL ERROR INHERENT IN IODINE CHEMISTRY

With the foregoing introduction to oxidant speciation, we can now proceed to consider the many potential sources of error that might enter into the analysis of chlorine produced oxidants at low concentrations.

NATURAL IODATE

Seawater contains about 0.06 mg/L of total elemental iodine. Rivers and lakes contain on the average about 0.002 mg/L. Iodine is probably very nearly conserved during mixing of rivers with the ocean, so estuaries would be expected to have intermediate iodine contents given approximately by

$$I = 0.00166S + 0.0018 \quad \text{(in mg/L)} \qquad (8)$$

where S is the salinity in g/kg. Wong and Brewer (9) and others have shown that most of the iodine present in oxygenated surface ocean waters is present as IO_3^-. This is consistent with thermodynamic predictions from our model. Every mg of IO_3^- has the same oxidizing capacity as 1.22 mg of chlorine. Thus, if an analysis is performed under conditions where IO_3^- is detected, then from this source there will be a background, or blank, oxidant level, expressed in mg/L chlorine, of up to:

$$\text{Background Oxidant} = 0.00203\ S + 0.0022\ (\text{mg/L Cl}) \qquad (9)$$

In full strength seawater, this is equivalent to 0.07 mg/L chlorine. Clearly, if chlorine produced oxidant levels are to be quantified below the 0.01 mg/L level, even a minor, sub-stoichiometric contribution of IO_3^- to the analytical signal could produce a large error, assuming that the quantity being sought is the amount of chlorine produced oxidant.

Generally speaking IO_3^- is too inert to be detected by most of the electrochemical and spectrophotometric procedures discussed in this report. However, it can be activated by I^-, which is added in many of the procedures. The reaction:

$$5I^- + IO_3^- + 6H^+ \rightarrow 3I_2 + 3H_2O \qquad (10)$$

has been shown by Abel and Fabian (10) to obey the rate law:

$$\text{Rate} = k\ (I^-)^2 (IO_3^-)(H^+) f \qquad (11)$$

where $k = 5.2 \times 10^8$ moles^4/liter^4-sec, and f is the activity coefficient for univalent ions. The time for this reaction to reach > 99% completion, and thus for the system to approach equilibrium as shown in figures 3-1 and 3-2, is plotted as a function of pH for various KI levels in Figure 3-3. These results agree quite well with the work of Carpenter et al (11), who reported the appearance of I_3^- from IO_3^- in solutions with high I^- content and acid pH. For example at pH 3.5 and KI = 4000 mg/L, a calculation would show that the reaction requires 7 minutes to reach > 99% completion, while Carpenter et al's (11) experimental work shows that I_3^- formation is essentially complete in ~8 minutes.

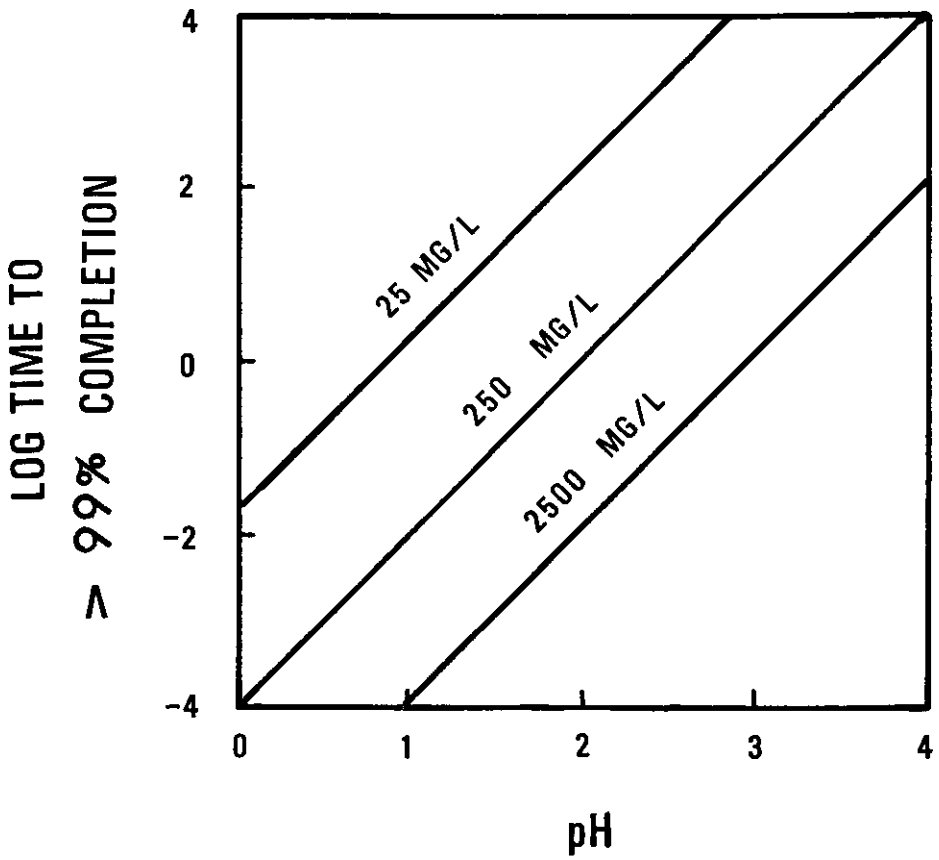


Figure 3-3. Time in minutes needed to convert IO_3^- to I_2 as a function of KI concentration which is represented by numbers on the contours. Temperature is 25°C.

Calculations also show that in seawater containing IO_3^- equivalent to 0.07 mg/L chlorine, 1% of this would be converted into the active, I_2, form in 0.2 min at pH 4.0 and KI = 250 mg/L. This pH and KI concentration is commonly employed for analysis of total chlorine produced oxidants. Conversion of the background iodate to analytically active I_2 can be diminished by increasing pH or reducing the KI concentration, but these strategies lead to other analytical problems.

OXYGEN INTERFERENCE

Potassium iodide stock solutions are subject to oxidation by the following type of reaction:

$$4I^- + O_2 + 4H^+ \rightleftarrows 2I_2 + 2H_2O \qquad (12)$$

This is so slow, however, that in neutral solutions it is not a problem. The reaction is accelerated by decreasing pH, by light, and by traces of cupric ion and nitrogen oxides which are known to catalyze the oxidation of iodide. The oxidation of I^- is potentially a very serious interference when low level analyses are to be performed. We found that an amount of oxidant equivalent to more than 1.0 mg/L Cl can be generated in a day in a ~0.1 M KI stock solution in the laboratory. In bright sunlight such as may be encountered in the field, we find that this level of oxidant can appear in less than 1 hour. It causes a marked yellowing of the KI solution. Even though this stock solution may be greatly diluted when added to a sample, its oxidant can still overwhelm the actual oxidant concentration in the sample when levels in the 0.01 mg/L Cl range are being determined. Thus KI solutions should be made fresh each day and stored in a dark place. Any visible yellowing of the solution requires that it be discarded if low level determinations are being made. Many analysts who are engaged in chlorine analysis under field conditions have occasionally observed background "chlorine" levels in excess of 0.01 mg/L unchlorinated water. Some of these observations are probably due to oxidized KI reagent rather than to such true background oxidants as IO_3^-.

OTHER INTERFERING OXIDANTS

Table 3-1 presents a list of half cell potentials for a variety of substances which under standard conditions are stronger oxidizing agents than I_3^-. These substances would be capable in principle of generating I_3^- from I^- if present in sufficient concentration. However, as with O_2 and IO_3 which have already been discussed, many of these will react only slowly under normal analytical conditions. More than half the reactions shown in Table 3-1 involve species which would normally be absent in natural water but which might be produced by chlorination. These are species with which I^- must react if analytical methods for chlorine produced oxidants are to function properly. Of the remaining species, those involving Fe and Mn may be most important on an abundance basis. Cu^{2+} could be important in some power plant situations where high corrosion rates are involved. In waters polluted by wastewaters or heavy agricultural runoff, nitrite and nitrate might become important. Bongers et al (12) investigated three possible interfering substances in concentrations up to and exceeding those expected in estuarine water. They observed that no I_2 was formed when systems containing 50 ppm Fe_2O_3 or 50 μ M/L nitrite were treated with KI, buffer, and PAO. In the case of MnO_2, high concentrations of KI (up to 20 g/L) combined with 2 mg/L MnO_2 produced detectable I_2 concentrations. However, at the 0.3 g/L KI concentrations routinely used, no interference was observed with MnO_2 contents up to 50 mg/L.

All of the potential interferences that have been discussed so far produce positive analytical errors, assuming that the quantity being sought is the amount of chlorine produced oxidant. The extent to which these interferences will actually be a problem at a particular power plant depends on the details of the analytical procedure used and the nature of the local water. An obvious general way of avoiding this type of error is simply to analyze unchlorinated intake water and then use this measurement to correct the values found in the discharge. For such a procedure to be valid, however,

Table 3-1

SELECTED STANDARD ELECTRODE POTENTIALS

Half-Reaction	E^o (volts)
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	2.01
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	1.77
$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O$	1.695
$HOCl + H^+ + e^- \rightleftharpoons 1/2Cl_2 + H_2O$	1.63
$OBr^- + 2H^+ + 2e^- \rightleftharpoons Br^- + H_2O$	1.59*
$HOBr + H^+ + e^- \rightleftharpoons 1/2Br_2 + H_2O$	1.58*
$BrO_3^- + 6H^+ + 5e^- \rightleftharpoons 1/2Br_2 + H_2O$	1.52
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{+2} + 4H_2O$	1.51
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	1.359
$NCl_3 + 3H^+ + 6e^- \rightleftharpoons 3Cl^- + NH_3$	1.30*
$NHCl_2 + 2H^+ + 4e^- \rightleftharpoons 2Cl^- + NH_3$	1.27*
$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{+2} + 2H_2O$	1.23
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	1.229
$NH_2Cl + H^+ + 2e^- \rightleftharpoons Cl^- + NH_3$	1.22*
$BrCl + 2e^- \rightleftharpoons Br^- + Cl^-$	1.21*
$BrCl_6^{5-} + 2e^- \rightleftharpoons Br^- + 6Cl^-$	1.20*
$IO_3^- + 6H^+ + 5e^- \rightleftharpoons 1/2I_2 + 3H_2O$	1.195
$BrCl_2^- + 2e^- \rightleftharpoons Br^- + 2Cl^-$	1.16*
$NBr_3 + 3H^+ + 6e^- \rightleftharpoons 3Br^- + NH_3$	1.09*
$Br_2Cl^- + 2e^- \rightleftharpoons 2Br^- + Cl^-$	1.09*
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	1.087
$NHBr_2 + 2H^+ + 4e^- \rightleftharpoons 2Br^- + NH_3$	1.08*
$NH_2Br + H^+ + 2e^- \rightleftharpoons Br^- + NH_3$	1.08*
$OCl^- + 2H^+ + 2e^- \rightleftharpoons Cl^- + H_2O$	1.04*
$HNO_2 + H^+ + e^- \rightleftharpoons NO + H_2O$	1.00
$NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O$	0.94
$H_2O_2 + 2e^- \rightleftharpoons 2OH^-$	0.88
$Cu^{+2} + I^- + e^- \rightleftharpoons CuI$	0.86
$Fe^{+3} + e^- \rightleftharpoons Fe^{+2}$	0.771
$O_2 + 2H^+ + 2e^- \rightleftharpoons 2I^-$	0.620
$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$	0.564
$I_3^- + 2e^- \rightleftharpoons 3I^-$	0.536

*Calculated from free energy data tabulated in Sugam, 1977 (13). All other values from Skoog and West, 1969 (7).

the two measurements must be conducted in exactly the same way. Since the foregoing discussion emphasizes that kinetic factors are important, such features of the analysis as the order in which reagents are added and the time taken for the various analytical steps must be as uniform as possible.

VOLATILIZATION

In addition to positive errors, there are a large number of potential negative errors. Volatilization is one of those most commonly cited. Figures 3-1 and 3-2 indicate that molecular I_2 will be the principal iodine species in acidic solutions when the total KI added to the sample is less than about 250 mg/L. I_2 is relatively volatile:

$$I_2(aq) \rightleftharpoons I_2(g) \quad \log K = -0.518 \tag{13}$$

Dilling (14) studied the rate of loss of a number of volatile organic compounds from stirred beakers at 25°C and showed that the first order rate constant, k, could be reasonably predicted from an equation:

$$\frac{1}{k} = \frac{\sqrt{M}}{126} + \frac{\sqrt{M}}{(12700)K'} \tag{14}$$

where M is the molecular weight in g/mole and $K' = K/RT$ = the unitless partition coefficient. For I_2, k = 4.41 cm/hr. Figure 3-4 shows the percentage of I_2 that would be lost from a 10 cm deep stirred beaker, based on the above equations. The calculated rate of loss is certainly not a completely accurate assessment of the rate in real power plant cooling waters under various test conditions, but it is probably not in error by more than a factor of 2 or 3. Thus, it is likely that if the analysis is completed within a few minutes after KI has been added to a sample, the error due to volatilization will be only a few percent.

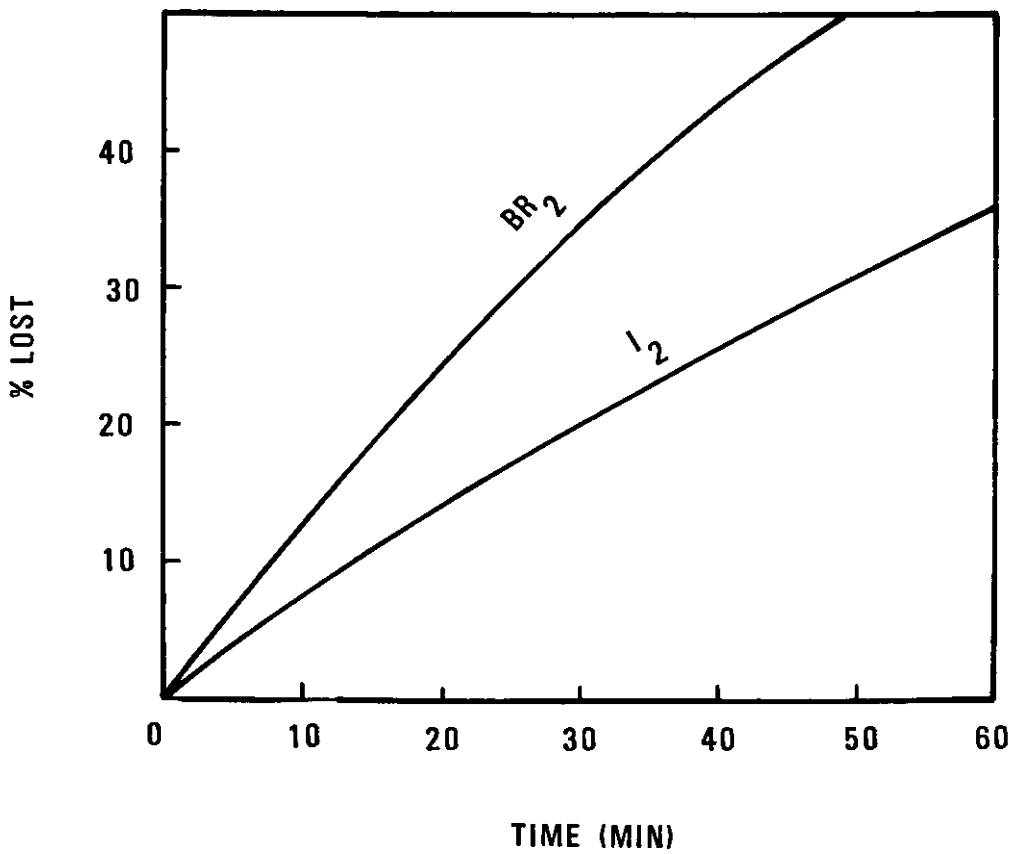


Figure 3-4. Volatilization loss rates for Br_2 and I_2 at 25°C.

An important characteristic of this and most of the following negative errors is that the absolute magnitude of the error diminishes as the concentration decreases. Thus, they are no more troublesome in low level analytical work than they are in high level analytical work. This contrasts with positive errors, such as that due to background IO_3^-, where the magnitude of the error becomes quite large in relation to the analytical signal at very low levels.

In addition to loss of I_2 after KI has been added to the sample, some of the chlorine produced oxidants themselves can be volatilized from the sample. Data needed to calculate volatilization rates for most of the species in Figures 3-1 and 3-2 are not available. However, the rate has been calculated for Br_2, which might be an important species in chlorinated marine waters if they are acidified during the analytical procedure. It can be seen in Figure 3-4 that Br_2 volatilizes at roughly twice the rate of I_2.

Probably the best way to minimize errors due to volatilization is to analyze the sample as quickly as possible. Addition of an acidic buffer and a large (>250 mg/L) concentration of KI so as to convert all the chlorine produced oxidant into non-volatile I_3^- (c.f. Figures 3-1 and 3-2) will help minimize volatilization, but this strategy increases the positive errors due to IO_3^-, O_2 etc. Another approach for minimizing errors due to volatilization and similar effects is to add an excess of reducing agent to the sample at the time it is collected and then titrate the extra reducing agent with an oxidant. We will consider this approach later, but one of its disadvantages is loss of precision.

ADSORPTION OF I_2

Bradbury and Hambly (9) report that I_2 is adsorbed on glassware to the extent of 7.8×10^{-11} mole/cm^2. The magnitude of error introduced by a loss of this type would depend upon the particular apparatus and procedure involved. However, for

illustrative purposes, a volume of 250 ml of solution in a 300 ml beaker would be in contact with roughly 200 cm^2 of glass. This glass could remove 1.6×10^{-8} mole of I_2, which is equivalent to about 0.004 mg/L chlorine. Unless a sample is subject to repeated transfers from one vessel to another (which is inadvisable on several grounds), adsorption on glassware is likely to contribute only minor error.

Adsorption on suspended particles could be more serious in the case of muddy or highly organic-rich waters. For example, the lower Mississippi, an extreme case, commonly carries 300 mg/l clay. If one assumes that this clay consists of spherical particles 2 μm in diameter or less, then their aggregate surface area would be 1000 cm^2/L or more. If their ability to adsorb I_2 is as good or better than that of glass, they would be capable of removing at least 7.8×10^{-8} mole/L. The actual removal might be much larger than this due to either a smaller mean particle size or to a stronger adsorption affinity for I_2.

In addition to adsorption by clay surfaces, I_2 might be adsorbed by organic particles. The well known and analytically useful complex which forms between I_2 and starch illustrates the tendency of polysaccharides to adsorb I_2. Similar interactions occur between I_2 and aromatic compounds. These effects have never been investigated in natural waters. They may be quite significant in highly turbid or colored waters.

REACTION OF I_2 WITH ORGANIC MATTER

In addition to simple adsorption, I_2 can react with organic matter, forming carbon-iodine bonds. This effect is thought to be an important loss mechanism for iodine during the analysis of chlorine produced oxidants in sewage treatment plant effluents. However, there seems to be little actual evidence for the mechanism in the form of identified iodocarbons. The importance of iodine-organic matter reactions will depend critically on water quality. Since most power plant cooling waters are of substantially better quality than sewage

effluents, the problem may not be of importance in many cases at power plants. Bunn and Haas (15) were able to show that iodine, generated by oxidizing a KI solution prepared with drinking water from the Missouri River, produced iodine containing haloforms. This establishes that iodine can indeed react with the traces of organic carbon in relatively good quality water. The total yields, however, in experiments such as these are usually only a few percent of the halogen added and it takes hours for the products to accumulate to final levels. Thus it remains to be established how important iodine-organic matter reactions might be in previously chlorinated waters on the time scale of an analysis, i.e., minutes at most. Some data bearing on this question will be presented later.

Analytically, it is quite difficult to compensate for errors introduced by adsorption on or reaction with organic and clay particles. Internal calibration in the sample by standard additions will help, but since the system may be a dynamic one, the time between when the sample is taken, when various reagents (including the standard spike) are added and when the final analytical measurement is made must be rigidly uniform for the unspiked aliquot of the sample and for each of the spiked aliquots. For example, it would not be acceptable to simply divide a sample into four aliquots, spike 3 with varying amounts of a standard I_2 solution and then analyze the aliquots sequentially. In such a procedure, the contact time of the spikes in the different aliquots would be different and the analysis would be invalid unless the samples have no iodine demand. (If they have no iodine demand then, of course, the standard additions procedure is unnecessary in the first place.)

Of the methods we examined in the laboratory, only the N.B.S. chlorine flux monitor has been designed to compensate for negative errors due to volatilization, adsorption or iodine-organic reactions by the standard additions method.

UNDETECTED OXIDANTS

Potentially the most serious threat to analytical accuracy in the determination of chlorine produced oxidants arises from the possibility that some oxidative chlorine by-products are inert in the time period of an analysis and so go undetected. If such by-products exist in a discharge water and later react slowly in the environment, they may create problems, so methods that detect them are needed. Alternatively, the unreactive products might be produced during the analytical manipulations. In either case, the final analysis is not representative of the chlorine produced oxidant present in the discharge water. Unfortunately, problems of this type have only recently been recognized in chlorine analysis, and they are not yet very well understood. Several papers appeared during the period of this project.

Carpenter et al (16) pointed out that when chlorinated seawater was titrated with thiosulfate to its endpoint and then allowed to sit for a period of minutes, additional oxidant gradually appeared. If this were removed by further addition of titrant, the whole process would repeat so that more than 24 hours was required to remove all the oxidant in the sample. They believed that the slow-reacting oxidant was not O_2, but rather a chlorine by-product.

Subsequently, Macalady et al (17) showed that BrO_3^- could be formed in chlorinated seawater which was photolyzed by sunlight, but they found no evidence of BrO_3^- formation in the absence of photolysis. They pointed out that because BrO_3^- reacts only sluggishly with iodide, it would be largely missed in the usual chlorine analysis.

In a further report, Carpenter et al (11) showed that when KI is added to chlorinated seawater, not only is I_2 or I_3^- produced (as expected), but some IO_3^- is also produced. Depending

upon the precise pH, KI concentration, and speed used during subsequent analysis, the IO_3^- may be wholly missed, partially missed or quantitively determined. To avoid this potentially serious error, they suggested either using a lower pH and higher KI concentration than usually recommended, or else using a back titration method. In a back titration, excess reducing agent is added before the KI; the analysis is then made by determining the amount of reducing agent left over after the reduction of the chlorine produced oxidants is complete. The first option has the drawback of tending to increase the contribution to the analysis from O_2 and other natural oxidizing agents in the sample. Particularly when very low oxidant levels are being sought, this can create quite a serious problem. Furthermore, any method which detects the IO_3^- generated during analytical manipulation will also detect the natural IO_3^- in marine waters, and, as already pointed out, this may result in a background oxidant level on the order of 0.07 mg/L Cl. A high blank level such as this would greatly impair accuracy and precision when chlorine produced oxidants were being determined at levels below 0.01 mg/L Cl.

Much remains to be learned about problems of this kind, especially for the case where marine waters are being analyzed. Atmospheric chemists, who use a method involving KI for the analysis of ozone in air, have been aware of such problems for some period of time (e.g. 18, 19). There is evidence for the production of H_2O_2 during the analysis of O_3. In marine waters, species such as $S_2O_8^{6-}$, peroxydisulfate, might be plausible by-products of H_2O_2. Whether chlorine can produce these types of by-products remains to be determined. There is also evidence from the O_3 analytical literature that trace contaminants in reagent grade KI and in buffers can produce both positive and negative errors. Research is needed on these topics as they relate to chlorine produced oxidants in marine waters. Until the reactions of KI with oxidants are totally understood, the accuracy of all the methods described in this report will be subject to challenge.

Section 4
ELECTROCHEMICAL METHODS

INTRODUCTION

In this section we will describe four electrochemical methods for chlorine analysis. In our original project design we planned to devote approximately equal time to testing each method. However, in the first few months it became apparent that this would be unproductive because two of the methods, the membrane probe and the potentiometric electrode, did not possess the necessary sensitivity for low level chlorine determinations and because to give equal time to all methods would not have allowed us to gain expertise with any. Furthermore, the manufacturer of an instrument needed for a third method, the N.B.S. chlorine flux monitor, was unable to deliver this instrument to us throughout the entire project period. Thus our work became focused on the amperometric titration method, which at this point appears the most promising method for power plants. We have improved the sensitivity of this method by an order of magnitude compared to that obtainable with conventional equipment. Our method is similar in sensitivity to a widely used, but unpublished, method employing a polarograph. However, the instrument we use is somewhat more automated and thus probably better suited for routine use. It can be used in either the standard or the back titration modes. Because of the information contained in the paper by Carpenter *et al* (16) which appeared during the project period, we amplified the original project plan to include a critical comparison of the standard (forward) and back titrations in natural estuarine waters.

STANDARD (FORWARD) AMPEROMETRIC TITRATION METHOD

The standard amperometric method is based on the reduction of free chlorine or the reduction of I_2 by phenylarsine oxide (PAO).

$$C_6H_5AsO + Cl_2 + 2H_2O \rightarrow C_6H_5AsO(OH)_2 + 2\ HCl \quad (15)$$

$$C_6H_5AsO + I_2 + 2H_2O \rightarrow C_6H_5AsO(OH)_2 + 2\ HI \quad (16)$$

Differentiation of the various oxidant species is based upon their ability to react with PAO and KI. In non-saline waters, only free chlorine can be reduced directly by PAO at pH 7. At pH 7, NH_2Cl will react with KI to form I_2 which will react with PAO. $NHCl_2$ will react with KI only at pH 4 to produce I_2. Thus, by appropriate use of KI and pH buffers one can determine free chlorine, free chlorine + NH_2Cl, and total chlorine. However, the utility of segregating oxidant in this way in seawater has been questioned (11, 16).

The instrumentation used by us for the amperometric titration is an improvement upon the commercially available amperometric titrators. The most difficult problem encountered in using the commercial titrators is the accurate identification of the endpoint. Considerable care is needed when approaching the endpoint so that it will not be passed. This is a common problem with all types of manual titrations, but it is compounded in this system by the lack of a clear, definitive endpoint.

To avoid the problems associated with manually titrating a large number of samples in the field and to increase sensitivity, a system was developed using an automatic titrator (Brinkmann Potentiograph E436). This allows the operator to obtain a record of the complete titration curve in the form of a strip-chart recording showing the amount of titrant added vs. the current measured (Figure 4-1). Titrant is added with a motor driven syringe. The titrator can be powered in the field by a 12V lead storage battery connected to a 12V DC to 115V AC inverter. Thus, it is usable in field applications, although hardly portable.

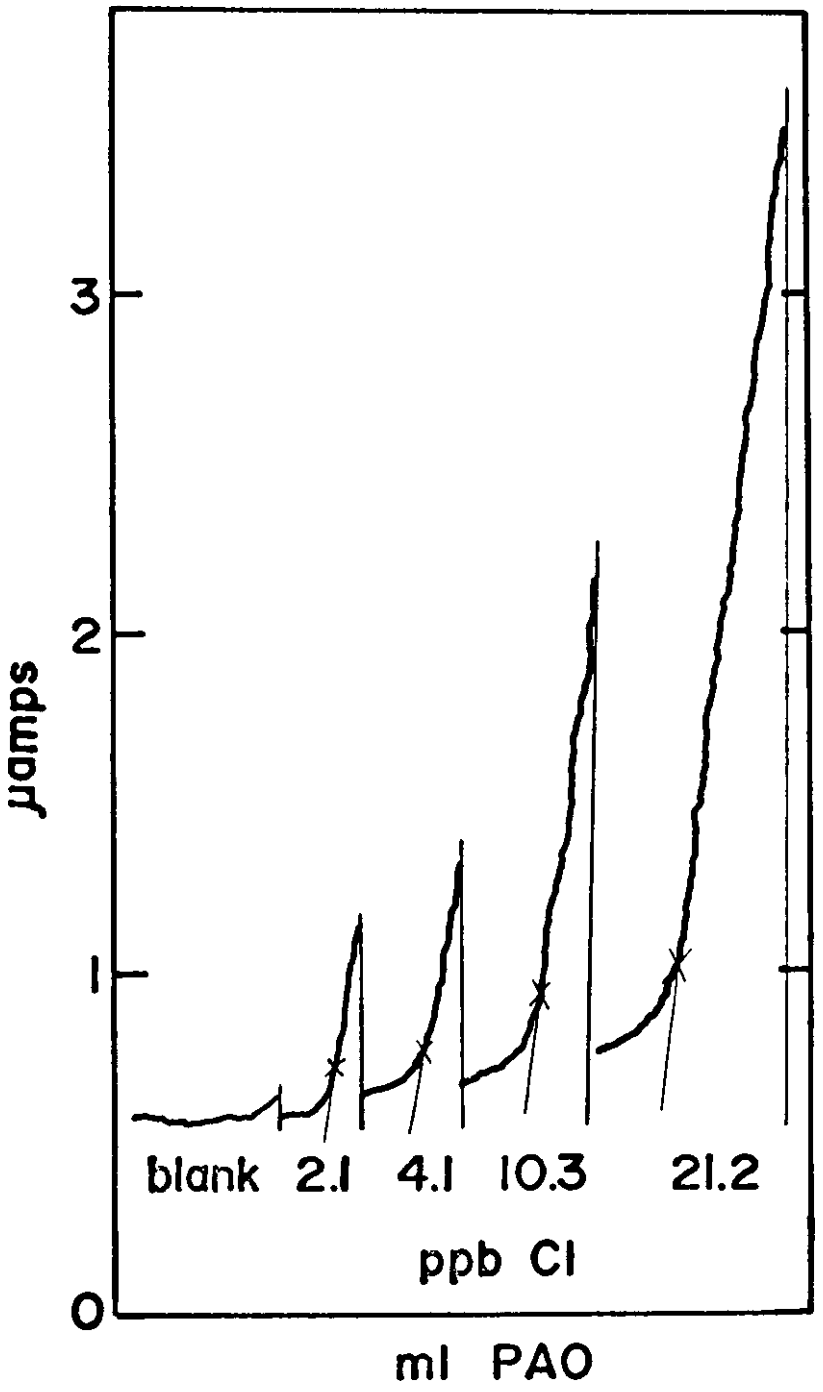
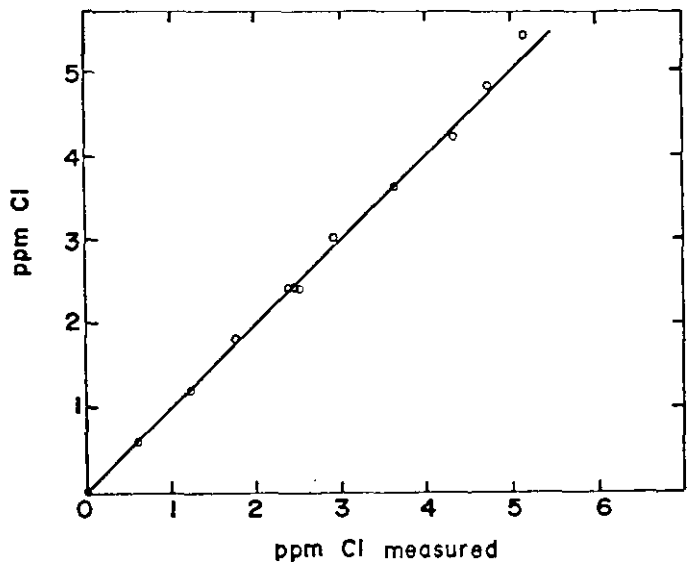


Figure 4-1. Typical strip-chart recording of the response of titrator to chlorine. The endpoint is established at the point where the curve begins to deviate from the initial slope (shown by the X on the graph).

The electrode assembly consists of a stationary Pt anode (Beckamn Pt inlay electrode) and a spiral Pt cathode (Englehard Industries #43000 8602 FSG 602) mounted on a Sargent-Welch synchronous rotator. Of several electrode combinations that were tested in this laboratory, this pair was the only one that approached a sensitivity in the μg/L range. Using a voltage of 200 mv across the electrodes and a current range of 0.5 μA, it is possible to detect the presence of 1 μg/L Cl in natural samples. Titrations were carried out using 0.000282N PAO, so that 1 mL PAO = 10 μg Cl. Under these conditions it is possible to obtain a precision of ± 1.5 μg/L Cl over the range of 0-100 μg/L Cl. By adjusting the concentration of PAO, higher levels of residual chlorine can be measured more efficiently with a precision depending primarily on the concentration of the reagent used. Two calibration curves for total residual chlorine obtained by titrating known solutions of chlorine at pH 4 with KI added are shown in Figure 4-2. Standard solutions of chlorine are prepared by dilution of a stock solution of NaOCl with distilled, deionized water. The concentration of the stock solution was determined by an iodometric titration with standardized $Na_2S_2O_3$. The top curve illustrates the calibration over the range of 0 to 5.0 mg/L Cl using 0.00564 N PAO. The bottom curve illustrates the calibration over the range of 0-100 μg/L Cl using 0.000282 N PAO.

Previously (13), we examined which oxidants in seawater are likely to be detected by amperometric titration. These experiments revealed that at pH 4.2 with 250 mg/L KI added free chlorine, free bromine, inorganic chloramines and inorganic bromamines were all quantitively determined. Negligible response was obtained from IO_3^-, $S_2O_8^{2-}$ and Fe^{3+} at 1 mg/L but H_2O_2, BrO_3^- and ClO_3^- gave a non-quantitive, yet measurable response. At pH 7 without any KI (conditions traditionally used for free chlorine), both free chlorine and free bromine were detected, but in addition bromamines and H_2O_2 gave non-quantitive responses. The response to bromamines, which under the conditions



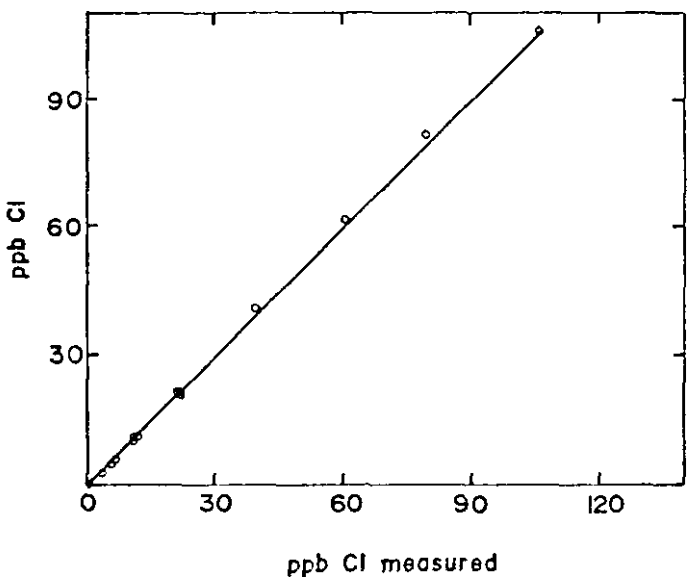


Figure 4-2. Calibration curves for total residual chlorine analyses. Upper diagram is for high Cl concentrations and lower diagram for low-Cl concentrations.

modelled in Figures 3-1 and 3-2 are the dominant species in seawater, cannot be clearly separated from free chlorine and bromine responses using amperometric titrations.

Additional experiments have been conducted to get a better feeling for the way some of the substances discussed in the previous chapter behave during analysis. In these experiments, the amperometric titration was tested under two circumstances, with pH adjusted to 4 and to 2. Analyses were made immediately after addition of the test oxidant and after a 10 minute contact time. The data are given in Table 4-1, along with comparative data for the N.B.S. chlorine flux monitor. Parallel tests were made with the Delta membrane probe, but as no response was obtained, it was not included in Table 4-1. Relative to the titrator, the N.B.S. chlorine flux monitor had consistently lower responses, except in the case of Cu^{2+}. Generally, the responses to these oxidants were non-quantitative under the conditions tested.

It is difficult to estimate the accuracy of the amperometric titration procedure in actual natural waters because standard spikes added to such waters decay extremely rapidly, especially in the first minute or so. However, an estimate of the method's <u>precision</u> can be gained by examining the scatter of analytical data points around a smooth decay curve. Elsewhere (13, 26) we have described measurements by our amperometric method in the cooling water discharge canal of the Chalk Point power plant (PEPCO). It was found that after about 15 minutes the decay pattern became first order, that is, linear on a log Cl vs t plot. A representative data set is plotted in Figure 4-3. Even though residuals below 10 parts per billion were observed, the scatter of the data about the straight line decay trend is of the same magnitude observed in laboratory calibrations. Thus the method is applicable to natural estuarine water without significant loss in precision.

Table 4-1

SUMMARY OF RESPONSES USING ELECTROCHEMICAL METHODS. VALUES IN EQUIVALENT MG/L CHLORINE RESPONSE.

Species (in mg/L)		Brinkman Automatic Titrator		Titrator Response After 10 min.		Chlorine Flux Monitor
		pH 4 + KI	pH 2 + KI	pH 4 + KI	pH 2 + KI	
Iodate (20-60 ug/L)*						
DW	0.1	0.55		0.40		0.11
	1.0	3.30	3.30	1.57	>5	0.67
	10.0	>5		>5	>5	1.24
	100.0					
SW	0.1	0.45	0.54			
	1.0	0.42	3.06			
	10.0					0.93
	100.0	>5				
Bromate (65 ug/L)						
DW	1.0	0.18	3.00	0.22		<.01
	10.0	0.20		0.32		<.01
	100.0	0.39		0.50		0.03
SW	1.0		0.08	0.10		
	10.0	0.08	2.50			
	100.0	0.09	>5	0.20		0.01
$S_2O_8^{=}$ (885 mg/L $SO_4^{=}$)						
DW	1.0	.15	0.35	0.24	0.29	<.01
	10.0	.15	0.34	0.28		0.04
	100.0	.24	0.88	0.31		0.10
SW	1.0	.11				
	10.0	.14	1.90			
	100.0	.10				<.01

Table... cont.

Species (in mg/L)		Brinkman Automatic Titrator		Titrator Response After 10 min.		Chlorine Flux Monitor
		pH 4 + KI	pH 2 + KI	pH 4	pH 2	
Peroxide (40 μg/L)						
DW	1.0	0.15	0.30	0.30		
	10.0	0.31	0.82	>5		0.05
	100.0	1.75	>5			0.32
SW	1.0	0.18	0.31	0.30		
	10.0	0.27	0.50	1.52		
	100.0	1.40	>5	>5		0.37
Cu^{+2} (3 μg/L)						
DW	1.0	0.20	0.17	0.28		
	10.0	0.30	0.35	0.27	0.30	
	100.0	0.35	-	0.40		0.70
SW	1.0	0.10	0.17	0.10		
	10.0	0.26	0.30			
	100.0	0.60	0.61	0.41		2.05

Table... cont.

Species (in mg/L)		Brinkman Automatic Titrator pH 4 + KI	Brinkman Automatic Titrator pH 2 + KI	Titrator Response After 10 min. pH 4	Titrator Response After 10 min. pH 2	Chlorine Flux Monitor
Fe^{+3} (10 μg/L)						
DW	1.0	0.15	0.25	0.20		
	10.0	0.20	0.18	0.25		
	100.0	0.21		0.21		
SW	1.0	0.18	0.40			
	10.0	0.15	0.26			
	100.0	0.15	0.26			
Mn^{+4} (2 μg/L)						
DW	1.0	0.36	0.35			
	10.0	1.57	1.40		1.40	
	100.0	>5	>5			
SW	1.0					
	10.0					
	100.0					

Blank values denote no response.
*Average concentration in seawater, after Horne, 1969.
DW refers to distilled water solutions.
SW refers to seawater solutions.

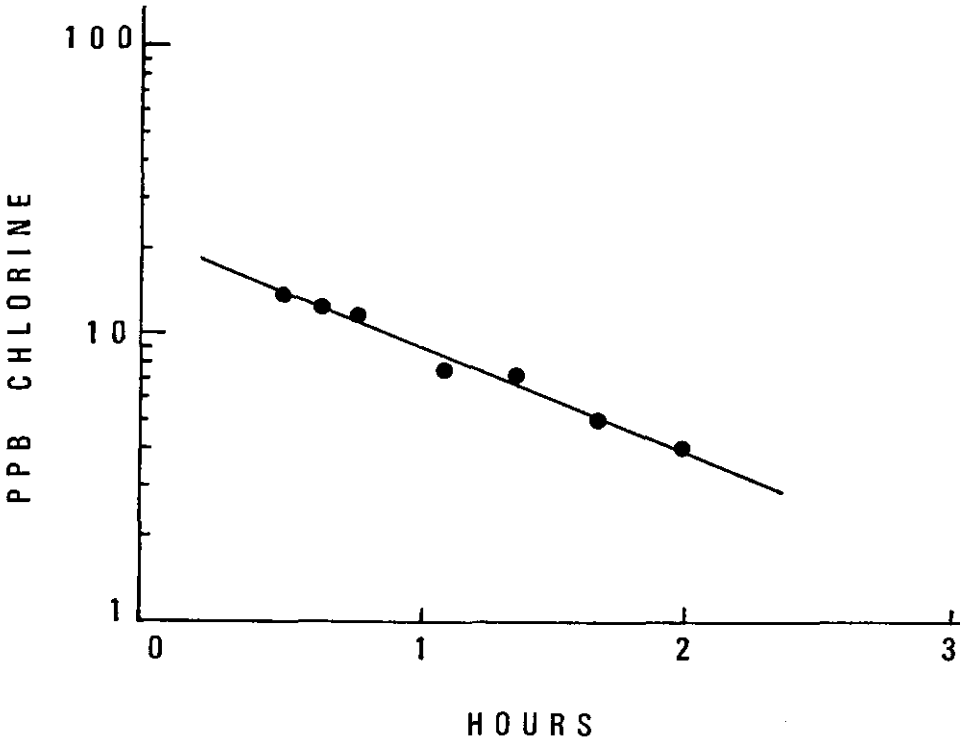


Figure 4-3. Chlorine decay in a power plant cooling canal.

AMPEROMETRIC BACK TITRATION METHOD

The amperometric back titration method differs from the standard amperometric technique in that excess reducing agent, such as phenylarsine oxide (PAO), is added to the sample prior to analysis to fix all the available oxidant. Excess PAO is then determined by back titration with iodine solution of known concentration. This technique has been recommended as the only reliable method for chlorine analysis in natural water systems (11, 12, 20), since the reagents are added at the time of sample collection to stabilize the chlorine present and permit an accurate determination.

The instrument and the electrodes used in these experiments are the same as in the previous section. Commercially available (HACH Chemical Company) 0.00564 N phenylarsine oxide (PAO) stock solution was used. The iodine titrant stock solution (0.10 N) was prepared by dissolving 40 g KI in distilled water, to which 13.0 g resublimed iodine were added and the volume brought to 1 L. The stock solution was stored in a brown glass bottle. A 0.001128 N I_2 titrant was made from the stock solution. The I_2 titrant was calibrated against the stable PAO solution every several hours. Potassium iodide solution was made by dissolving 50 g KI in distilled water which was diluted to 1 L and stored in brown glass bottles in a dark cabinet.

Acetate buffer (pH 4) was prepared by dissolving 243 g $NaC_2H_3O_2 \cdot 3H_2O$ into approx. 400 mL freshly boiled distilled water; 457.5 mL glacial acetic acid were added and the solution brought to 1 liter volume after equilibration to room temperature.

Sodium thiosulfate (0.00564 N $Na_2S_2O_3$) was investigated as a possible reductant in place of the PAO, but the latter produced a sharper endpoint. Potassium dichromate (0.0001 N) and potassium bi-iodate (0.0056 N) were tested as potential titrants in addition to the iodine solution. Neither the potassium dichromate nor the bi-iodate proved to be satisfactory titrants because they reacted too slowly for use in an automated method.

Chlorine standards were made from reagent grade sodium hypochlorite (NaOCl), the concentration of which was established iodometrically (1).

The back titration procedure that was found to be most satisfactory for chlorine concentrations in the range 0.1 to 1.0 ppm was as follows: 10 mL of 0.000564 N PAO (a 1:10 dilution), followed by 2 mL of 2 M KI solution and then 2 mL acetate buffer (pH 4) were accurately measured* into a beaker; 200 mL of sample were then added to the beaker, which was covered and allowed to react for several minutes. The titration with 0.001128 N iodine was done at the slowest possible speed (approximately) 1 mL/min) to allow maximum time for titrant mixing and recorder response. The endpoint under these conditions was sharp and highly reproducible. For chlorine concentrations in the range 0.01 to 0.1 mg/L, the PAO and I_2 were diluted by a factor of ten.

The sensitivity of this method is roughly comparable to that of the standard titration ($\pm$ 1.5 μg/L Cl), although some precision is lost because of the additional uncertainty associated with adding the excess reducing agent. Furthermore, unlike the standard titration where the poorest precision is associated with the most dilute sample, in the back titration poor precision may occur at relatively high oxidant concentrations if it happens that the aliquot of reducing agent which is added is only slightly more than required to completely remove the oxidant in the sample. To obtain a precise analysis by the back titration method it is necessary to make a preliminary

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*An accurate measurement of the PAO reductant is critical to reproducible results. We found that a 1:10 dilution and the subsequent use of a 10 mL pipette provided superior results relative to 1 mL pipette or Eppendorf micropipets with 0.00564 N PAO.

analysis for range finding purposes and then adjust the size of the reducing agent aliquot so that the excess will be an amount convenient to titrate precisely.

COMPARISON OF THE FORWARD AND BACK TITRATIONS

The calibration curves for chlorine in distilled water in the range 0.02 to 1.0 mg/L show no major differences between the two methods (Figs. 4-3), although the back titration appears to give slightly lower chlorine recovery than the standard procedure. In order to compare the capability of the two techniques in natural water, 0.5 mg/L chlorine was added to six samples collected at various places in Maryland. These ranged in salinity from 0 to 31 g/kg. They were analyzed by each method 10 minutes after the chlorine was added. All reagents were mixed with the samples at the time the samples were analyzed. The results in Table 4-2 indicate reasonable agreement between the two methods, although the back titration values are low relative to those from the forward titration in several cases. It is surprising to find that where the forward and back titrations disagree significantly (samples 1, 4 and 5), the forward titration gives higher results. The back titration procedure is advocated mainly as a means of overcoming the negative errors in the forward titration. These results suggest that such negative errors were negligible in some cases and overwhelmed by positive errors in others (samples 1, 4 and 5). An alternate, and possibly more plausible explanation is that the levels found by back titration in samples 1, 4 and 5 were falselv low because the I_2 titrant reacted with some reducing component in the sample in addition to reacting with excess PAO. Possible candidates would be Mn^{2+} or Fe^{2+}.

PAO (15 mL, 0.00564 N) was added to three liters of Choptank River water (salinity = 12.65 g/kg) from Horn Point, Maryland, and titrated with iodine after various periods of delay to determine the stability of PAO in a brackish water. The KI and pH 4 buffer solutions were mixed with 200 mL aliquots at

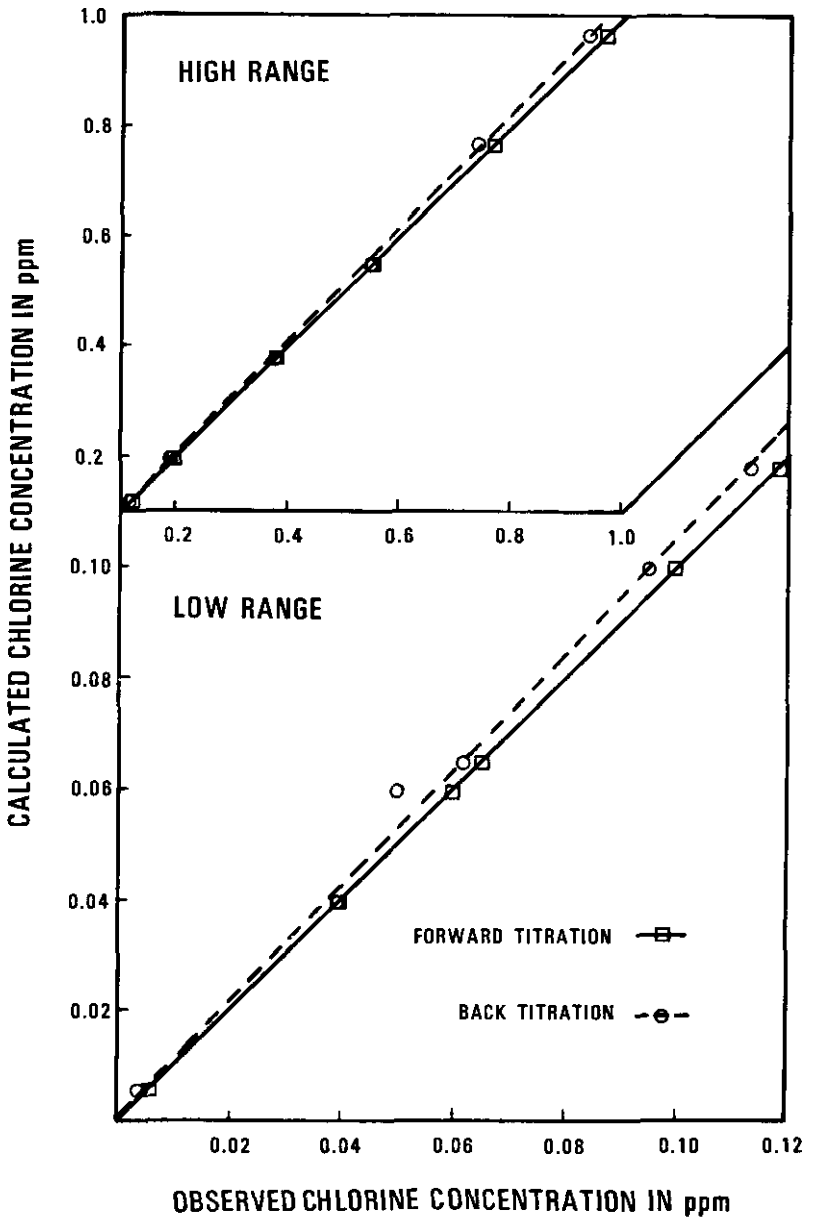


Figure 4-4. Comparison of forward and back titrations using standards prepared in distilled water. The forward titration yields slightly higher analytical values.

Table 4-2

COMPARISON OF FORWARD AND BACK TITRATION METHODS WITH NATURAL WATER SAMPLES.[a]

SAMPLE NUMBER	SALINITY (S g/kg)	ORGANIC CARBON (mg/L)	TOTAL NITROGEN (mg/L)	FORWARD TITRATION (mg/L)	BACK TITRATION (mg/L)
1	0	4.20	2.59	.280	.250
2	1	3.24	0.95	.380	.380
3	4	3.24	0.81	.180	.178
4	7	3.36		.195	.168
5	10	3.24	0.48	.200	.164
6	31	2.88	0.43	.185	.190
		6.12	-		

[a]All analyses were made 10 min. after the addition of chlorine (0.5 mg/L). Reagents (KI, buffer and PAO) were added at 10 min. Total Nitrogen = $N_{org} + N_{NO_3^-} + N_{NO_2^-} + N_{NH_4^+}$.

the time of analysis. The results indicate that PAO is stable in the river water for periods of at least two weeks (Table 4-3). The average amount of iodine needed for the titration was 3% lower than that required for the same amount of PAO in distilled water. This suggests that a PAO demand may exist in some natural, unchlorinated, waters which would indicate the presence of oxidants other than those artificially added to the system.

Natural waters commonly exhibit a chlorine demand. However, if PAO, KI and pH 4 buffer are added to the water prior to chlorination, there should be no oxidant decay, or demand. This is also the case with good quality distilled water. For the back titration method to be effective in the field, it must be capable of "freezing" or stabilizing the chlorine content as of the moment of collection. To demonstrate this capability PAO, KI and buffer were mixed with a chlorinated sample after a 15 minute delay. The decay curve for this sample is illustrated in Figure 4-5, along with decay curves for chlorine in a chlorinated water with reagents added prior to chlorination, and a chlorinated water with no reagents added. These results indicate that there is no further change in the measured chlorine concentration once the reagents and natural chlorinated water react.

Forward titration chlorine decay curves were prepared for comparison with the back titration data. A sample of Choptank River water was chlorinated (0.75 mg/L Cl_2) and the KI and buffer solutions were added at the time the sample was analyzed. In a second aliquot of Choptank water, KI and buffer reagents were added prior to chlorination. All samples were stored in closed polyethylene bottles away from direct sunlight. The results in Figure 4-6 demonstrate that chlorinated samples combined with KI and buffer alone arrest chlorine decay for up to 24 hours. In other words, the addition of KI and pH 4 buffer serves to stabilize the oxidant content at the time of collection and would permit returning a suite of

Table 4-3

PAO STABILITY IN A BRACKISH WATER[a]

Time	Amount of titrant[b] per ml of PAO[c]
10 min.	4.79
20 min.	4.75
30 min.	4.91
60 min.	4.87
2 hrs.	4.79
3 hrs.	4.95
4 hrs.	4.83
24 hrs.	4.88
48 hrs.	4.94
2 wks.	4.85
in distilled water	5.00

a. Choptank River, Horn Point, Maryland

b. mL of 0.001128 N iodine

c. 0.00564 N

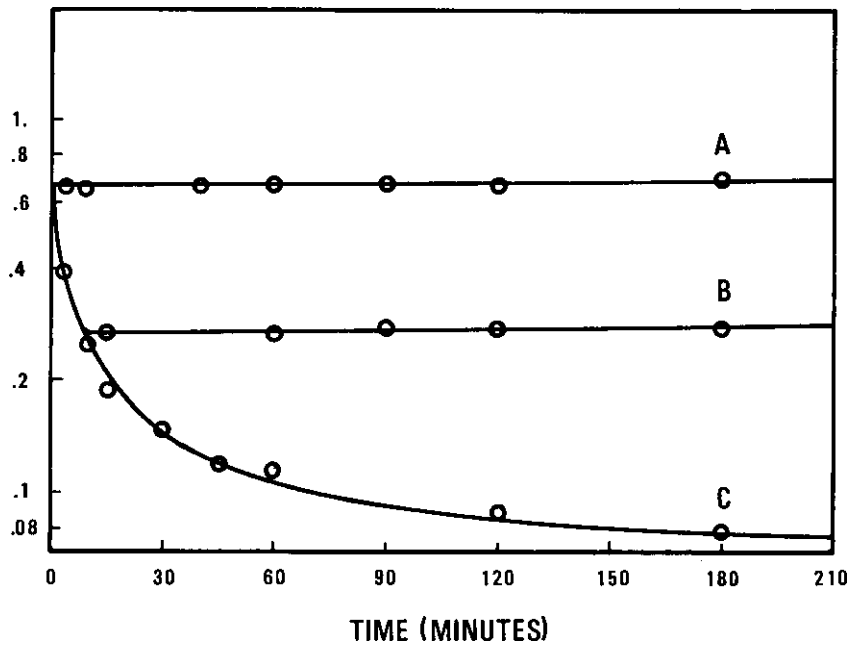


Figure 4-5. Residual oxidant determined by back titration under 3 experimental conditions: (a) chlorine added to estuarine water containing KI and excess PAO; (b) chlorine added to estuarine water with excess PAO added after 15 minutes; and (c) chlorine added to estuarine water with excess PAO added at time of analysis. Abscissa is the time after initial chlorination that the sample was analyzed.

samples to a nearby laboratory for analysis later the same day. Curve A in Figure 4-5 is actually the decay curve of I_2 or I_3^-, and shows no decrease with time. Indeed there is a very slight rise in oxidant residual, probably reflecting reaction of I^- with IO_3^-. This result agrees with estimates made in the discussion on Iodine Chemistry (Sec. 3). This rise is insignificant here but could pose a problem in low level analysis. In summary, our experimental data show that the addition of reagents (KI and buffer for forward titration, or PAO, KI and buffer in the back titration procedure) at the time of sample collection serves to stabilize the chlorine content, although in the forward titration case there is a slight increase in residual with time. The data in Table 4-2 do not substantiate the claimed superiority of the back titration method relative to the forward titration procedure for determining oxidant levels in saline waters (11).

NATIONAL BUREAU OF STANDARDS CHLORINE FLUX MONITOR

The so-called Chlorine Flux Monitor was developed at the National Bureau of Standards to measure low levels of total residual chlorine in water. It is a self-contained, battery powered portable system designed for field analyses. The instrument measures iodine which is generated by the reaction of I^- with chlorine in a continuous flowing water sample. The flux monitor is equipped with a pump which not only draws the sample through the instrument, but also adds the appropriate amount of buffered KI reagent to it (Fig. 4-6). An electrochemical cell coupled to an electronic measurement system provides direct concentration readout down to chlorine concentrations of 0.002 mg/L $\pm$ 0.001 (2). The instrument includes an internal calibration system in which standard additions of known amounts of iodine are made coulometrically. Since no external standards are required, this instrument has a clear advantage for on-site residual chlorine measurements.

The electronic circuitry also includes a battery charger. This maintains the battery and during AC use will recharge the battery within a 16 hour period. At the time that this project was originally proposed, one commercial manufacturer was advertising

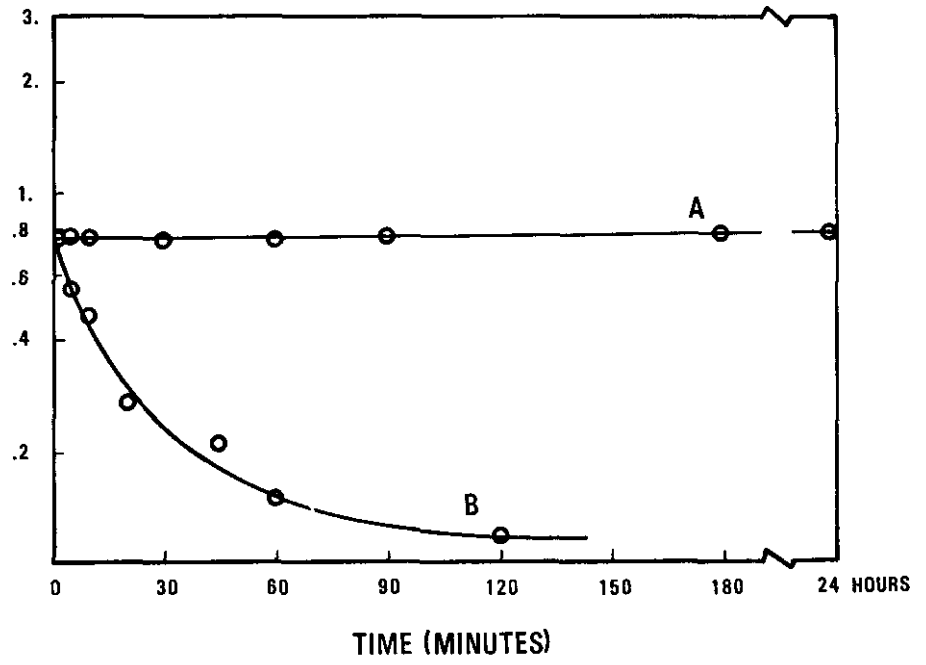


Figure 4-6. Forward titration chlorine decay curves in Choptank River water. (a) KI and pH 4 buffer added before chlorination; and (b) KI and pH 4 buffer added at time of analysis. Vertical scale is ppm Cl.

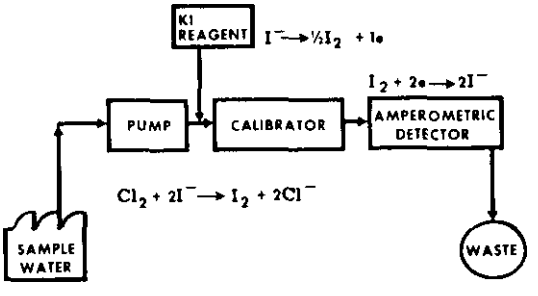


Figure 4-7. Schematic of the NBS chlorine flux monitor.

an improved version of this monitor and several were considering producing it. However, during the entire period of this project, the company advertising the instrument was unable to deliver one and no other companies entered the market. We were finally able to borrow a prototype made at the Bureau of Standards in order to gain some experience with it.

The following reagents are recommended for use in the sample stream. Three M KI solution is made by dissolving 500 g of KI and 50 mg of THAM (tris(hydroxymethyl)-aminomethane) in one liter of distilled water. Buffer is prepared by dissolving 125 g of KH_2PO_4 and 300 g of KBr in one liter of chlorine-free water. The pH is then adjusted to about 3 with phosphoric acid. This provides a final solution of pH of 4 when the buffer is diluted by a factor of 20 in the sample stream.

Because the 3M KI solution produced a large background, a more dilute 1M KI solution was used for 0.5 to 1.0 mg/L chlorine determinations. Below 0.5 mg/L chlorine, a 0.1 M KI solution was used. No further dilutions were made since the background current was insignificant at the 0.1 M KI concentration.

An equal flow rate of both the buffer and KI solutions is also an important parameter for proper operation of the instrument. In order to equalize the viscosities, and thus the flow rates, of the two solutions, both the KI and buffer reagents were saturated with NaCl.

These reagents were found to be stable for at least one week if kept unmixed in the reagent compartment, sealed from light and air. Within the reagent mixing chamber, the KI oxidized to iodine overnight, producing a brown color. This solution was removed each morning through the auxillary port in the mixing aparatus with a syringe, which reduced the initial time required to purge the system.

To make a measurement, a sample of distilled water is pumped through the cell to establish a zero point. The calibration circuit is then activated and a generator current is selected to provide an iodine equivalent concentration similar to the chlorine concentration expected in the samples to be measured. The cell output is adjusted so that the meter reads the calculated chlorine concentration. Alternatively, the calibration can be made on the sample stream itself by manual standard additions. After calibration, the calibration current is turned off and a sample is pumped through the cell. The digital meter will then indicate the sample chlorine content in mg/L. Since the amperometric response, or cell current, depends not only on the amount of iodine generated but also on the hydrodynamic flow, the instrument must be calibrated for each sample type.

Between sample measurements, the sample intake hose should be transferred rapidly in order to minimize the amount of air pumped into the instrument. If the hose pumps too much air, the pump must be reprimed using the flush mode. Some caution should also be exercised when utilizing the rapid flush mode. When allowed to operate for long periods of time, the reagents cannot meet the demand, so that air flows from the mixing tube changing the sample to reagent ratio. Also, the agitation produced during the rapid flush can introduce air bubbles into the electrical cell, which causes spurious measurements. Adequate time must also be allowed for the system to restabilize after a fast flush. Because of these potential problems and instability, we recommend patience and a gradual flush between samples.

The flow meter should be checked frequently to insure that the value remains constant throughout a series of measurements. One serious flaw in the model we tested was a marked instability in the flow rate. An accurate flow rate can be determined by measuring the volume of sample outflow per unit of time. One minute measurement times were found to provide adequate accuracy.

Two sets of calibration curves were prepared showing quite different results. The first was made by diluting normal chlorinated tap water with distilled water; 0.1 M KI reagent was used in the instrument. The calibration curve is a straight line with only slight negative deviation (Fig. 4-7a). In the second case, chlorine standards of known concentration were prepared using distilled water and artificial seawater; a 1 M KI solution was used. These second calibration curves exhibited a strong negative deviation (Fig. 4-7b), although the deviation was less pronounced at lower Cl concentrations. Furthermore, the response for chlorine in the seawater was about 15% less than that for chlorine in distilled water. The most obvious sampling difference between these two sets of data (one month apart) was the sample flow rate. The rates were 76.8 mL/min for tap water and 102 mL/min for the distilled and seawater standards. These flow rates are higher than the recommended 54 mL/min due to the wearing of the pump. The rapid pump decline was in fact a serious problem with this instrument. The lack of linearity with increased flow rates suggests that insufficient I_2 is produced at the generating electrode to give a complete measurement response at rapid flow rates.

A calibration of the amount of iodine produced versus current generated and readout (Table 4-4) indicates that the relationship between these two parameters is linear over the 50 to 1000 μA current range (Fig. 4-8). This current range corresponds to values of 12 to 270 μg/L, and indicates that the theoretical detection limit for our instrument is close to 1 μg/L (5 μA response).

The interferences with the chlorine flux monitor are the same as those for other methods employing iodide. That is, any strong oxidant present in a water sample is likely to oxidize iodide to iodine in the same manner as chlorine. The species investigated were iodate, bromate, peroxide, persulfate,

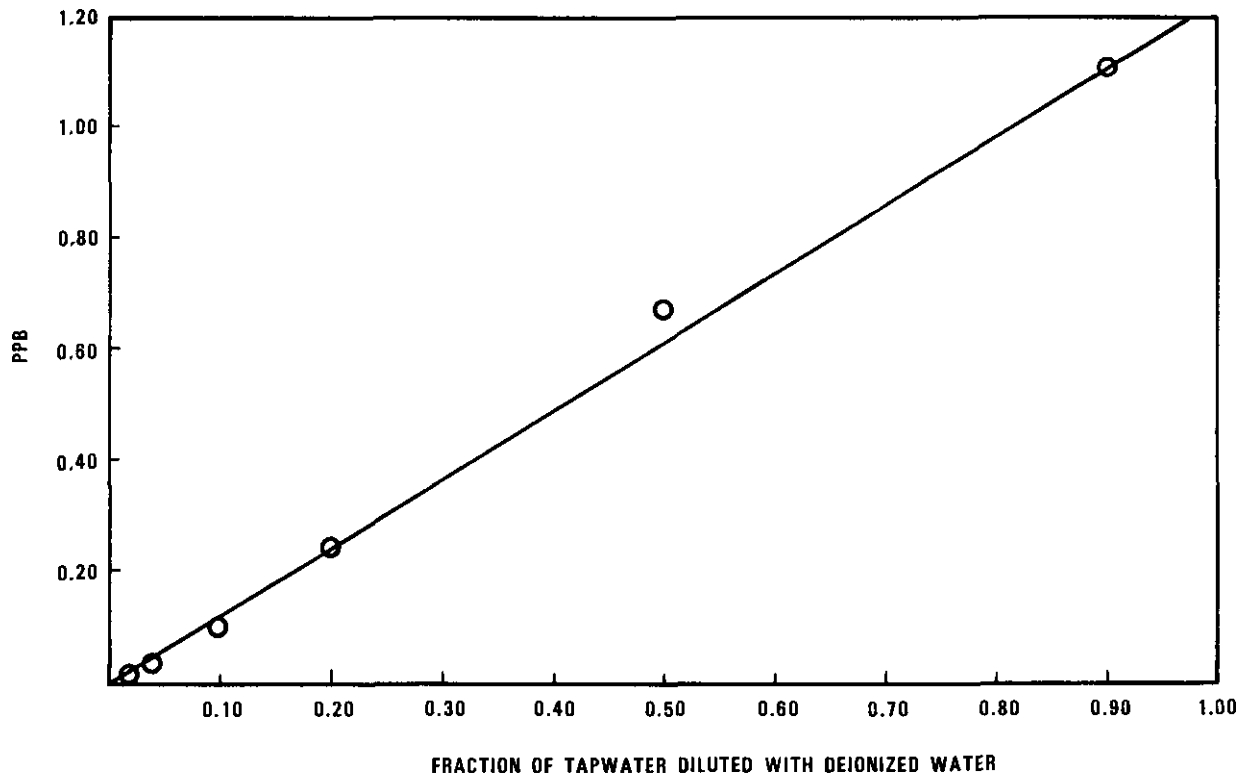


Figure 4-7a. Analytical data for College Park tap water diluted with distilled water. Determinations made by NBS chlorine flux monitor.

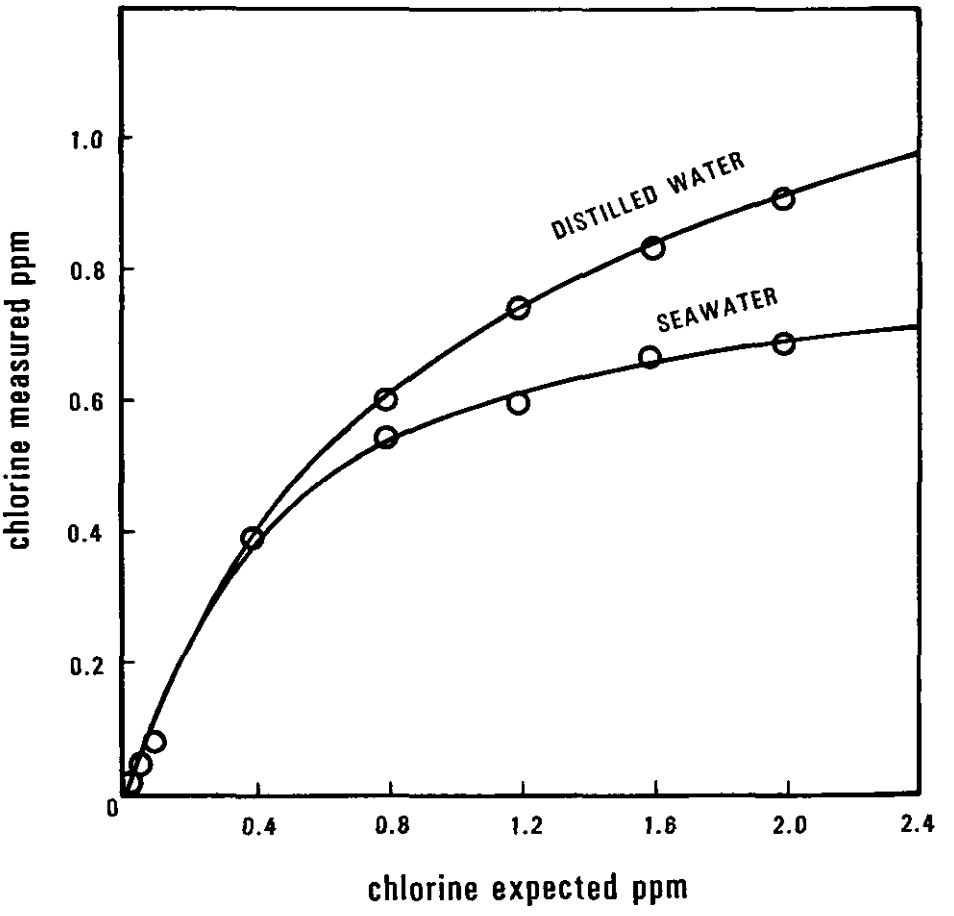


Figure 4-7b. Chlorine calibration curve for NBS chlorine flux monitor after it began to malfunction.

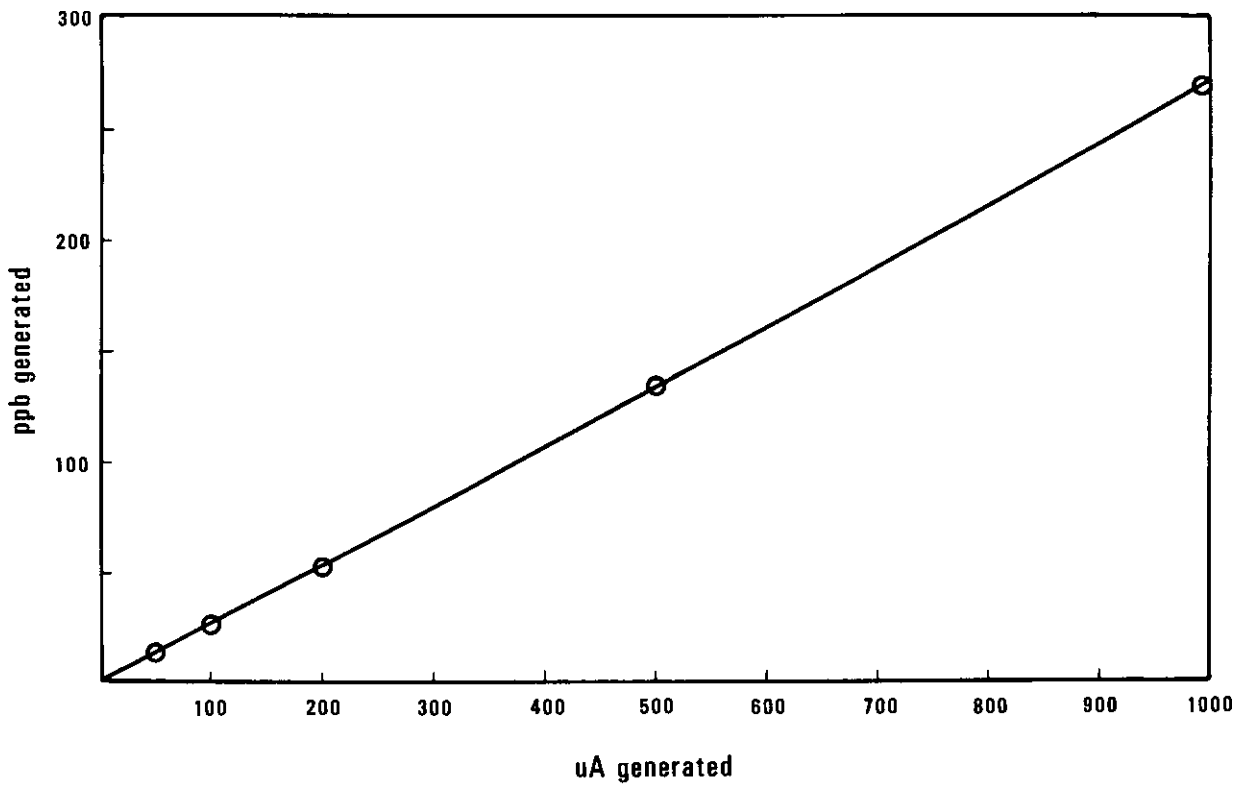


Figure 4-8. Relationship between coulometrically generated I_2 and the amperometric current.

Table 4-4

CALIBRATION OF CALCULATED CURRENT GENERATED RELATIVE TO DIRECT READOUT RESPONSE.

Current generated (in μA)	Readout response* μg/L
50	12.1
100	24.9
200	51.5
500	132.5
1000	269.0

*Relative error for duplicate readings was 2%.

Cu^{+2}, Fe^{+3} and Mn^{+4}. The data show that the chlorine monitor has approximately one tenth the interference response relative to the automatic titrator for the same solutions (Fig. 4-1). This observed effect is reasonable since the KI and buffer solutions are added to the sample stream in the flux monitor just before the actual measurement is made. Additional experiments with the automatic titrator indicated that delay time is an important factor in degree of interference.

It should also be noted that the flux monitor calibration procedure tends to limit the interference problem. When the system is calibrated by the standard additions method, the measurement is made on the sample matrix itself. This procedure should correct any multiplicative errors contributed by the sample matrix.

The description and specifications for the NBS chlorine flux monitor suggest that it is the ideal instrument for determining total chlorine in water samples. Its advantages are that it is a compact, portable system with internal addition and calibration; the required reagents are stable for up to one week in the reagent compartment; and the electronic system provides rapid direct chlorine concentration readout.

In actual practice, we found that the instrument did not perform as expected and was susceptible to repeated malfunctions. It was unstable electronically and subject to erratic measurement values. Also, the intake pump motor declined rapidly (within one month), which contributed to spurious results and prevented good calibration over the specified range. The internal standard addition method of calibration sufficiently disrupted the system so that extensive adjustments were required before stable sample measurements were obtained. The internal measurement cell tended to leak, creating electrical problems.

It is apparent that many of these limitations can be eliminated by a competent manufacturer, and that the instrument is potentially superior to other electrochemical methods for on site chlorine analyses.

DELTA SCIENTIFIC CHLORINE PROBE

The chlorine probe is a specialized type of voltammetric system which uses a self contained cell for measurement. The cell consists of a reference electrode and a cathode where the reduction of the hypochlorous acid takes place. The current produced is proportional to the hypochlorous acid concentration in the solution. The oxidized and reduced species diffuse in and out of the membrane until a steady state is achieved. This requires several minutes of vigorous stirring. The teflon membrane has the property of selectivity passing uncharged species through to the inner chamber. This means that the probe responds fully to HOCl, and minimally to OCl^- and combined chlorine species (5% or less compared to the HOCL response).

If one wishes to measure total free chlorine, it is necessary to reduce the pH below about 5.5 so as to convert all OCl^- to HOCl. In marine waters where HOBr would be more important, a higher pH will suffice because HOBr is a weaker acid.

The selective HOCl response is an advantage when attempting to measure disinfecting power. The manufacturer asserts that only the amount of hypochlorous acid should be considered when measuring the disinfecting power. This is due to the belief that charged species like OCl^- do not pass freely through the cell membranes of bacteria. In waters in which there is a high ammonia concentration, the predominant form of chlorine is monochloramine, to which the probe responds poorly.

Initial attempts to standardize the instrument using the recommended pH 5.5 buffer proved inadequate. Subsequently, the use of a pH 4 acetate buffer (243 g $NaC_2H_3O_2 \cdot 3H_2O$ + 457.6 ml glacial acetic acid brought up to 1 L volume) provided satisfactory results. Chlorine standards were prepared from reagent grade sodium hypochlorite (NaOCl), the chlorine concentration of which was established by the iodometric method (1).

The probe must be calibrated using both a blank solution (distilled water plus 1 mL pH 4 buffer) and an upper limit standard. During calibration and sample measurement, the solutions were stirred with a magnetic stirring bar. The instrument calibration may require 3 or 4 zero-calibration adjustments before satisfactory agreement is obtained. To make a chlorine measurement, the probe is inserted into a beaker containing 200 mL of sample and 1 mL acetate buffer. The free chlorine concentration is read directly from the meter after a stable value is attained. Between samples, the probe should be carefully blotted with a tissue in order to remove remnants of the preceding sample.

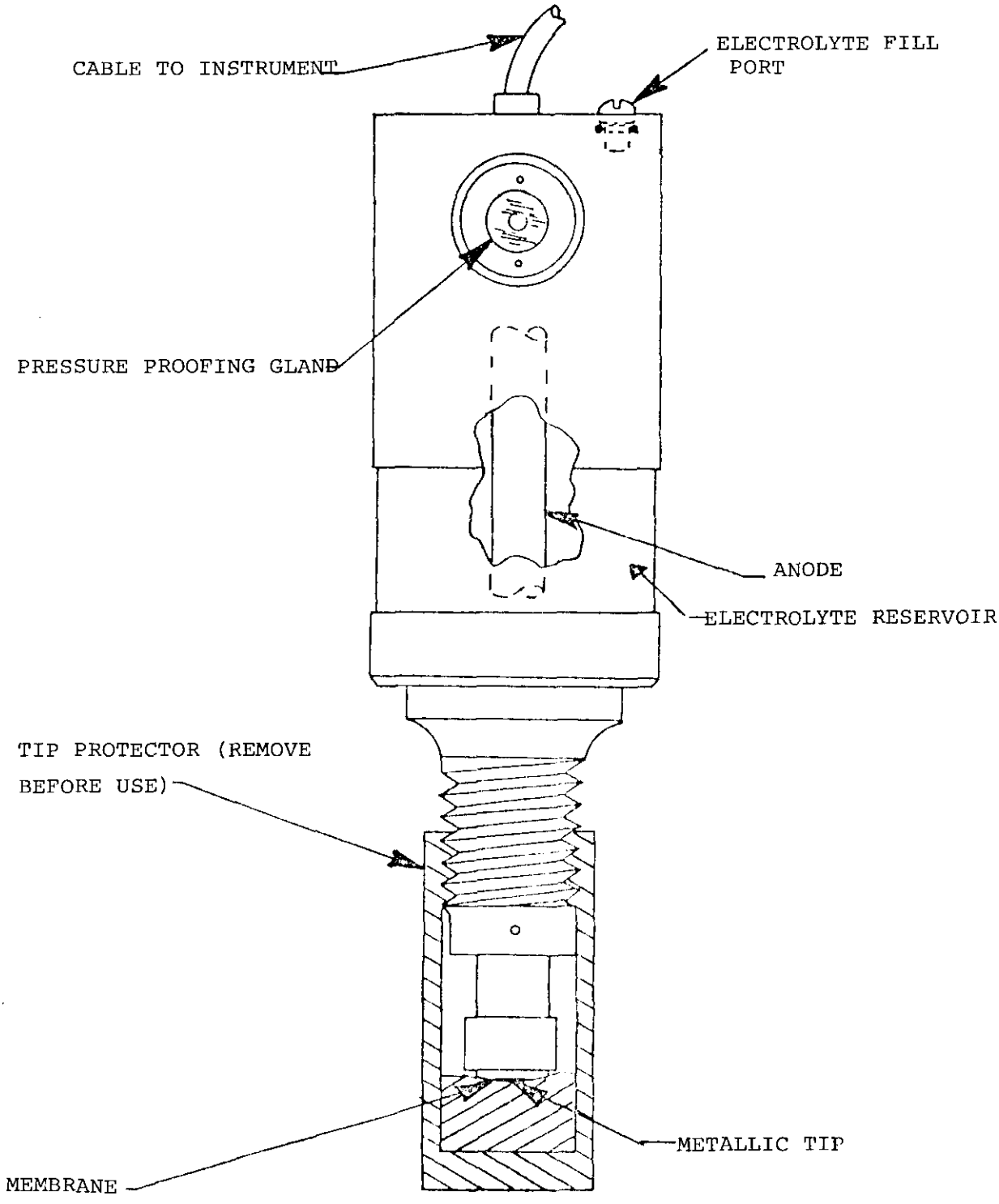


Figure 4-10. Schematic Diagram of the Delta probe.

The calibration curve for chlorine in the range 0.1 to 1.0 mg/L exhibits a high degree of linearity (Fig. 4-10). Experiments to determine the response of the Delta Probe to iodate, bromate, peroxide, borate, persulfate, and Cu^{+2}, Fe^{+3} and Mn^{+4} ions indicate that the instrument is indeed unaffected by these potential interferences. These results confirm the manufacturer's claims to the effect that charged species in solution do not penetrate the outer membrane of the probe.

Although the instrument readout meter is calibrated down to 0.01 mg/L, the instability of meter readings made the use of this lower scale impossible. Furthermore, scale drift required the instrument to be zero-calibrated before every sample measurement, making this an impractical routine instrument.

The main advantages of the Delta probe are its portability and its selective response to HOCl. However, in marine waters, the latter advantage diminishes because bromamines will tend to be detected just as HOBr is. The main disadvantages are its inadequate stability and sensitivity for low level analysis. Only in a situation where discharge regulations require measurement of "free chlorine" and where relatively high chlorine levels are being sought by analysis would this instrument be attractive for power plants.

ORION CHLORINE ELECTRODE

The Orion total residual chlorine electrode is a small portable chlorine probe which permits rapid analysis at the sampling site using an ordinary portable pH meter. The electrode consists of an internal iodide reference element with a platinum sensing element at the tip (Fig. 4-11). The Orion instrument measures the redox potential generated by iodine produced by reaction between chlorine solutions and an iodide reagent in an acidic (pH 4) medium. Electrode potentials developed in the iodine-containing solutions are plotted on the linear axis of semi-logarithmic graph paper against chlorine concentration (mg/L Cl_2) on the logarithmic axis.

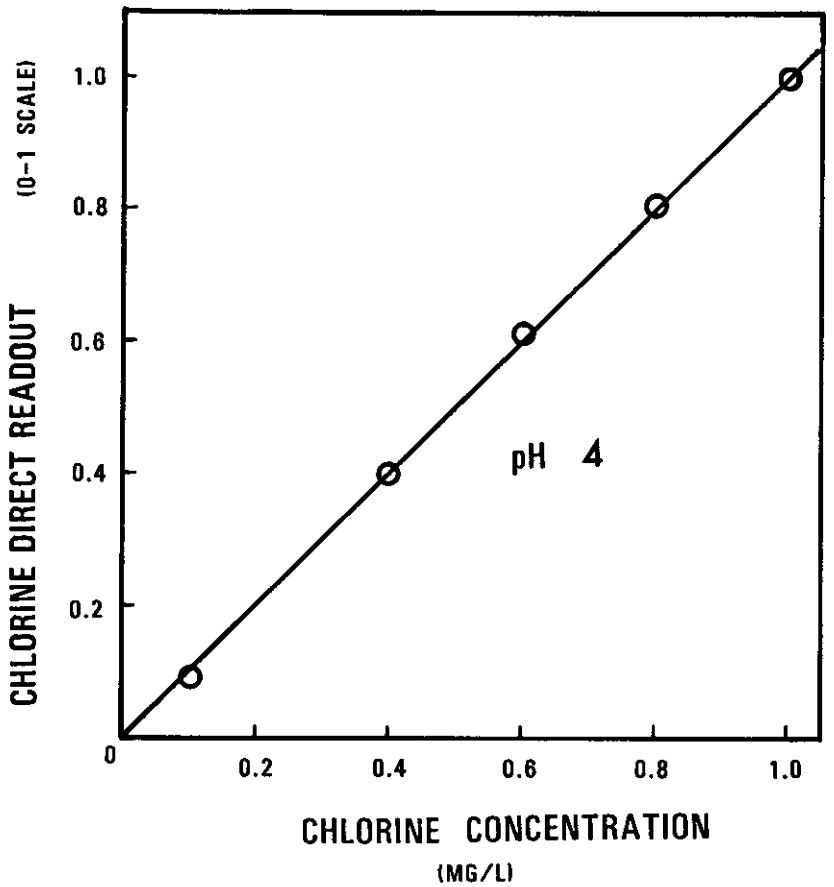


Figure 4-11. Chlorine calibration curve for Delta chlorine probe.

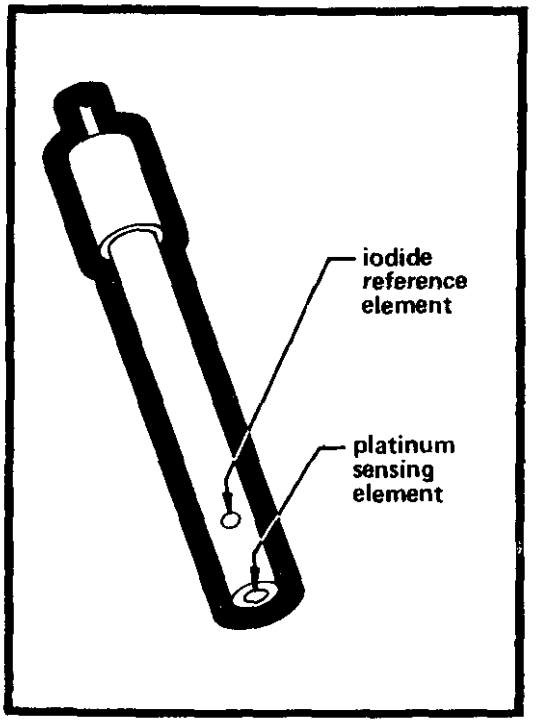


Figure 4-12. Diagram of the Orion electrode.

Standard solutions (200 mL), containing 1 mL 2M KI reagent and 1 mL pH 4 acetate buffer, were used to prepare a calibration curve of electrode potential (mV) versus chlorine concentration for the instrument. The chlorine concentration in a sample was determined by placing 200 mL of sample in a beaker containing 1 mL acetate buffer and 1 mL 2M KI reagent. The mixture should be stirred for about 2 minutes to allow complete reaction before inserting the electrode. The calibration curve of electrode potential versus log of chlorine concentration is linear in the range 0.05 to 1.0 mg/L Cl_2 (Fig. 4-12). The electrode calibration proved to be extremely stable with respect to time and is therefore suitable for large numbers of sample measurements. Although the electrode response to possible interferences was not examined in these analyses, the response should be similar to those for amperometric titration techniques as discussed previously. Platinum electrodes are quite susceptible to poisoning in natural waters. This alters their response and produces drift. We did not conduct tests of this electrode in natural waters because it appeared that the sensitivity was inadequate for power plant applications even under optimum conditions in the laboratory. While the electrode might be useful at concentrations above 0.1 mg/L Cl, especially if used simply as an indicator in a redox titration, we would recommend that it be tested extensively in the water of interest before being adopted.

At the time that this report was being written, a paper (22) appeared in which residual chlorine was determined to $\pm$0.002 mg/L in the range 0.003-0.100 mg/L. To achieve this increased sensitivity, the authors used an on-line mini-computer coupled to an automatic titration buret. The method of standard additions was used to calibrate the electrode below its region of Nernst reponse. While this work demonstrates that much lower detection limits may be obtained with this method, they are achieved only by sacrificing two of the method's most attractive features, its portability and its low cost.

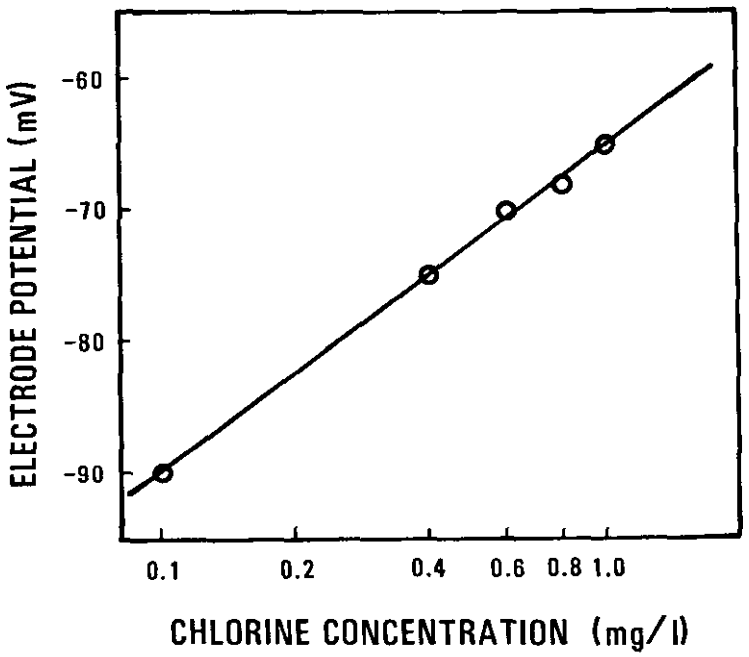


Figure 4-13. Chlorine calibration curve for Orion electrode.

DISCUSSION

Table 4-5 presents a comparison of the electrochemical methods available for chlorine. Which method would be most suitable for power plant monitoring would depend very much on the sensitivity required. If one is faced with monitoring concentrations above 0.1 mg/L, then all the methods are adequately sensitive and cost considerations would favor either a conventional amperometric titrator, the Delta membrane probe or the Orion electrode. Of these, the Delta measures mainly free chlorine (i.e. HOCl, OCl^-, HOBr, and OBr^-), the Orion measures only total chlorine, and the conventional titrator can measure either one in freshwaters but only total chlorine in marine waters. The detection limit of the conventional titrator listed in Table 4-5 is based on conversations with users and may be optimistic; we did not test these instruments. The detection limit for the Orion is a conservative estimate based on the range over which Nernst response is observed. By employing more elaborate calibration procedures, this detection limit can be reduced. While the Delta probe appears to be roughly comparable to the Orion in both price and detection limit, we found the latter to be far more stable and generally satisfactory. Furthermore, in marine waters the fraction of total oxidant measured by the Delta probe often will not be clearly definable.

If analyses below the 0.1 mg/L Cl level must be made, then we would not recommend any of the above methods, but instead either of the two more sensitive amperometric titration procedures, or the method using the N.B.S. flux monitor. We did not experiment with the manual titration method which uses a polarograph as an endpoint detector. However, the electrode system normally used in this procedure is the same as the one we used with the automatic titrator; hence the detection limit and general behavior should be the same for these two methods. The automatic titrator has two advantages over the manual titration procedure - it requires less operator

Table 4-5

COMPARISON OF METHODS

Method	Approximate Equipment Cost	Approximate Detection Limit (mg/L Cl)	Portable
Amperometric Titration			
a) Conventional Equipment*	$ 800	0.01	yes
b) Manual Titration Polarograph*	$4500	0.002	no
c) Automatic Titrator	$6500	0.002	no
N.B.S. Flux Monitor	$3000	0.002	yes
Delta Membrane Probe	$1000	0.05	yes
Orion Electrode w/Meter	$ 800	0.05	yes

*Not tested in this study.

skill and a permanent record of the result is produced in the form of a chart recording (e.g. Fig. 4-1). Its advantages with respect to the less expensive conventional amperometric titrator include a much lower detection limit, and, at least in our instrument, the capability to change titrant rapidly. This latter feature is valuable if samples with a wide range of chlorine concentrations must be dealt with, because in this case several different concentrations of PAO titrant will be needed for optimum precision at all levels. This feature also permits both the standard and back titration procedures to be used on the same sample if this is desired. The main disadvantages of the automatic titrator are that it is not portable, that it is complicated enough to confuse unskilled operators, and that it is expensive. However, since an automatic titrator is a flexible, general analytical instrument that is not restricted to chlorine in its applications, the expense factor may be partly offset if it can be used to solve multiple analytical problems. Furthermore, the experiments reported earlier on preserving oxidant level by adding either KI or PAO suggest that sometimes it is feasible to collect samples, dose them on the site with one of these reagents, and then bring them to the instrument. Thus portability may not be a serious drawback. At this time we recommend this method as best for low level chlorine analyses.

Our experience with the N.B.S. flux monitor was unsatisfactory. The prototype which we borrowed for testing had a number of defects, enumerated earlier, which make it unacceptable for routine use. All of these defects could be corrected.

In its basic design, this instrument has a number of advantages over other instruments. Most obvious are portability and low price compared to instruments of comparable sensitivity. While the calibration procedure may be slightly complicated, this could probably be automated with microprocessor circuitry for a price which would still be competitive with the automatic titrator. Among the numerous advantages of this instrument

are the following. The sample can be pumped into the instrument directly from the discharge stream or other sample source with no handling or transfers, thus minimizing opportunities to contaminate the sample with oxidizing or reducing agents or to lose oxidants by volatilization. The time between addition of reagents and analysis is only a few seconds, so there is little time for I_2 loss, or for background IO_3^- in a marine sample to interfere. Another advantage is that the buffer and KI are mixed before being added to the sample (see below). Finally, by being calibratable by the method of standard additions, poorly understood problems such as those described at the end of Section 3 will be minimized. Thus, if an improved version of this instrument should come on the market, it will merit careful consideration.

If we assume, however, that at present the best approach for low level chlorine analysis is that employing an automatic titrator, would it be best to employ this in the standard, or the back titration mode? The back titration procedure is inherently more cumbersome than the standard titration and thus less precise. It is recommended when negative errors in the forward titration due to loss of free I_2 from solution by volatilization, adsorption, reactions with organic matter or formation of undesirable by-products such as IO_3^- are a problem. However, our direct comparison of the forward and back titration procedures on a suite of natural samples spanning the range from freshwater to seawater revealed general agreement between the two methods. In the worst case, differences between the two methods amounted to 20%. We did not observe, as reported in the literature (11), that adding KI to chlorinated seawater results in underestimation by more than threefold of the chlorine produced oxidants due to iodate formation from iodine. Indeed, we find that the iodine so generated is stable for hours (see Fig. 4-4). Furthermore, when the forward and back titration did differ, the back titration yielded lower, rather than higher amounts of oxidant (the opposite was observed by Carpenter *et al*, 11.) The conclusion that must be drawn from our experiments is that in samples such as those studied, negative

errors in the forward titration are not large enough to justify undertaking back titrations as a normal procedure. However, whenever accurate data are desired, there would be merit in analyzing samples by both methods since this is easily done with an automatic titrator.

It is not clear that valid reasoning underlies the suggestion that the back titration be used to avoid spurious IO_3^- formation. In the back titration, the I_2 titrant is normally several orders of magnitude more concentrated than I_2 concentrations created by adding KI to waters which have been chlorinated at normal levels. During a back titration this titrant mixes with the sample over a time period of perhaps 10 seconds. Although the mechanism by which iodate forms is not known, the rate may well be 2nd or 3rd order in I_2 since, stoichiometrically, 3 moles of I_2 are required to make one mole of IO_3^-. Consequently, it is possible that much more iodate could be formed in a period of seconds around a concentrated, slowly dispersing I_2 titrant than would be formed in a period of minutes in a solution containing a uniform, much lower I_2 concentration. Thus, back titrations actually could be more sensitive to negative errors than the standard titrations. Our results suggest that this is true.

The conditions under which Carpenter et al (11) observed extensive iodate formation were not representative of those which would commonly be encountered in analysis at power plants. Their seawater contained very little organic matter and amino nitrogen and the KI was added within 1 min after the chlorine. Both of these factors tend to maximize the contact of KI with potent oxidants like HOCl and HOBr. With a higher amino nitrogen content and longer delay before addition of KI, the odds become greater that KI will encounter only weaker, bromamine oxidants such as those depicted in Figures 3-1 and 3-2. There is also some evidence (Crecelius, personal communication) that iodate formation is minimized if the buffer and KI used in the standard titration are premixed before being added to the sample. This prevents contact between the oxidant and KI under

neutral conditions where our calculations show IO_3^- to be stable (c.f. Figs. 3-1 and 3-2).

Section 5
OPTICAL METHODS

Diethyl-p-phenylenediamine (DPD) and syringaldazine belong to a group of amines which can be oxidized in solution by an agent such as chlorine to form semiquinones. The semiquinones from these compounds are highly colored free radicals and the intensity of color in the solution is dependent on the concentration of the free radicals formed. This concentration is a function of the original concentration of the oxidizing species in solution.

Analytical methods based on DPD (diethyl-p-phenylenediamine) are considered the most advanced of the colorimetric methods for chlorine and its daughter oxidants. Syringaldazine is the newest of the oxidant indicator dyes and has previously received only preliminary evaluations. The following experiments were designed to determine the basic physical parameters of the DPD and syringaldazine (FACTS) colorimetric methods which affect chlorine analysis in natural waters, and to evaluate the effect of possible interferences.

DPD METHOD

The diethyl-p-phenylenediamine (DPD) colorimetric method of chlorine analysis, developed by A. Palin (23) is capable of differentiating between the free and combined chlorine through a sequence of measurements before and after the addition of potassium iodide. In a comparative evaluation of several methods of residual chlorine analysis, Nicolson (24) reported that the DPD colorimetric method had good reproducibility and linearity, a low limit of detection, and satisfactory sensitivity. Its main drawbacks were the instability of the indicator solution and the difficulty in the production of stable solution colors.

The DPD indicator solution used in the following analyses was prepared by dissolving 1.0 g DPD oxalate (Cat. No. D24260 Pfaltz and Bauer, 126-04 Northern Blvd., Flushing, N.Y. 11368.) in chlorine-free distilled water containing 8 mL of 3N H_2SO_4 and 0.20 g disodium ethylenediamine tetracetate dihydrate. The solution was brought up to 1 liter volume and stored in a brown glass bottle. A phosphate buffer, which is usually recommended for this procedure, was made by dissolving 24 g anhydrous disodium hydrogen phosphate (Na_2HPO_4) and 46 g anhydrous potassium dihydrogen phosphate (KH_2PO_4) in distilled water containing 0.80 g disodium ethylenediamine tetracetate dihydrate. The solution was diluted to 1 liter with distilled water (1). However, when the seawater was used, Ca^{+2} and Mg^{+2} formed precipitates with phosphate, destroying the buffer, and causing the pH to be lowered out of the range desired for analysis. A citric acid buffer was found to be an acceptable alternative. It formed no insoluble precipitates in seawater and had a pH range similar to but slightly lower than the phosphate buffer. This buffer consisted of ~1M disodium citrate which was prepared from reagent grade citric acid and NaOH. The NaOH was added in slight excess of 2:1 to achieve a final buffer pH near 7. One advantage of this buffer is that it should help minimize interferences from trace metals such as Fe^{3+} or Cu^{2+}. This buffer was used in place of the phosphate buffer throughout the section of the study involving seawater samples.

Solutions of all interfering substances, except for H_2O_2, were prepared by making a stock solution from a soluble salt and making the calculated dilutions. 30% H_2O_2 was diluted and standardized iodometrically using the same reagents that were used for the chlorine standardization. 100 mL samples were made from this stock solution by appropriate dilutions. Interference samples were analyzed in the same manner as the chlorine solutions.

The artificial seawater was made by dissolving the following in 1 liter of distilled water:

NaCl	23.477g	KCl	0.664g
$MgCl_2 \cdot 6H_2O$	10.626g	NBr	0.0968g
Na_2SO_4	3.917g	KI	0.000075g
$CaCl_2$	1.102g		

Samples were prepared for analysis by pipetting 5 mL of DPD stock solution and 5 mL of buffer into a beaker, and adding 100 mL of sample. A Bausch and Lomb Spectronic 700 was used for all spectrophotometry except for the initial scans which were done on a Varian Scanning Spectrophotometer. A flow system attachment with a 1 cm cell was found to be convenient for the measurement of large numbers of samples. For spectrophotometric titrations, a colorimetric attachment for the Brinkmann automatic titrator was used.

The absorption maxima at 512 and 555 nm were found by scanning the colored solution through the range of DPD absorbance. Three sets of chlorine solutions were tested at 512, 515, and 555 nm to determine differences in absorbances (Table 5-1). The absorbances at 512 and 555 nm were essentially equivalent and slightly higher than those at 515 nm, the wavelength recommended in Standard Methods (1). Subsequent measurements were taken at 512 nm.

The linearity of the absorbance-chlorine concentration function was determined by measuring the absorbances of a series of chlorine solutions in the range 70 to 1200 μg/L (Fig. 5-1). A linear regression analysis was done on the points to determine the line A - b(conc.) + a and the goodness of the fit, as reflected in the correlation coefficient, r. The values of a, b, and r were:

$$a = -1.781 \times 10^{-3}$$
$$b = 2.67 \times 10^{-6}$$
$$r = .9971$$

Table 5-1

COMPARISON OF DPD ABSORBANCE AT 3 WAVELENGTHS

Solution	Wavelength (nm)		
	515	512	555
Blank	.020	.020	.021
1	.054	.058	.058
2	.061	.062	.062
3	.080	.082	.082
4	.089	.091	.092
5	.108	.112	.114

The precision of the linear function was determined by calculating the standard deviation of the constants a and b and the total standard deviation in determining absorbance from the calibration line. For the line in Figure 5-1 these values were calculated to be:

$$s_a = 3.87 \times 10^{-3}$$

$$s_b = 7.23 \times 10^{-6}$$

$$s_t = 8.10 \times 10^{-3}$$

The s_a value indicates that the line will pass through the origin. The relative standard deviations of the chlorine concentration at 100 ppb and 1000 ppb were calculated to be 33% for the 100 ppb and 3.1% for the 1000 ppb. The 100 ppb deviation seemed high, since Nicolson (24) reported a 5% standard deviation at this concentration. A second linear regression analysis, calculated using only the first six points, showed that the relative standard deviation for the 100 ppb concentration would be 15%, about half the deviation calculated from the first line.

The optimum concentration of the indicator DPD was established by adding varying amounts of DPD to five solutions containing 1.5 mg/L chlorine. These results showed that the color

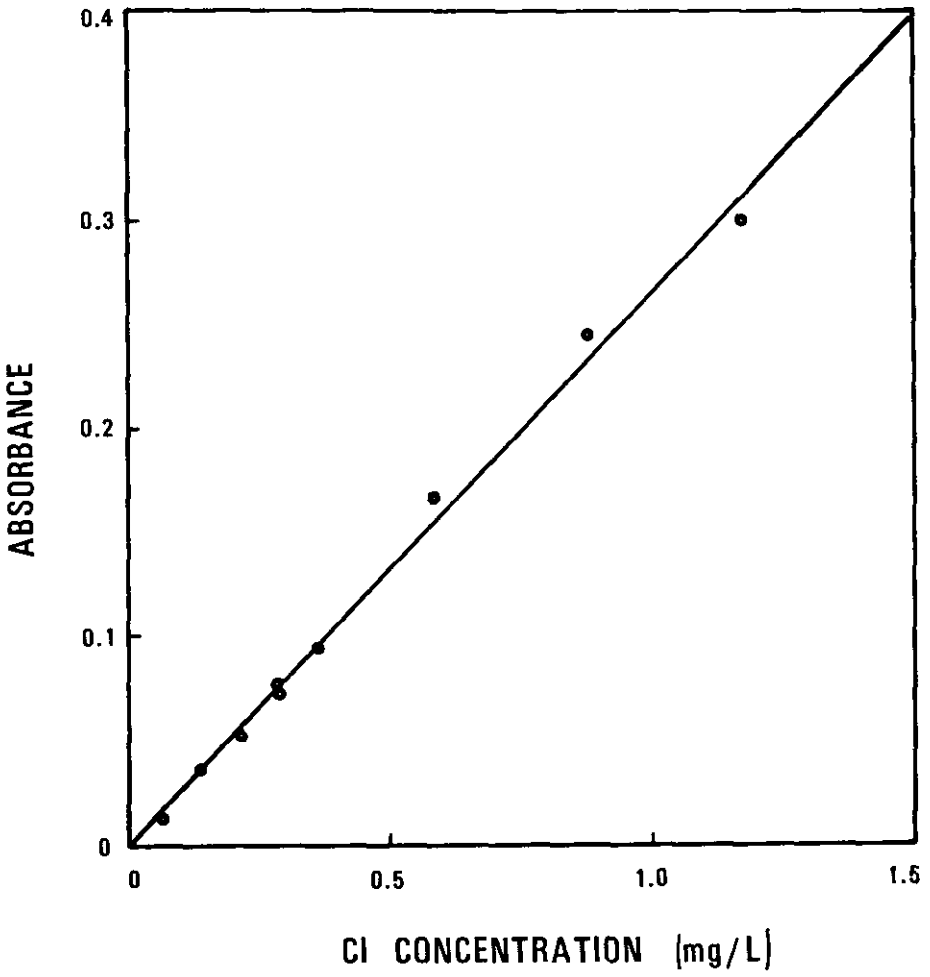


Figure 5-1. Calibration curve.

intensity became independent of the DPD concentration above the 5 mL of indicator recommended (Fig. 5-2).

To illustrate the practical detection limits for the DPD colorimetric technique, we used the absorptivity of 2.67×10^{-4} L/μg-cm from the first calibration line to calculate the chlorine concentrations that would be observed at 1% and 10% absorption. These concentrations are in Table 5-2. The 1% absorption level is equivalent to 4.26×10^{-3} absorbance which is on the same order as the standard deviation of the calibration lines. Although the larger path length (10 cm) theoretically increases the sensitivity of the method, in actual practice the background absorbance increased correspondingly and reduced the net gain.

Table 5-2
CALCULATED CHLORINE CONCENTRATIONS AT 1% AND 10% ABSORPTION

Cell Length	% Absorption	
	1%	10%
1 cm	16.3	163
10 cm	1.63	16.3

The instabilities of both the indicator stock solution and prepared sample solutions have been reported previously (24). The DPD amine undergoes a two step oxidation process, first to the colored free radical and then to the colorless imine. In the presence of a small amount of chlorine, the first step is the primary reaction. However, the DPD will react with any substance which is a strong oxidizing agent. Dissolved oxygen in water is the main interferent. In neutral solutions, we observed color begin to develop in about 15 minutes. Addition of a small amount of acid greatly slows the reactions so that the solution remains colorless for about a month. There is still

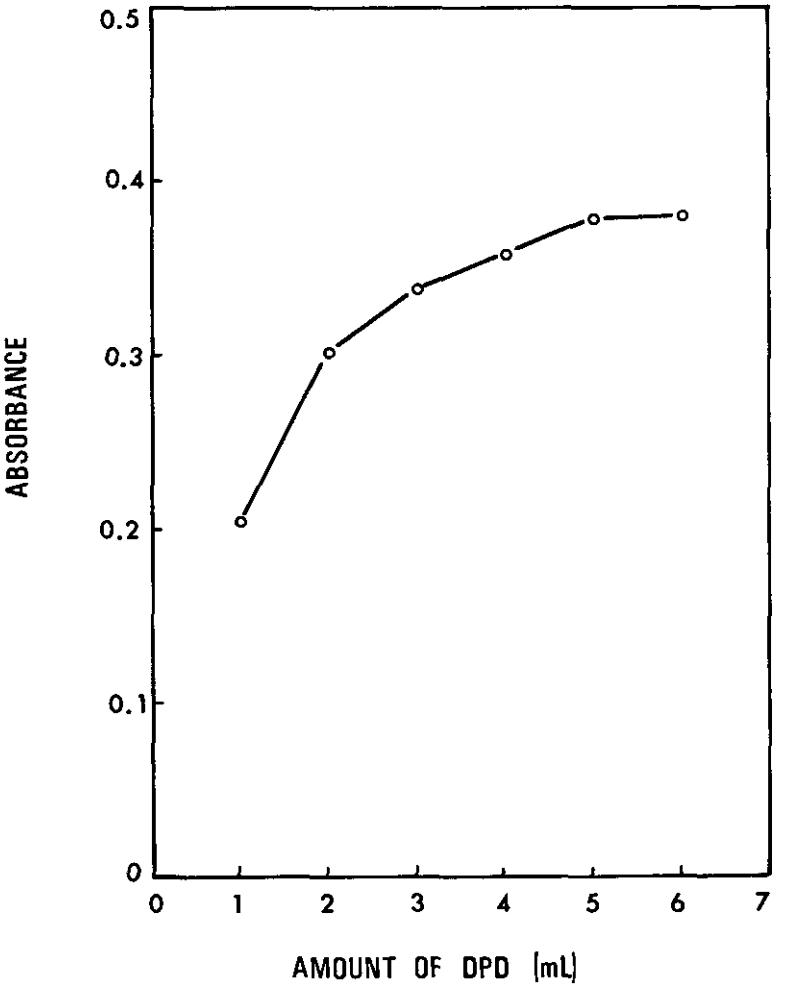


Figure 5-2. Effect of DPD concentration on absorbance.

a slow deterioration of the indicator being oxidized to the imine. As the DPD ages, its sensitivity toward chlorine decreases. This is illustrated by the differences in absorbances and absorptivities in a series of chlorine solutions analyzed using freshly prepared DPD and DPD that was 21 days old (Table 5-3).

It was also noticed that, if a mixture of DPD and phosphate buffer were allowed to sit, the solution quickly became colored. Two experiments using blank solutions containing DPD, buffer, and distilled water were performed to determine the factors controlling the rate of this drift.

In the first experiment, the increase in color, as a function of time, was measured for DPD solutions of three different ages (Fig. 5-3). Since DPD stability is sensitive to pH, the next experiment was designed to determine the optimum pH. These results indicate that the DPD is very susceptible to oxidation at pH 7 (Fig. 5-4). The drift decreases with decreasing pH so that measuring samples at lower pH (5.9) would minimize the possible error caused by the blank drift.

The chlorine samples themselves increased in color over a period of time. Whether or not this increase could be ascribed to the blank drift (presumably reaction with dissolved O_2) was tested by measuring the absorbances of two concentrations of chlorine over a period of time (Fig. 5-5). Measurements were taken at the same two minute intervals as the blanks to obtain a net absorbance or blank-corrected absorbance. The results from the fresh DPD solutions in Table 5-3 were used as the blank values.

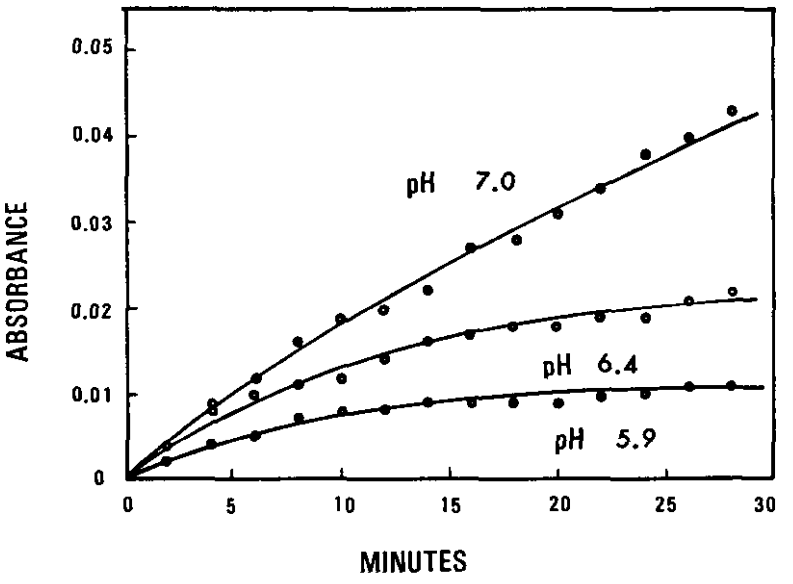


Figure 5-4. Stability of DPD in phosphate buffer as a function of pH.

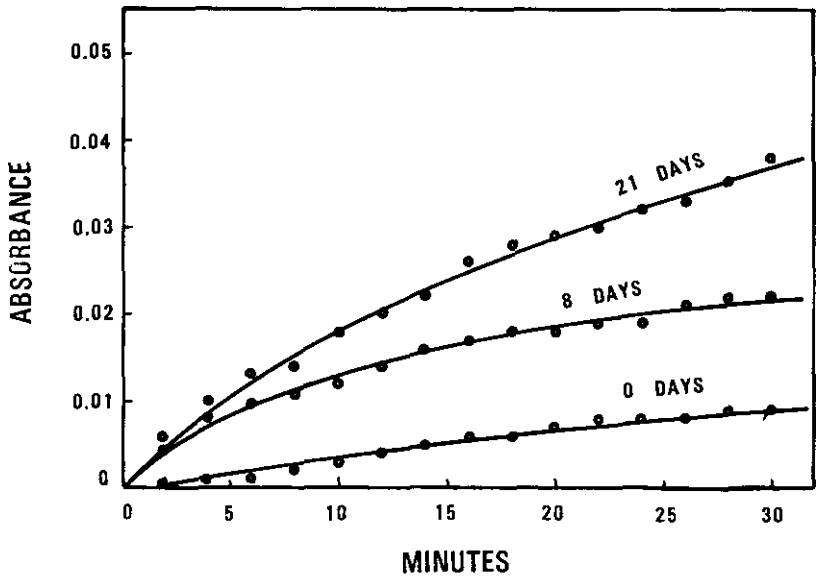


Figure 5-3. Stability of DPD Blanks at pH 6.4.

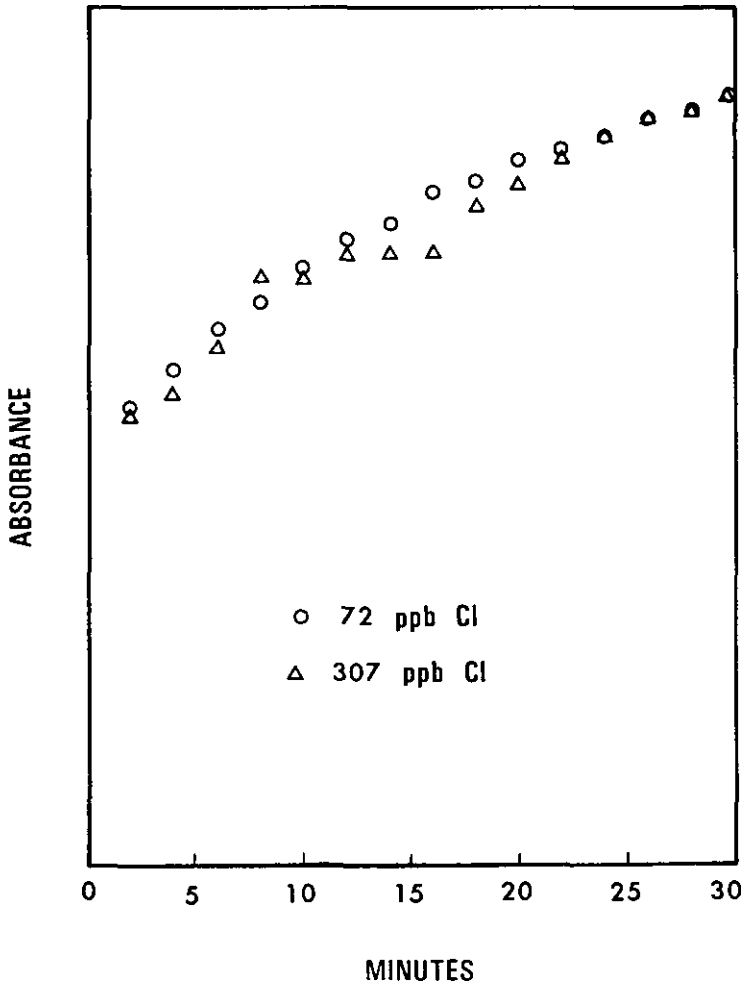


Figure 5-5. Solution stability vs. time at two different total oxidant levels. Data normalized to same absorbance range.

Table 5-3

COMPARISON OF DPD SOLUTIONS OF DIFFERENT AGES

Cl Conc. ppb	Net Absorbance	
	Fresh DPD Solution	21 Day old DPD Solution
293.1	.071	.076
586.3	.167	.153
879.4	.245	.215
1172.6	.299	.272
1465.7	.378	.328

The change in the net absorbances and absorptivities shows that the increase in color was not due entirely to the blank oxidation. The change in the absorptivities of each solution indicates that some further oxidation of DPD by chlorine occurred, though at a much slower rate than the initial formation of the colored solution. The rate of change in the absorptivities of the two solutions was approximately the same, indicating that the drift was dependent only on the concentration of DPD. Using fresh DPD stock solution and keeping the pH of all test solutions below 7 will minimize the drift, but will not eliminate it. Measurements on all solutions should be made at the same time interval after mixing to minimize errors caused by the drift.

The effect of pH on the blank drift was already described in the discussion of indicator stability. The effect of pH on apparent chlorine concentration was determined by measuring sets of chlorine solutions at three pH values (Fig. 5-6). The results at pH 5.9 and 6.4 are within experimental error. At pH 7.0, the sensitivity is significantly decreased, though the precision remains about the same. Consideration of these results and the effect of pH on the blank drift indicate that the best results are obtained by measuring samples buffered in the pH range of 6 $\pm$ 0.5.

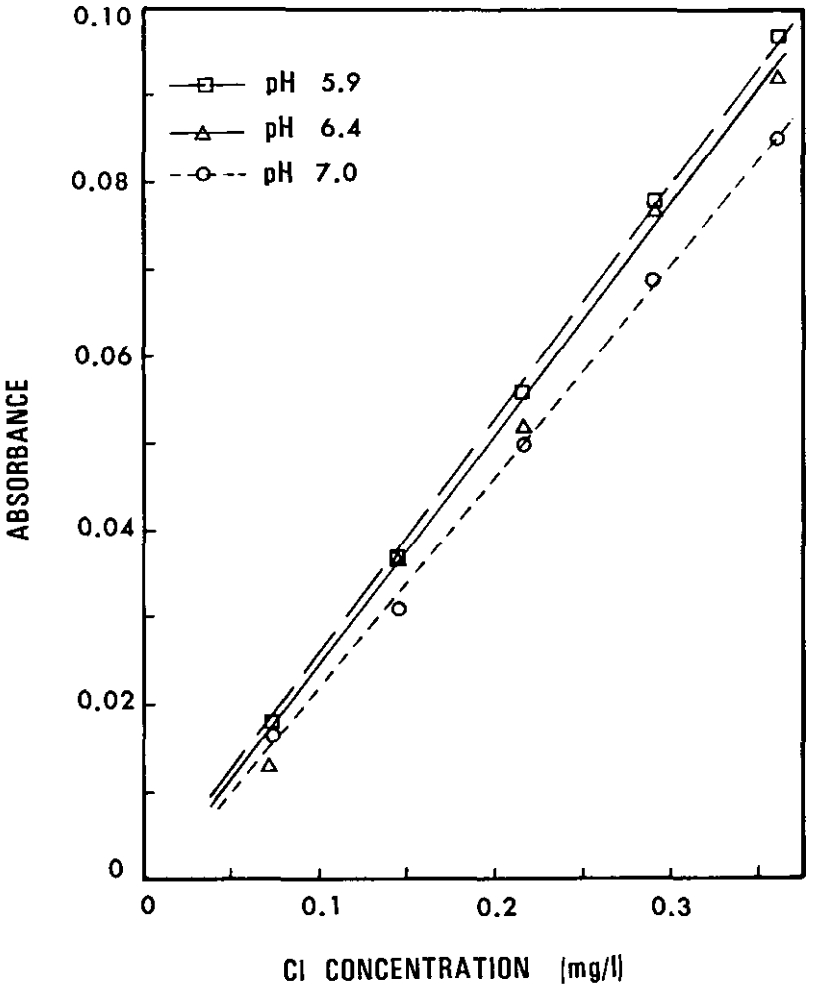


Figure 5-6. Effect of pH on Cl absorbance.

The effect of temperature on chlorine determination was shown by a series of chlorine measurements at 12, 19, 25, and 30°C (Fig. 5-7). There is a slight trend in the results due to temperature between 12° and 30°C. At the 1 mg/L level, there is approximately a 5.3% difference in the absorbances measured from the 12° and 30°C calibration lines. To reduce potential errors due to temperature variation, samples and standards should all be brought to the same temperature before analysis. This effect would be of importance in power plant applications of this technique.

In a comparison of the measured absorbance of samples made with distilled water and artificial seawater, it was found that there was either a large chlorine demand by the seawater, or that the apparent sensitivity of the DPD was reduced markedly. The former is more likely because high chlorine demand has been observed by independent methods even in simple KBr solutions (17). The presence of KI had no significant influence on the sensitivity of the response. The data are shown in Figure 5-8.

INTERFERENCES

Six potential oxidants were tested for their response in distilled water and seawater, with and without KI. These were BrO_3^-, IO_3^-, Cu^{+2}, Fe^{+3}, $S_2O_8^{-2}$ and H_2O_2.

The species were analyzed at 1 mg/L concentrations. Equivalent chlorine concentrations were determined using the absorptivity from the distilled water + KI line and reported in parentheses, as µg/L (Table 5-4), for those absorbances which were above the detection limit (.004 A). Blanks of buffer and test sample were run at all concentrations to compensate for the natural color in the test samples. Since there was a small difference in the volumes of blanks and solutions containing DPD, the reported blanks were adjusted to a value that would be measured at the DPD solution volume. Of the six species tested, BrO_3^- showed no response.

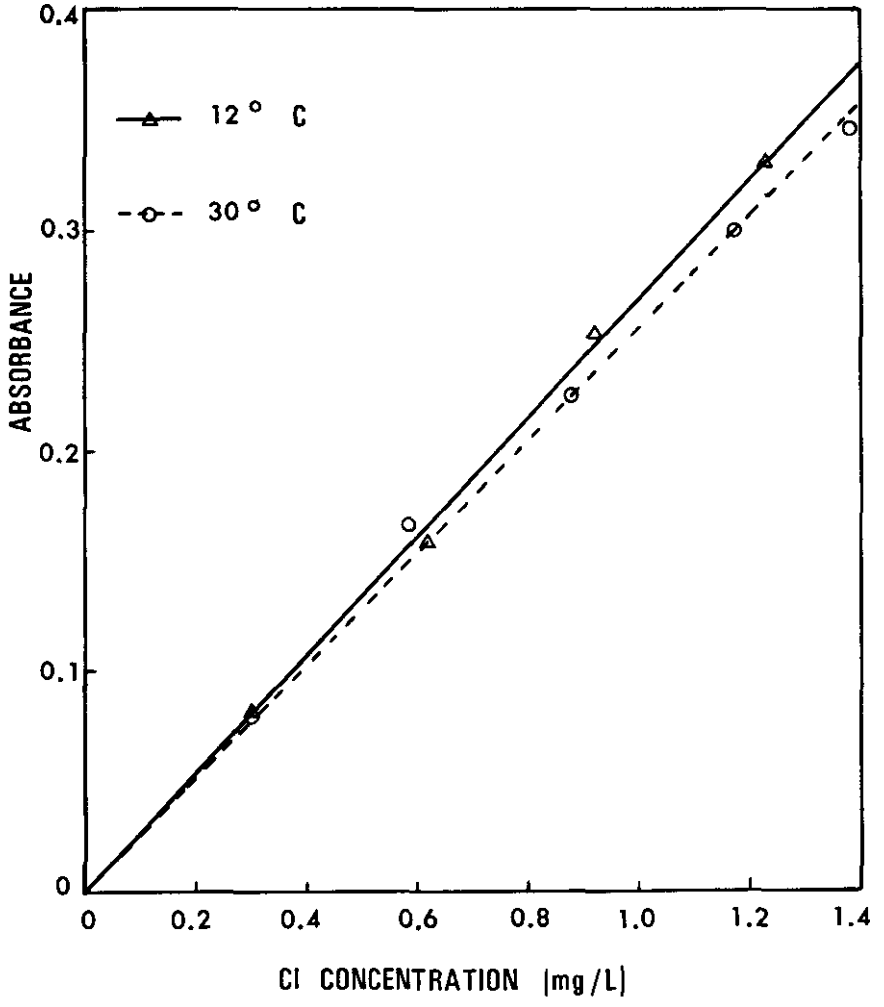


Figure 5-7. Effect of Temperature on Chlorine-DPD reaction. Additional data obtained at 19° and 25° yielded intermediate isotherms.

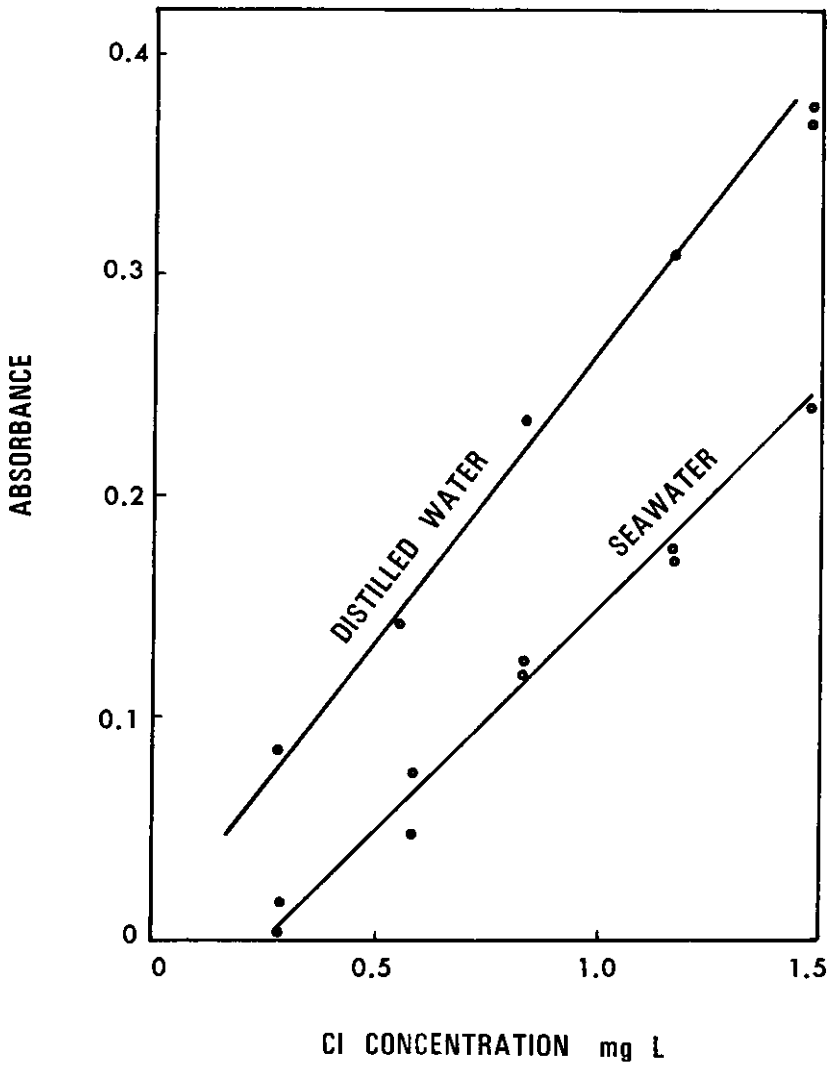


Figure 5-8. Calibration of Cl_2 in Citric Buffer. Absorbance vs. Dose of Cl_2. Addition of KI to these samples resulted in identical calibration curves.

Table 5-4

NET ABSORBANCE OF INTERFERENTS

	Distilled Water		Seawater	
Species	w/o KI	with KI	w/o KI	with KI
BrO_3^-	.001	.001	.001	.000
IO_3^-	.001	.003	.003	.005 (19.69)
Cu^{+2}	.003	.006 (23.62)	.007 (27.56)	.007 (27.56)
Fe^{+3}	.008 (31.50)[a]	.007 (27.56)	.004	.008 (31.50)
$S_2O_8^{-2}$	.002	.050 (196.9)	.008 (31.50)	.072 (283.5)
H_2O_2	.003	.092 (362.2)	.000	.090 (354.3)

a. Numbers in parentheses refer to equivalent chlorine concentration (μg/L) determined from the distilled water + KI curve in Fig. 5-8.

In distilled water, the measured absorbances for Fe^{3+} were due to the color of hydrolyzed $Fe(OH)_3$ rather than the oxidation of DPD. Using seawater as a solvent gave similar results. Persulfate is a strong oxidizing agent, but its reaction in distilled water with DPD was relatively slow. In seawater, the reaction was even slower and measurements could be taken before the persulfate reacted with DPD to any great extent. The response was slightly changed when KI was added to the prepared samples. The persulfate caused a significant response in the KI solutions even at 1 mg/L level, due to the formation of I_2. Its presence would prevent the accurate determination of combined chlorine fractions and the residual chlorine by the DPD method.

The analysis of peroxide solutions produced great instability of the absorbance readings. This was probably due to the large amount of dissolved oxygen in the solutions. Like persulfate, peroxide underwent a reaction with I^- and caused a serious interference in the analysis of combined chlorine and total chlorine even when it was present in small concentrations.

It was evident that DPD is not specific to chlorine, nor is it limited to a small number of interferences. Other strongly oxidizing substances may oxidize DPD under some conditions. If the concentration of the oxidant is large enough, the DPD is completely oxidized to the imine and the method is useless. The generation of iodine was the cause of the responses of the five substances that showed measurable interference at the 1 mg/L level. Persulfate and peroxide were strong enough to cause large DPD responses even at 1 mg/L.

Conclusions

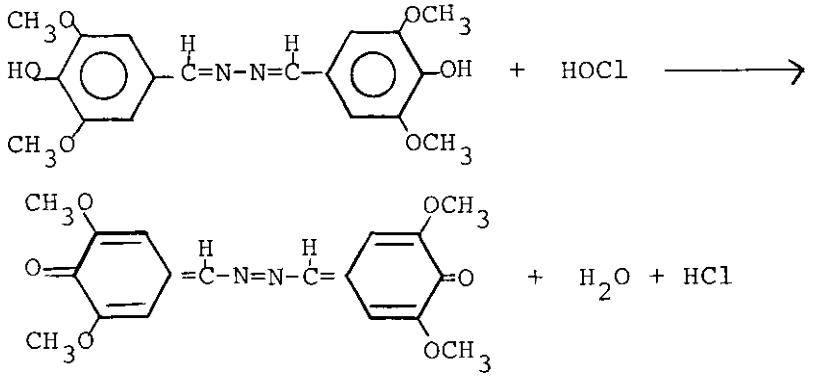
Of the parameters evaluated, DPD concentration, temperature and pH have limited effect on analytical response. Indicator instability can cause serious errors, this being an inherent limitation of the method. Best results are obtained by measuring the absorbance of samples immediately after addition of the

indicator. Using fresh DPD solution and buffering the samples to pH 6.0 slows the drift and, thus, the error is minimized. The non-specificity of the DPD reagent could lead to serious interferences when other halogens or oxidizing species are present. In seawater, the method is feasible if the amount of other oxidizing ions are present only in trace amounts. The use of KI to improve response to combined halogen caused both a radical change in the calibration line and a large increase in the number of substances to which the indicator responded.

SYRINGALDAZINE METHOD (FACTS)

The syringaldazine (FACTS) method is a colorimetric procedure which is advocated for determining free available chlorine (hypochlorous acid, hypochlorite ion) in water buffered to pH 6.8. The reagent is reportedly not sensitive to bound chlorine, such as chloramines (25), although other strong oxidizing agents such as iodine, bromine and ozone will produce a color. Very high concentrations of monochloroamine (> 35 mg/L), oxidized manganese (> 2.6 mg/L), and ferric iron (> 10 mg/L) will slowly produce a color with syringaldazine. Nitrite (≤ 250 mg/L), nitrate (≤ 100 mg/L), sulfate (≤ 1000 mg/L) and chloride (≤ 1000 mg/L) do not interfere with the FACTS procedure (1).

The oxidation of syringaldazine (3,5-dimethoxy-4-hydroxy-benzaldazine) by chlorine reacts on a mole to mole basis. The reaction may be represented as follows (25):



The purple color produced has an absorption maximum at λ = 530 nm. The minimum detectable concentration is approximately 0.1 mg/L, making it unsuitable for most power plant monitoring problems.

The syringaldazine indicator solution was made by dissolving 115 mg of 3,5-dimethoxy-4-hydroxybenzaldazine (No. 17 753-9, Aldrich Chemical Co., Inc., Cedar Knolls, N.J. 07927) in 1 liter of 2-propanol. Since the solute is only slightly soluble, it must be heated gently for several hours until the syringaldazine dissolves.

Chlorine standards (0.1 mg/L) were prepared from stock sodium hypochlorite solution whose chlorine concentration was established by the iodometric method. Chlorine standard solutions were checked by amperometric titration just prior to use.

A sample containing combined bromine was made to check the method for bromoamine response. Potassium bromide (KBr) was added to 1 mg/L Cl solution to equal 60 mg/L Br^- to form hypobromous acid as in the following equation:

$$HOCl + Br^- \rightarrow HOBr + Cl^-$$

Ammonia was then added to equal 5 mg/L NH_3 to form bromoamine as follows:

$$HOBr + NH_3 \rightleftarrows NH_2Br + H_2O$$

Fifteen ml of standard, or sample, and 0.5 ml buffer were added to a test tube containing 5 ml syringaldazine indicator solution. The solution was capped immediately, inverted several times to mix, and 60 sec. were allowed for the full color to develop. The samples should be analyzed within 10 minutes to minimize color fading and instrument drift. A Bausch and Lomb Spectronic 700, equipped with 1 cm quartz cells, was used for all measurements. The instrument was zeroed with blank solutions containing buffer and indicator (5 ml).

The standard curve for the chlorine-syringaldazine reaction deviates only slightly from Beers Law (Fig. 5-9) in the concentration range 0.1 to 2 ppm chlorine. Specifically, the curve in this region is a straight line, but it does not actually pass through the zero point. The chlorine detection limit for this method is ~0.1 mg/L.

The bromoamine sample reacted with syringaldazine to produce an orange color. After three days, addition of the syringaldazine indicator produced a bright yellow solution, characteristic of the reaction of syringaldazine and ammonia, or haloamines. Solutions with and without chlorine, bromide, and ammonia were also prepared. The results of reactions with syringaldazine are summarized in Table 5.5. The orange color in the bromoamine sample is apparently due to a mixture of ammonia-syringaldazine and oxidant-syringaldazine phases. The syringaldazine indicator solution remained clear in the absence of both oxidant and amines, and produced a yellow color (λ = 368 nm) when only amines were present. Bauer and Rupe (25) reported that combined chlorine (chloroamine) does not interfere with the free available chlorine determination and recommended the FACTS method for situations where disinfection was a primary consideration. The formation of bromoamines rather than chloroamines in seawater (2,3) indicates that the specificity of the syringaldazine method would be decreased in seawater.

DISCUSSION

The most critical problem encountered when applying colorimetric procedures to natural waters is interference from turbidity and color in the water. One strategy to avoid this is to employ a titrimetric variation in which the critical analytical measurement is one of titrant volume rather than light absorbance. In this capacity, the Brinkman automatic titrator used for amperometric chlorine determinations (Sec. 4) can be used as a colorimetric titrator by replacing the reference and platinum electrodes with a Brinkman colorimetric probe.

Table 5-5

SYRINGALDAZINE RESPONSE

	No Br-	60 mg/L Br-
No NH_3	Purple	Purple
5 mg/L NH_3	Yellow	Orange

a) 1 mg/L Cl in initial solution

	No Br-	60 mg/L Br-
No NH_3	Clear	Clear
5 mg/L NH_3	Yellow	Yellow

b) No Cl in solutions

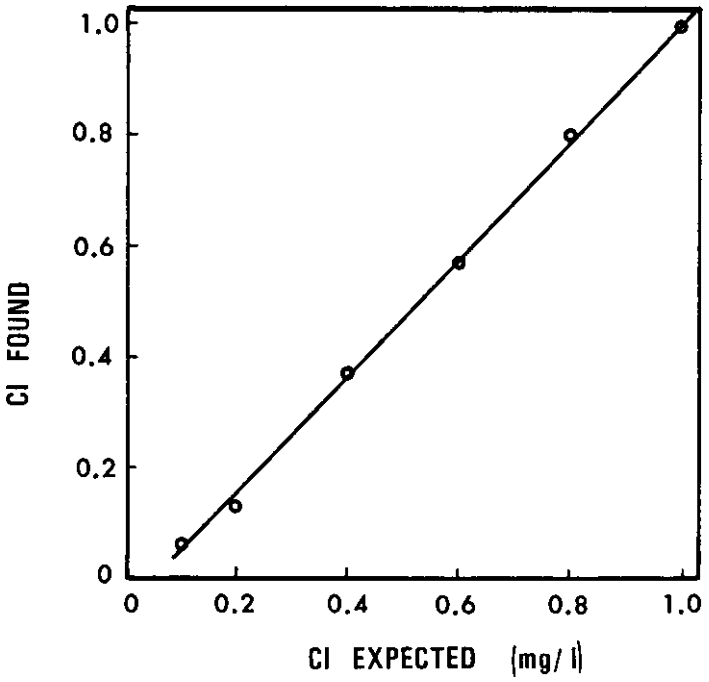


Figure 5-9. Calibration curve for chlorine-syringaldazine reaction.

The flexible probe colorimeter permits measurements to be made directly in test tubes or bulk containers, a useful feature in sequences of repetitive tests. The probe tip light path in a fluid is 2 cm. The percent transmittance is read directly from the voltage output meter after the meter has been zeroed on a blank solution. Terminals for connection to an external chart recorder are also provided, which allows an accurate determination of the volume titrated. Since it is not necessary to measure the actual value of the absorbance at this point, interferences due to natural color and turbidity are unimportant.

At this time it appears that DPD methods will be of limited usefulness to power plant operators who require extremely low level analyses. We found the absorptivity of oxidized DPD to be 2.67×10^{-4} $(\mu g/L\ Cl)^{-1}\ cm^{-1}$. If we assume that the smallest % absorption shift which is useful for detecting an endpoint is 1%, then the smallest amount of chlorine which could be detected under these conditions using a 1 cm path length is 16.3 μg/l Cl for DPD. For the FACTS method (syringaldazine indicator), the limit under these conditions is 12 μg/L. The detection limit can be reduced by increasing the path length, but practical considerations probably limit this improvement to about one order of magnitude (10 cm pathlength). Our commercial apparatus for automatic colorimetric endpoint detection is limited to a 2 cm pathlength. Thus the absorptivity of DPD and syringaldazine are such that under optimum circumstances, a quantitive measurement at 5 μg/L Cl would be marginal. It should be stressed that this is a theoretical limit. Actual limits would not be as good due to problems with color fading, O_2 interference, etc.

Because the problem is in the absorptivity, we sought ways of increasing this. In separate sets of experiments, we investigated the effect of light wavelength, DPD concentration, KI catalysis, solution temperature and pH. Unfortunately, none of these experiments revealed a way by which the absorptivity of DPD might be significantly enhanced (small improvements were made, however).

Work on chemical interferences in distilled water and synthetic seawater revealed negligible or small interferences from BrO_3^- and IO_3^-, although some interference from the latter occurred when KI was added to the seawater sample. Hydrogen peroxide and peroxydisulfate produced marked responses in the presence of KI. In order to use the DPD method with seawater it was necessary to replace the standard phosphate buffer with a citric acid buffer.

After examining both the DPD and FACTS methods, it is our opinion that optical methods offer very little hope of providing reliable data at the very low levels which will be needed by power plant operators.

Section 6

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