# Use of an Ion-Selective Electrode for Determination of Free Chloride Ions in Water-Based Drilling Fluids

**F. Kaland**
**U. Hakli**
**P. Ruoff**
Rogaland Regional College

# Use of an Ion-Selective Electrode for Determination of Free Chloride Ions in Water-Based Drilling Fluids

**F. Kaland,** *SPE, Rogaland Regional College
**U. Hakli,** Rogaland Regional College
**P. Ruoff,** SPE, Rogaland Regional College

**Summary.** The use of an ion-selective electrode (ISE) for the determination of chloride ions in water-based drilling fluids has several advantages: the measurement is simple, fast, easy to perform, and inexpensive. An ISE can be used for continuous chloride ion logging and allows analysis of colored samples where the traditional API-recommended method is difficult to use.

## Introduction

The determination of the chloride ion concentration in drilling fluids is very important. For example, the effect of sodium chloride on a water-based bentonite mud can be rather dramatic, as shown in Fig. 1. The increase of viscosity in Region A is generally believed to be caused by flocculation of the bentonite particles, while the decrease of viscosity in Region B is a result of aggregation of the clay.[1]

To determine the amount of chloride ion in a water-based drilling fluid, API recommends titration of the filtrate with a standardized silver nitrate solution that uses chromate ions as an indication of the equivalence point.[2] This method, also called the "Mohr method"[3] after its inventor, requires pH adjustment. If the pH is too low, dichromate ions are formed and do not react with silver ions, making the detection of the endpoint impossible. On the other hand, when the pH of the sample is too high, silver oxide is preferentially formed instead of silver chloride. To avoid these problems, phenolphthalein, acid, and calcium carbonate are normally used to adjust the pH to about 8.3. In addition, serious endpoint-detection problems can arise when the sample is miscolored. An alternative titration method, which avoids the problems of the chromate indicator, is the use of silver or chloride ISE's working as indicator electrodes for the determination of the endpoint.[3]

We were looking for a method, however, that is easy and quick to perform, applies to miscolored samples, is relatively independent of pH, is inexpensive, and can be used as a continuous mud logging device for chloride ions. It appears to us that a chloride ISE alone fulfills all these requirements in a satisfactory way.

## Method and Apparatus

The use of ISE's has become an important tool in quantitative chemical analysis in many fields of industrial and laboratory applications—e.g., air and water pollution; toxicology; industrial hygiene; analysis of soil, water, and

pharmaceuticals; and other industrial purposes.[4] Thus we found it natural to apply a chloride ISE for the determination of chloride ions in water-based drilling muds.

The chloride ISE consists of a membrane made out of a matrix of silver chloride and silver sulfide. When the membrane is in contact with a solution containing chloride ions, the electrode develops a potential because of the chloride ion concentration. The potential is measured against a constant reference potential with a digital volt meter or a specific ion meter.[5] The measured potential corresponds to the chloride ion level in the solution and is described by the Nernst equation[4,6]:

$$E_{pE} = E_{pr} + m \log C_e, \quad \dots \dots \dots \dots \dots \dots (1)$$

where $E_{pr}$ is a constant and $m$ is about 59 mV per log unit at 20°C [68°F].

The chloride ion activity, $C_e$, is related to the chloride ion concentration of free chloride ions, $C_f$, by the ionic activity coefficient, $\gamma$:
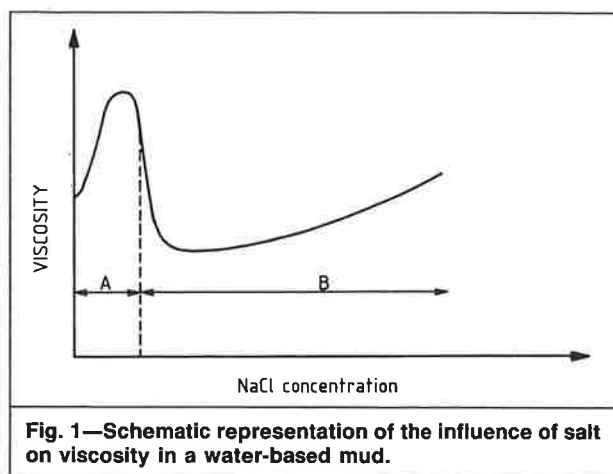
$$C_e = \gamma C_f. \quad \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (2)$$

Ionic activity coefficients are variable and largely dependent on total ionic strength. Ionic strength is defined as

$$I = 0.5 \sum_{i=0}^{i=n} C_i (Z_i)^2. \quad \dots \dots \dots \dots \dots \dots (3)$$

If the background ionic strength is high and constant relative to the sensed ion concentration, the activity coefficient is constant and the chloride ion activity is directly proportional to the concentration. An ionic-strength adjuster should be added to all samples so that the background ionic strength is high and constant relative to variable concentrations of chloride. We used $NaNO_3$ as the ionic-strength adjuster, but other solutions can be used as long as they do not contain ions that would interfere with the electrode's response to the chloride ion.[6]

*Now with Baker Production Technology.

Fig. 1—Schematic representation of the influence of salt on viscosity in a water-based mud.
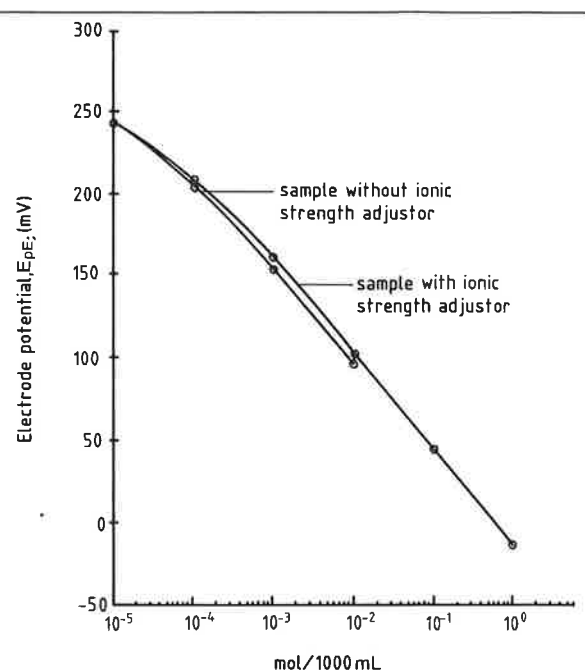


Fig. 2—Calibration curve that shows electrode potential of a chloride ISE as a function of NaCl concentration (mol/1000 mL of solution) with and without ionic-strength adjuster.

In our experiments, we used an Orion chloride ISE Model 94-17A™ (chloride).[6] As a reference we used a silver/silver-chloride double-junction electrode (Orion, Model 90-02™) to avoid the contamination of chloride ions in the sample. Any other reference electrode can be used, however, as long as it does not release interfering ions. A calomel electrode, for example, should be avoided because chloride ions will diffuse from the salt bridge of the calomel electrode into the sample.

The electrode setup described operates within a chloride ion concentration range of about $10^{-4}$ to 10 $M$, which exceeds the actual chloride ion concentration range of drilling muds by several orders of magnitude on each side. For measurements in the linear region—i.e., for chloride ion concentrations of $2 \times 10^{-4}$ $M$ or 7 ppm (chloride) and above—the procedure is practically independent of pH. For quantitative analytical requirements —i.e., for an accuracy of about 2 to 3%—standards and samples should be within 1°C [1.8°F] of one another. Slope $m$ (Eq. 1) increases in magnitude by 1 mV per 5°C [9°F] change in temperature.[6] A drawback of the Mohr method is that it can be used only at room temperature because the solubility of silver chromate increases with rising temperature and its sensitivity as an indicator undergoes a corresponding decrease.[3]

The electrode couple can be connected to a specific ion meter for direct readings of ion concentrations.[5] In our measurements, however, a simple millivolt meter was used.

## Experimental Procedure and Results

By use of several solutions with known NaCl concentrations, the electrode characteristic was established ($m = -57.3$ mV/log unit and $E_{pr} = 249.5$ mV). Fig. 2 shows the measured electrode potential against known NaCl solutions with and without ionic-strength adjustment. The figure clearly demonstrates that for quantitative work, ionic-strength adjustment is absolutely necessary. The relationship between NaCl concentration in mol/1000 mL of solution and parts per million (NaCl) is calculated by the following relationship:

$$C_{NaCl} = C_{[Cl^-]} \times M_{NaCl} \times 1000/\rho, \quad \ldots \ldots \ldots \ldots (4)$$

where $M_{NaCl}$ is the molecular mass of NaCl in g/mol and $C_{NaCl}$ is the NaCl concentration in mol/1000 mL solution.

Several parallel experiments were carried out to see whether the chloride ion concentration in water-based test muds can be determined by the use of an ISE with the desired accuracy of about 2 to 3%. In these test muds, the chloride ion concentration was determined by use of both the Mohr method and the electrode method with various salt concentrations. As a final test, we determined chloride ion concentrations in some drilling fluid samples from the North Sea where the additives were unknown to us.

The test muds were made up of 22.5 g of Wyoming bentonite, 350 mL water, and NaCl. Bentonite and water

| Mud Sample* | NaCl Added (g) | $E_{pE}$ (mV) | NaCl From Electrode (ppm) | NaCl From Mohr (ppm) | Deviation (%) |
|---|---|---|---|---|---|
| 2 | 9 | 8.48 | 29,600 | 26,500 | 10.5 |
| 3 | 18 | −9.0 | 53,600 | 52,000 | 3.0 |
| 4 | 27 | −18.86 | 79,700 | 76,900 | 3.5 |
| 5 | 36 | −25.51 | 104,100 | 100,800 | 3.2 |

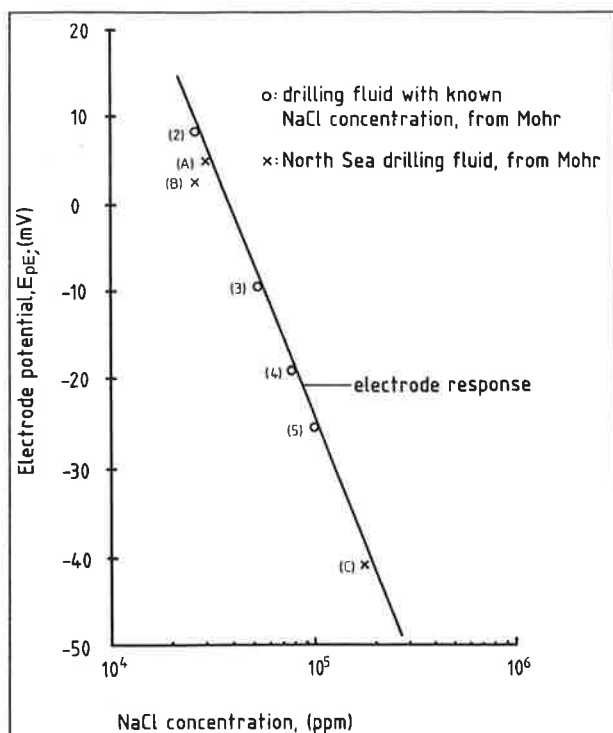TABLE 1—RESULTS FROM LABORATORY-PREPARED MUDS

*Mud Sample 1 contains no NaCl.

**Fig. 3—Determined chloride ion concentration on filtrates of laboratory-prepared muds and North Sea field muds by chloride ISE and the Mohr method.**

**TABLE 2—RESULTS FROM NORTH SEA FIELD MUDS**

| Mud Sample | $E_{pE}$ (mV) | NaCl From Electrode (ppm) | NaCl From Mohr (ppm) | Deviation (%) |
|---|---|---|---|---|
| A | 4.3 | 31,400 | 29,000 | 7.6 |
| B | 2.3 | 34,100 | 25,700 | 24.6 |
| C | −40.6 | 190,900 | 174,100 | 8.8 |

trode. To compare chloride ion concentrations from Mohr with the electrode values, chloride ion concentrations from the electrode are found when the chloride ion concentration is read from $E_{pE}$ values that are connected through the straight curve of the electrode response.

Table 2 gives the results from measurements on three different North Sea water-based drilling muds. We received these muds from three different operators. Mud Sample A was described by one operator as a salt-water/polymer/gypsum mud. Mud Sample B was a lignite/lignosulfonate mud. No information about polymers, clay, or electrolytes was available. Mud Sample C was described by another operator as a combined polymer/lime [$Ca(OH)_2$]/brine ($CaCl_2$) mud. We found that the deviation between the Mohr method and the electrode method is larger for the field muds than for the drilling fluid test samples we made. The deviation is especially high for Sample B. The results from the North Sea drilling muds are also shown in Fig. 3 together with the data of our test samples.

## Discussion

When the chloride ion concentration is lower than 7 ppm, the electrode deviates from the linear Nernst response, as can be seen from Fig. 2. For an actual mud, however, chloride ion concentrations lower than 7 ppm can normally be neglected.

Because the ion-strength adjuster should normally be added to achieve reasonably accurate measurements, it can be difficult to use the electrode for continuous quantitative chloride ion analysis of drilling muds. If, on the other hand, the accuracy requirements are relaxed, then ion-strength adjustment can be omitted, and the possibility exists for a continuous semiquantitative chloride ion indication in the mud.

If it is desirable to do a quick quantitative chloride ion analysis without first preparing the drilling fluid filtrate, this can be done by adding the ion-strength adjuster directly to the drilling fluid and then measuring the electrode potential. We tried this method on the North Sea drilling fluids and on Sample 4. The deviation from Mohr is higher than on the measurements taken on the filtrate, but the values are within reasonable limits. Fig. 4 shows these results and the results from measurements taken directly on the drilling fluid without any ion-strength adjuster.

In addition to the chloride ion, the chloride ISE is also sensitive to other anions, especially iodide, sulfide, and cyanide ions. Table 3 shows the maximum allowable ratio of interfering ion concentrations to the chloride ion concentration.[6] Because iodide, sulfide, and cyanide form rather sparely soluble precipitates with silver ions, these anions also interfere in the Mohr method.

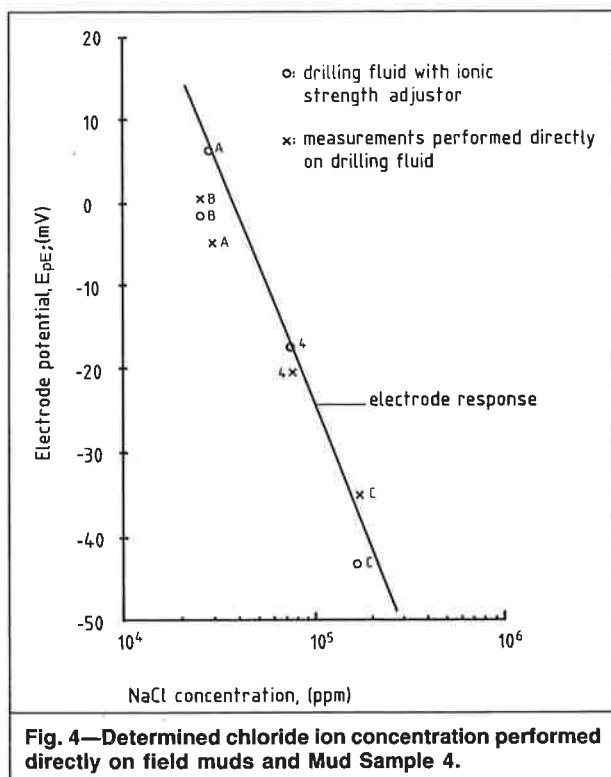Care should also be taken in the presence of cations that readily form complexes with chloride ions—e.g., $Tl^{+3}$,

were mixed for 5 minutes before NaCl was added; then the mud was mixed an additional 5 minutes. Table 1 shows the NaCl content used in each sample.

Then the test muds were filtered according to the standard API procedure that uses a low-temperature (21°C [70°F]) filter press. The samples used for the determination of the chloride ion concentration by the electrode method consisted of 10 mL mud filtrate and 90 mL of a 1-$M$ $NaNO_3$ solution for ionic-strength adjustment. This solution was poured into a 150-mL low-form beaker, and the electrode potential was measured when both the ISE and the reference electrode were immersed into the sample. A magnetic stirrer is recommended to avoid potential fluctuations caused by local inhomogeneities in inert electrolytes, which come from the double-junction reference electrode.

Table 1 shows the results of the measurements and the deviation from the Mohr method. The concentration of NaCl in parts per million is calculated by

$$C_{NaCl} = 1.65 \times 10^{E_{pE} - E_{pr}/m}. \qquad \dots (5)$$

In Eq. 5, differences in sample densities, $\rho$, are neglected; all sample densities were set to water's density—i.e., $\rho = 1.0$ g/mL.

As in Fig. 2, the electrode potential plotted against NaCl concentration on semilogarithmic paper gives a straight line with slope $m$. This is shown in Fig. 3 together with the corresponding results from Mohr's titration. For each sample, a chloride ion concentration value is obtained from the Mohr method (abscissa in Fig. 3) together with a potential reading $E_{pE}$ (ordinate in Fig. 3) from the elec-

**Fig. 4—Determined chloride ion concentration performed directly on field muds and Mud Sample 4.**

Plot legend:
o: drilling fluid with ionic strength adjustor

x: measurements performed directly on drilling fluid

electrode response

Electrode potential, $E_{pE}$, (mV)

NaCl concentration, (ppm)

taken when this method is used on drilling fluids that contain significant amounts of complexing agents and/or interfering ions. But normally these interfering ions will also cause difficulties when the Mohr method is used because they will form either extremely sparely soluble precipitates with silver ion or tightly bounded complexes with chloride ions.

## Nomenclature

$C_{[Cl^-]}$ = chloride ion concentration, $M$

$C_e$ = chloride ion level in solution, effective concentration, $M$

$C_f$ = concentration of free chloride ions, $M$

$C_i$ = concentration of Ion $i$, $M$

$C_{NaCl}$ = NaCl concentration, ppm

$E_{pE}$ = measured electrode potential, mV

$E_{pr}$ = reference potential, mV

$I$ = ionic strength, $MC^2$

$m$ = electrode slope, mV per log unit

$n$ = number of ions

$Z_i$ = charge of Ion $i$, C

$\gamma$ = ionic activity coefficient

$\rho$ = specific density of sample, g/mL

## References

1. "Drilling Fluid Engineering Manual," Magcobar Div., Oilfield Products Group, Dresser Industries Inc., Houston (1977) Chap. 3.
2. *Standard Procedure for Testing Drilling Fluids*, tenth edition, API, Dallas (1984) 23.
3. Skoog, D.A. and West, D.M.: *Fundamentals of Analytical Chemistry*, Holt, Rinehart & Winston Inc., London (1974).
4. Koryta, J.: *Ion-Selective Electrodes*, Cambridge U. Press, Cambridge, MA (1975).
5. *Instruction Manual for Model 901 Microprocessor Ionalyzer*, Orion Research Inc., Cambridge, MA (1979).
6. *Instruction Manual for Halide Electrodes*, Orion Research Inc., Cambridge, MA (1977).

**SPEDE**

$Cd^{+2}$, $Pb^{+2}$, and $Bi^{+3}$ ions. Because the electrode responds only to free chloride ions, the presence of any chloride ion complexing agent lowers the measured apparent chloride ion content.

The electrode's service life will depend on both mechanical and chemical wear. Chemical wear is dependent on how corrosive the environments are in which the electrodes are placed—e.g., pH. Values of pH higher than 12 are expected to reduce the electrode's lifetime to some extent, although no precise measure can be given. Mechanical wear is, of course, dependent on the solid content and the particle-size distribution in the drilling fluid when the measurements are taken directly on the mud. From our experiences in the laboratory with different ISE's, we expect the lifetimes of the electrodes to be in the 1- to 5-year range.

## Conclusions

The use of an ISE for chloride ion determination in water-based drilling fluids is a real alternative to the well-known Mohr method. In the expected chloride ion concentration range of water-based drilling muds, no adjustment of pH is necessary. The price for the apparatus is comparable to ordinary digital pH meters. The method is well suited when the drilling-fluid filtrate is miscolored by additives; it also gives possibilities for fast quantitative chloride ion analysis without first preparing the drilling-fluid filtrate. In addition, the method seems able to work as a continuous chloride ion mud logging device. Caution must be