Chemical Analysis Instruction Book

Instruction Manual Part No. 209802 Revision B

NOTE

Fann reserves the right to make improvements in design, construction and appearance of our products without prior notice.

Fann Instrument Company
P.O. Box 4350
HOUSTON, TEXAS, U.S.A. 77210
TELEPHONE: (281) 871-4482
TOLL FREE:(800) 347-0450
FAX: (281) 871-4358

TABLE OF CONTENTS

SECTION **PAGE NO.**

TABLE

SECTION 1
INTRODUCTION

The Chemical Analysis Test Kits were developed for precise field analysis of drilling fluids used in oilwell drilling. These analyses may be used for formation identification, compatibility studies, quality control, or evaluation of pollution problems. These kits contain all chemicals, equipment and glassware for measurement in the field of the property or properties for which the kit was designed. Kits and the tests they cover are tabulated below. For results of these analyses to be accurate and reliable, care must be exercised in taking the drilling fluid samples.

Most chemical analyses are performed on the drilling fluid filtrate rather than the drilling fluid. To obtain a sample of drilling fluid filtrate, the drilling fluid is filtered using a standard API, 100 psi (690 kPa) filter press or a high temperature high pressure filter press. This operation removes all solids but leaves the dissolved salts. Some filtrates are so darkly colored the filtration endpoints cannot be seen. Procedure for clarifying these filtrates is described for each test.

SECTION 2
SAFETY CONSIDERATIONS

Chemicals in this kit may cause hazard to the user's health by direct contact, inhalation, ingestion, explosion or fire. Read all warnings, precautions and hazard classifications (fire, health, and reactivity) on the container label. For in depth information on handling, reactivity with other substances, storage and other safety related information refer to the "Material Safety Data Sheet (MSDS) for each chemical. If personal contact or an environmental accident occur use the counteractive measures outlined on the label and on the MSDS sheet.

Certain of the procedures described in this instruction require reactions which may release harmful gases, for example chlorine. These procedures must always be carried out in a well ventilated area or preferably under a laboratory hood.

Always use Pipette Pump (206730 or equal) to load chemicals into pipette.

CAUTION
NEVER PIPETTE ANY CHEMICAL BY MOUTH.

For safe operation of the Hot Plate, make sure the electrical cord is in good condition and equipped with a grounding plug.

Read and follow the operating instructions for the Hot Plate. Do not leave unattended while it is heating. Use caution while handling hot flasks and other laboratory containers.

SECTION 3
ALKALINITY AND LIME CONTENT P-M (METHOD)

Alkalinity of the mud or filtrate, (P_m — M_m) or (P_f — M_f) is a result of the presence of bicarbonate, carbonate, and hydroxides, of calcium magnesium, sodium and other cations. Inorganic ions which also contribute to alkalinity are borates, silicates, sulfides and phosphates. Of major consideration in Alkalinity build up are the organic thinners and filtrate reducers which contribute to M_f alkalinity thus making this test inaccurate and therefore requiring the use of the alternate P_1/P_2 test. However, in simple bentonite base systems without organic additives the P_f and M_f test are sufficient. The term alkalinity has little or no relation to pH of water. It refers to the acid neutralizing capacity of the water.

Alkalinity is determined by titrating a sample with standard sulfuric acid with the use of a pH indicator to determine the endpoints. With the use of indicators, one changing at a pH of 8.3 and another at 4.5 to 5.1, it is possible to make two titrations and determine by calculations the amounts of hydroxyl (OH^-), carbonate (CO_3^{-2}), and bicarbonate (HCO_3^-) in the sample. Phenolphthalein indicator gives the amount of carbonate alkalinity. The M_f or total alkalinity gives the total alkalinity; bicarbonate, carbonate, and hydroxyl. Phenolphthalein indicator is universally used for P alkalinity determinations. Methyl orange has been used as the total alkalinity indicator, however, its endpoint color change is difficult to distinguish with the eye, and furthermore, it changes color near a pH of 3.5, which is generally too low a value.

M or total alkalinities should be carried down to a pH of 5.1 of alkalinities of 1 epm or less, to 4.8 to alkalinities of around 3 epm, and 4.5 of alkalinities of around 10 epm. An indicator mixture of bromcresol green and menthyl red gives various shades of color changes from blue to pink in this pH range. For the range of alkalinities the following shades are used:

pH	Alkalinity Range	Color
5.1	Low alkalinities (1 epm or less)	Greenish blue-gray
4.8	Medium alkalinities (3 epm)	Light pink-gray with bluish cast
4.5	High alkalinities (10 epm or greater)	Light pink

A. EQUIPMENT

The following equipment and material is necessary for the P-M alkalinity testing:

Phenolphthalein Indicator Solution, 1 gm/100 cm^3 of H_2O — alcohol solution
Sulfuric Acid Solution, .02N (N/50)
Methyl Orange Indicator Solution, .1 gm/100 cm^3 of water
pH Sticks
Dish Titration, polyethylene, 140 ml
Graduated Pipette, 1 ml
Graduated Pipette, 10 ml
Stirring Rod

B. PROCEDURE, FILTRATE ALKALINITY, P_f AND M_m

1. Measure one or more cm^3 of filtrate into the titration vessel. Add two or more drops of the phenolphthalein indicator solution. If the Indicator turns pink, add 0.02 normal (N/50) sulfuric acid, drop by drop from the graduated pipette, while stirring, until the pink color just disappears. If the sample is so colored that the indicator color change is masked, the endpoint can be taken when the pH drops to 8.3 as measured with a pH meter.

2. Report the phenolphthalein alkalinity of the filtrate, P_f as the number of cm^3 of 0.02 normal acid required per cm^3 of filtrate.

3. To the sample which has been titrated to the P_f endpoint, add two or three drops of methyl orange indicator solution. Add the standard acid drop by drop from the pipette, while stirring, until the color of the indicator changes from yellow to pink. If the sample is so colored that the indicator color change is masked, the endpoint can also be taken when the pH of the sample drops to 4.3 as measured by a pH meter. Report the methyl orange alkalinity of the filtrate, M_f as the total cm^3 of 0.02 normal acid per cm^3 of filtrate required to reach the methyl orange endpoint including that amount required for the P_f endpoint.

C. PROCEDURE, DRILLING FLUID ALKALINITY: P_m

1. Measure 1.0 cm^3 of mud into the titration vessel using a syringe or volumetric pipette. Dilute the mud sample with 25-50 cm^3 of distilled water. Add 4-5 drops of phenolphthalein indicator solution and while stirring, titrate rapidly with 0.02 normal (N/50) standard sulfuric acid solution until the pink color disappears. If the endpoint color change cannot be seen, it can be taken when the pH drops to 8.3 as measured by a pH meter.

   NOTE: If cement contamination is suspected, the titration must be performed as rapidly as possible and the endpoint reported at the first disappearance of the pink color.

2. Report the phenolphthalein alkalinity of the drilling fluid, P_m, as the number of cm^3 of 0.02 normal (N/50) acid required per cm^3 of drilling fluid.

D. CALCULATIONS

1. P_f and M_f can be estimated using the following table:

TABLE 1
P_1 and M_1 ESTIMATES

CONCENTRATIONS, mg/L			
	OH^-	CO_3^{-2}	HCO_3^-
$P_F = 0$	0	0	$1220M_f$
$2P_f < M_f$	0	$1200P_f$	$1220 (M_f — 2P_f)$
$2P_f = M_f$	0	$1200P_f$	0
$2P_f > M_f$	$340 (2P_f — M_f)$	$1200 (M_f — P_f)$	0
$P_f = M_f$	$340M_f$	0	0

E. PROCEDURE, LIME CONTENT

1. Lime content F_w can be obtained by using the percent water from a retort analysis of the drilling fluid.

$$F_w = \frac{Volume\ percent\ water}{100}$$

2. Lime Content can be calculated by:

Lime, lb/bbl = 0.26 (P_m — F_wP_f)

Lime, kg/m^3 = 0.742 (P_m — F_wP_f

F. FILTRATE ALKALINITY DETERMINATION P1/P2 METHOD

The P1/P2 back-titration method was mainly developed in an attempt to overcome the limitations of the P_f/M_f alkalinity method. The P1/P2 method eliminates the interference in the "M" titration.

1. Determine P_f as in Section 3B-1 and 2.

2. Using a pipette, measure 1.0 cm^3 of filtrate into the titration vessel. Add 25 cm^3 of deionized water to the titration vessel.

3. Using a pipette, add 2.0 cm^3 of 0.1 normal (N/10) sodium hydroxide solution and stir well. Measure the pH with the high range pH paper (or pH meter). If the pH is 11.4 or greater, proceed to Section 3F-4. If the pH is less than 11.4 add 2.0 cm^3 more of 0.1 normal sodium hydroxide solution, then proceed.

   NOTE: Exact measurement of the sodium hydroxide is necessary to avoid serious errors.

4. Using a 10 cm^3 graduated cylinder, measure 3 cm^3 of barium chloride solution and add to the titration vessel. Add 2-4 drops of phenolphthalein indicator solution while stirring.

WARNING

BARIUM CHLORIDE IS POISONOUS!
DO NOT PIPETTE BY MOUTH, USE
BULB PIPET.

5. Immediately titrate the mixture as rapidly as practical with the standard 0.02 normal hydrochloric acid to the first disappearance of the pink color (or to a pH of 8.3 with a pH meter). The color may reappear after a short time. Do not continue the titration.

6. Report the P1/P2 alkalinity. P1, as the cm^3 of 0.02 normal acid to reach the phenolphthalein endpoint.

7. Determine the blank alkalinity, P2. Omit the filtrate, but otherwise repeat the procedure described in Section 3F-2 through 3F-6 for determining P1, using exactly the same quantities of water and reagents in preparing the sample.

8. Report the blank alkalinity, P2, as the cm^3 of 0.02 normal acid needed to titrate the reagent mixture to the phenolphthalein endpoint.

G. CALCULATIONS: P1/P2

This method reduces organic interferences and gives more accurate estimations of hydroxyl, carbonate, and bicarbonate concentrations.

These concentrations can be calculated as follows:

When P1>P2: OH^-, mg/L = 340 (P1 — P2)

CO_3^{-2}, mg/L = 1200 [P_f(P1 — P2)]

When P1<P2: HCO_3 —, mg/L = 1220 (P2 — P1)

CO_3^{-2}, mg/L = 1200 P_f

SECTION 4
CHLORIDE ION CONCENTRATION IN DRILLING FLUID FILTRATE

To determine the chloride content of a drilling fluid filtrate sample, the sample is titrated with a standard silver nitrate solution, using potassium chromate as an indicator. The silver nitrate precipitates the chloride ion producing a red color silver chromate, which is taken as the endpoint. Results are reported in mg/L.

A. EQUIPMENT

The following apparatus and reagents are used for determining chloride content:

Potassium Chromate Indicator Solution, 5 g/100 cm^3 of water.
Phenolphthalein Indicator Solution, 1 g/100 cm^3 of 50% alcohol and water solution
Sulfuric Acid Solution, 0.02 (N/50)
Silver Nitrate Solution, 4.79 g/L (equiv. to .001 g chloride ion [cm^3])
Silver Nitrate Solution, 47.91 g/L (equiv. to .01 g chloride ion [cm^3])
Calcium Carbonate, precipitated
Graduated Pipette, 1 ml
Graduated Pipette, 10 ml
Distilled Water
Titration Dish, polyethylene
Stirring Rod

B. PROCEDURE

1. Measure one or more cm^3 of filtrate into the titration vessel. Add 2-3 drops of phenolphthalein solution. If the indicator turns pink, add acid drop by drop using a pipette while stirring, until the color disappears. If the filtrate is deeply colored, add an additional 2 cm^3 of 0.020 normal (N/50) sulfuric or nitric acid and stir. Then add 1 g of calcium carbonate and stir.

2. Add 25-50 cm^3 of distilled water and 5-10 drops of potassium chromate solution. Stir continuously, while adding standard silver nitrate solution drop by drop from the pipette, until the color changes from yellow to orange-red and persists for 30 seconds. Record the number of cm^3 of silver nitrate solution that are used.

C. CALCULATIONS

Report the chloride-ion concentration of the filtrate in mg/L, calculated as follows:

$$Chloride\ mg/L = \frac{1000\,(0.001\ silver\ nitrate,\ cm^3)}{filtrate\ sample,\ cm^3}$$

NOTE: If the chloride-ion concentration of the filtrate exceeds 10,000 mg/L,

$$Chloride\ mg/L = \frac{10{,}000\,(.01\ silver\ nitrate,\ cm^3)}{filtrate\ sample\ cm^3}$$

To convert units:

$$Chloride,\ ppm = \frac{Chloride,\ mg/L}{Specific\ Gravity\ of\ Filtrate}$$

Salt (NaCl), mg/L = (1.65)(Chloride, mg/L)

As the specific gravity of the filtrate is not always conveniently measured the tables which follow can be used to make the conversions.

TABLE 2
CONVERSION OF MILLIGRAMS PER LITER CHLORIDE TO WEIGHT PERCENT SALT (NaCl) OR PARTS PER MILLION SALT

SOLUTION TEMPERATURE AT 68 Ff (20 C)			
Milligrams Per Liter Chloride	Weight Percent Salt	Milligrams Per Liter Salt	Parts Per Million Salt
3,040	0.5	5,020	5,000
6,100	1	10,050	10,000
12,300	2	20,250	20,000
18,600	3	30,700	30,000
24,900	4	41,100	40,000
31,599	5	52,000	50,000
37,900	6	62,500	60,000
44,200	7	73,000	70,000
51,200	8	84,500	80,000
57,600	9	95,000	90,000
64,900	10	107,100	100,000
71,800	11	118,500	110,000
79,000	12	130,300	120,000
86,100	13	142,000	130,00
93,400	14	154,100	140,000
100,900	15	165,500	150,000
108,200	16	178,600	160,000
115,800	17	191,000	170,000
123,500	18	203,700	180,000
131,200	19	216,500	190,000
139,200	20	229,600	200,000
147,300	21	256,100	210,000
155,200	22	256,100	220,000
163,600	23	270,000	230,000
169,400	24	279,500	240,000
171,700	25	283,300	250,000
188,700	26	311,300	260,000

TABLE 3
VOLUME OF SALT (NaCl) IN THE WATER PHASE OF MUD CALCULATED FROM CHLORIDE ANALYSIS

Chloride Content, mg/L	Salt Volume Percent	Specific Gravity
5,000	0.3	1.004
10,000	0.6	1.010
20,000	1.2	1.021
30,000	1.8	1.032
40,000	2.3	1.043
60,000	3.4	1.065
80,000	4.5	1.082
100,000	5.7	1.098
120,000	7.0	1.129
140,000	8.2	1.149
160,000	9.5	1.170
180,000	10.8	1.194
188,650	11.4	1.197

SECTION 5
TOTAL HARDNESS AS CALCIUM (VERSENATE METHOD)

The hardness of water or drilling fluid filtrate is due primarily to the presence of calcium and magnesium ions. When EDTA is added to the water, it combines both with the calcium and magnesium and the endpoint is determined with a suitable indicator. The total hardness of the water is expressed as mg/L calcium. An endpoint obscured by dark components can be remedied by oxidizing with a reagent such as sodium hypochlorite.

A. EQUIPMENT

The following apparatus and reagents are used in determining total hardness by the EDTA method.

Hot Plate (optional if boiling required)
Volumetric Pipette Pump
Hardness Indicator Solution, 1g/L ("Calmagite ®")
EDTA Titrating Solution (Versenate), Disodium Tetraacetate Dihydrate (1 cm^3 1,000 mg/L $CaCO_3$, 20 epm)
Buffer Solution, 7.5g ammonium chloride and 970 ml ammonium hydroxide (15N) diluted to 1 Liter
Acetic Acid (glacial - 10%)
Distilled Water
pH Paper Sticks
Titration Vessel
Pipette 10 ml X 1 ml
Sodium Hypochlorite Solution ("Clorox ®")
Masking Agent (optional)

B. PROCEDURE

1. Measure 1.0 cm^3 or more of sample into a 150-cm^3 beaker (if filtrate is clear or is only lightly colored, omit steps 2 through 5 below.

2. Add 10 cm^3 sodium hypochlorite solution and mix.

3. Add 1 cm^3 glacial acetic acid and mix.

4. Boil the sample for five minutes. Maintain the sample volume by adding deionized water as required during boiling. Boiling is required to remove excess chlorine. The absence of chlorine can be verified by immersing a strip of pH paper in the sample. If the paper is bleached white, continued boiling is required.

CAUTION:

WORK IN AN ADEQUATELY VENTILATED AREA
PREFERABLY UNDER A LABORATORY HOOD
CHLORINE GAS COULD BE RELEASED

5. Cool the sample and wash the sides of the beaker with deionized water.

6. Dilute the sample to 50 cm^3 with deionized water. Add about 2 cm^3 of hardness buffer and swirl to mix.

   NOTE: The presence of soluble iron may interfere with the endpoint determination. Should this be suspected, a mixture of triethalolimine, tetraethylenepentamine, and water (1:1:2 by volume, respectively) has proven to be a suitable masking agent. One cm^3 of the mixture is used per titration.

7. Add sufficient hardness indicator (2-6 drops) and mix. A wine-red color will develop if calcium and/or magnesium is present.

8. While stirring, titrate with EDTA solution to the proper endpoint. Calcium indicators will produce a red to blue change. The endpoint is best described as that point where additional EDTA produces no further red to blue color change. This is the EDTA volume used in the calculation in C below.

C. CALCULATIONS

$$\text{Total hardness as calcium, } mg\ /\ L\ = \frac{(400)\,(\text{EDTA volume, } cm^3}{\text{volume sample, } cm^3}$$

SECTION 6
CALCIUM (VERSENATE METHOD)

A. DESCRIPTION

When EDTA is added to water or mud filtrate containing both calcium and magnesium, it combines first with calcium. Calcium can be determined with EDTA when the pH of the sample is sufficiently high, so that magnesium is precipitated as the hydroxide, and as indicator specific for calcium is used. Several indicators will give color changes when all of the calcium has been complexed by EDTA at a pH of 12-13. An endpoint obscured by dark organic components can be remedied by oxidizing with a reagent such as sodium hypochlorite.

B. EQUIPMENT

The following equipment and material is necessary for the calcium only by the Versenate Method.

Hot Plate (optional if boiling required)
Volumetric Pipette Pump
Hardness Indicator Solution, 1 g/L ("Calmagite ®")
EDTA Titrating Solution (Versenate), Disodium Tetraacetate Dihydrate (1 cm^3 1,000 mg/L $CaCO_3$, 20 epm)
Buffer Solution, 7.5g ammonium chloride and 970 ml ammonium hydroxide (15N) diluted to 1 Liter
Acetic Acid (glacial - 10%)
Distilled Water
pH Paper Sticks
Titration Vessel, poly dish
Pipette 10 ml X 1 ml
Sodium Hypochlorite Solution ("Clorox ®")
Masking Agent (optional)

C. PROCEDURE

1. With a pipette, add 1.0 cm^3 or more of sample to a 150-cm^3 beaker. This sample volume will be used in the calculation below. If filtrate is colorless or is only slightly colored, omit steps 2 through 5 below.

2. With serological pipette, add 10 cm^3 hypochlorite solution and mix.

3. With serological pipette, add 10 cm^3 glacial acetic acid and mix.

4. Boil the sample for five minutes. Maintain the sample by adding deionized water as required during boiling. Boiling is required to remove excess chlorine. The absence of chlorine can be verified by immersing a strip of pH paper in the sample. If the paper is bleached ;white, continued boiling is required. A sufficiently boiled sample will show a pH of 5.0.

CAUTION:

WORK IN AN ADEQUATELY VENTILATED AREA
PREFERABLY UNDER A LABORATORY HOOD
CHLORINE GAS COULD BE RELEASED

5. Cool the sample and wash the sides of the beaker with deionized water.

6. Dilute the sample to approximately 50 cm^3 with deionized water. Add 10-15 cm^3 of NaOH buffer solution, or sufficient NaOH to produce a pH of 12-13.

NOTE: The presence of soluble iron may interfere with the endpoint determination. Should this be suspected, a mixture of triethanolamine, tetraethylenepentamine and water (1:1:2 by volume, respectively) is a suitable masking agent. Add 1.0 Cm^3 of the mixture after above.

7. Add sufficient calcium indicator (0.1-0.2g) to produce a pink to wine-red color if calcium is present. Too much indicator will obscure the endpoint.

   NOTE: The addition of several drops of methyl orange along with the calcium indicator may improve the visibility of the endpoint.

8. While stirring, titrate with standard EDTA to the proper endpoint. Calcium indicators will produce a red to blue change. The endpoint is best described as that point where additional EDTA produces no further red to blue color change. The EDTA volume will be used in the calculation below.

D. CALCULATION

$$Calcium\,(mg\,/\,L)\ =\ \frac{400\,(EDTA\ volume,\ cm^3)}{volume\ sample,\ cm^3)}$$

SECTION 7
SULFATE ESTIMATION

Sulfate ion may be present in drilling mud filtrates (especially in filtrates where sulfur compounds are present). The indicator method may be used to determine if further testing is necessary.

A. EQUIPMENT

The apparatus and materials used for testing the approximate amounts of sulfate ion in the water are as follows:

Sulfate Indicator Solution
Distilled Water
10 ml pipette

B. PROCEDURE AND CALCULATION

1. Measure 2 ml of filtrate sample into a clean test tube and add a few drops of Sulfate Indicator. Shake well and let stand 2 minutes.

2. Judge the quantity of precipitate formed and estimate the sulfate ion according to the following table:

   Translucent white suspension 0-10 sulfate ion
   Milk white suspension 10-20 epm sulfate ion
   Heavy white suspension. Above 20+ epm sulfate ion.

3. Sample can be diluted with distilled water for a more accurate estimation when the concentration exceeds 20 epm sulfate ion.

SECTION 8
PARTS LIST

PART NO.	DESCRIPTION
209834	Buffer solution, 4oz
209940	Calcium Carbonate Powder, 2oz
101440812	Calver® II Indicator Powder, 20gm
205902	Dish, Titration Polyethylene, 140ml
209945	Distilled Water, 16oz
208763	Glacial Acetic Acid Solution, 4oz
205741	Hot Plate, 115 Volt, 325 Watt
209885	Methyl Orange Indicator Solution, 2oz
101450380	pH Sticks, 0-14, 100/box
209855	Phenolphthalein Indicator Solution, 2oz
206730	Pipette Pump, 10ml
206029	Pipette, 10ml X 1ml
206026	Pipette, 1ml X .01
206028	Pipette, 5ml
209850	Potassium Chromate Indicator Solution, 2oz
206031	Rods, Stirring Polyethylene, 4 inch
209910	Silver Nitrate Solution .001, 8oz
209922	Silver Nitrate Solution .01, 4oz
209896	Sulfate Indicator Solution, 2oz
209863	Sulfuric Acid N/50, 8oz
209839	Versenate Hardness Buffer Solution, 2oz
209821	Versenate Hardness Indicator Solution, 2oz
209828	Versenate Hardness Titration Solution 20epm, EDTA, 4oz
209826	Versenate Titration Solution, 40 mg/L, 8oz

Warranty

Fann Instrument Company warrants the product to be free from defects in material and workmanship for a period of twelve months. If repair or adjustment is necessary, and has not been the result of abuse or misuse within the twelve month period, please return, freight prepaid, and correction of the defect will be made without charge.

For your protection, items being returned must be carefully packed to prevent damage in shipment and insured against possible damage or loss. Fann will not be responsible for damage resulting from careless or insufficient packing.

Out of warranty products will be repaired for a nominal charge.

Return of Items

Before returning items for any reason, authorization must be obtained from Fann Instrument Company. When applying for authorization, please include information regarding the reason the items are to be returned.

The correspondence address is:
Fann Instrument Company
P.O. Box 4350
Houston, Texas 77210
U.S.A.
Telephone: (281)871-4482
Toll Free: (800)-347-0450
Fax: (281) 871-4358

The shipping address is:

Fann Instrument Company
15112 Morales Road
Houston, Texas 77032
U.S.A.