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EVALUATION OF LABORATORY PROCEDURES FOR DETERMINING SOIL-WATER CHLORIDE

by

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ABSTRACT

Five laboratory tests were designed and conducted to assess the validity of procedures being used to determine soil-water chloride content in ground-water recharge studies. The tests utilized locally available, naturally occurring examples of sand and mud. The gravimetric method was found to provide moisture-content values identical to or only 0.0003 g/g higher than actual (artificially induced) values. Although total removal of chloride from samples was not achieved in flushing tests, only approximately 3 mg/L remained in sand-sample extracts and 4 mg/L remained in mud-sample extracts after as much as 20 hrs of shaking with deionized water. A study of soil-water-chloride content versus shaking time revealed that 8 hours is an optimum shaking (extraction) time. Determination of soil-water-chloride content by specific-ion electrode was found to compare favorably with that by colorimetric titration. Amount of ionic strength adjustor (ISA) added to samples in the electrode method is not a significant factor in chloride measurements obtained. Although the tests were made without the benefit of a constant-temperature laboratory, the effects of evaporation appear to have been negligible.

INTRODUCTION

Several studies recently conducted by the Bureau have estimated ground-water recharge from the average chloride content of the unsaturated zone (Stone, 1984a, b, c). One of the major steps in such estimations is the determination of the chloride content of the soil water (Clsw) in numerous core samples. After soil-water contents are determined gravimetrically, chloride contents are measured using extracts produced by shaking oven-dried soil-moisture samples with known amounts of deionized water. A number of questions arise concerning the procedures used in these determinations:

1. How good is the gravimetric soil-moisture analysis?
2. Is chloride effectively extracted?
3. What is the optimum shaking time for extraction?
4. What is the best way to measure chloride content?
5. Are the results reproducible?
6. What are the effects of evaporation in a non constant-temperature laboratory?

Five laboratory tests were designed and conducted to address these questions. One test evaluated the accuracy of gravimetric moisture-content determination. Two tests dealt with the effectiveness of chloride-extraction procedures. Another test compared chloride-content-measurement techniques. Finally, the effects of laboratory climate were examined. The purpose of this report is to describe the nature and results of these tests.

Materials Tested

The tests were run on materials of two different textures:

sand and mud. Locally available natural materials were utilized. The sand was collected from an area of modern dune deposits northeast of Socorro. More specifically, samples were collected south of the road to Johnson Hill, just north of Pueblito (across the Rio Grande, east of Escondida). The mud was collected from an area of modern playa-like deposits in the northern part of Socorro where runoff periodically ponds. The area lies west of El Camino Real, north of Gianera Street, and east of a major north-south irrigation ditch.

Average texture (percentage of sand, silt, and clay) of the two materials was determined by standard methods of sieve and pipette analysis as outlined by Royce (1970). The sand was low in silt and clay content, whereas, the mud was predominantly clay (Table 1).

Equipment and Procedures Used

Soil samples were collected, stored, and tested in 1-, 2-, and 4-oz, wide-mouth, polypropylene (Nalgene) jars with screw caps. Gravimetric moisture content was determined by means of a Fisher Isotemp 127G oven. Wet and dry weights were obtained using a Mettler PC400 electronic, top-loading balance. The balance was interfaced with a Mettler GA23 desk-top, printing calculator to facilitate recording weights. Extraction of chloride from soil samples was accomplished by means of a custom-made shaker consisting of 10 clear plexiglass columns (3 in. in diameter) in a rack which rotates end for end around a horizontal axis at a rate of 10 rpm.

Chloride-ion concentrations were measured either by

Table 1. Average texture of sample material used. Percentages in parentheses are observed range of values.

Material (No. of samples)	% Sand (>4 phi)	% Silt (<4 phi, >8 phi)	% Clay (<8 phi)	Total %
Sand (10)	92.04 (90.45-95-73)	4.74 (3.06-7.43)	2.06 (0.58-4.91)	98.84
Mud (5)	5.01 (4.08-5.70)	30.57 (23.79-36.71)	64.41 (58.35-72.13)	99.89

colorometric titration with mercuric nitrate or using an Orion 94-17B chloride electrode and a model 407A specific ion/pH meter. Procedures for titration were those of Franson (1976) and those for the electrode method were those prescribed by the manufacturer (Orion, 1982). Specific conductance of extracts was measured using a Yellow Springs Instruments model 33 salinity/conductivity meter.

MOISTURE-CONTENT DETERMINATION

A major control of the amount of chloride in the soil is the amount of soil water in the sample. Thus, a reliable measure of moisture is important. A test was conducted to evaluate the gravimetric method employed in moisture-content determination.

Procedure

Ten sand samples were oven dried overnight at 105°C and weighed. Next, 10 ml of deionized water were added to each and the samples were reweighed. Then they were oven dried overnight again and reweighed as soon as they were removed from the oven the next morning. Soil moisture content (θ) is calculated from the relationship:

$$\theta = \text{wet wt} - \text{dry wt} \; / \; \text{dry wt} - \text{jar wt}.$$

Wet and dry weights include the weight of the jar. This gives gravimetric wetness or mass wetness; the resulting value may also be referred to as dry-soil wetness because it is calculated on a dry-soil basis (Hillel, 1971).

Results and Discussion

Table 2 gives results of the gravimetric-moisture-method accuracy test. The data show very little error or difference between actual and observed moisture content. Only four of the samples yielded any difference and these were all very small differences. Interestingly, in all these cases the observed values were higher than the actual values. Perhaps this is due to the fact that the balance used only reads to two decimal places, but calculations were carried out to four decimal places.

Table 2. Results of soil-moisture-method accuracy test. All samples used are sand. Plus sign indicates observed value is greater than original value by amount listed.

Sample No.	Jar Wt. (g)	Orig. Wt. (g)	Wet Wt. (g)	Orig. Moisture (g/g)	Dry Wt. (g)	Observed Moisture (g/g)	Error
1	30.92	80.86	90.84	0.1998	80.85	0.2000	+0.0002
2	30.94	84.09	94.01	0.1866	84.08	0.1869	+0.0003
3	31.12	77.17	87.10	0.2156	77.17	0.2156	0.0000
15	31.28	83.09	93.00	0.1913	83.09	0.1913	0.0000
16	31.30	77.25	87.15	0.2154	77.25	0.2154	0.0000
17	31.10	79.49	89.43	0.2054	79.48	0.2057	+0.0003
37	31.49	77.34	87.24	0.2159	77.33	0.2162	+0.0003
38	31.44	73.24	83.13	0.2366	73.24	0.2366	0.0000
41	31.34	82.38	92.29	0.1942	82.38	0.1942	0.0000
43	31.13	75.90	85.82	0.2218	75.90	0.2218	0.0000

It is concluded that the gravimetric method is accurate enough for purposes of the soil-water-chloride determinations required.

EXTRACTION OF CHLORIDE FROM SOIL

Two aspects of chloride extraction were addressed. First, could all of the chloride in a sample be removed? Next, what is the optimum shaking time for the extraction process?

Total Removal of Chloride

In order to test the accuracy of chloride extraction and measurement, an attempt was made to 1) flush existing chloride from natural samples of sand and mud (by repeated episodes of shaking with deionized water), 2) add a known amount of solution of known chloride content, and 3) go through the normal extraction procedure, comparing results with the concentration of chloride added to the presumably flushed sample. The flushing portion of the test provided useful insight into how much of the chloride in a sample can be removed.

Procedure

Fifteen samples each of sand and mud were placed in tared 4-oz plastic jars and approximately 60 ml of deionized water were added to each. The samples were then shaken mechanically five different times for a total time ranging from 13 hrs 25 min to 20 hrs 13 min. After all but the first shaking episode, the samples were allowed to settle overnight. The supernatant liquid (extract) was decanted, another 60 ml of deionized water was added to the sample, and the sample was shaken again. Specific conductance of the extract from every other sample was monitored as a measure of the success of flushing out salts.

Results and Discussion

The specific conductance values obtained after each of the five flushing runs are given in Table 3. The sands are characterized by lower specific conductances than the muds and also by less decrease in conductance with repeated flushing. Mud samples 2 and 4 exhibited the greatest decrease in conductance. This is probably a consequence of settling time. After the first flushing run, the first five mud samples were only allowed to settle for a few minutes before the extract was decanted. Thus, much of the finer portion of the soil was removed in suspension, decreasing the soil sample size.

A more specific measure of chloride flushing efficiency is provided by a comparison of initial chloride contents of the natural samples and the chloride content after the five episodes of flushing (Table 4). Indications are that a small but detectable concentration of chloride remains even after as much as 20 hrs 13 min of flushing. However, these background chloride values are so low as to be of little consequence in soil-water-chloride measurements. In fact, they are only slightly higher than the chloride content of deionized water plus the indicator used in the titration procedure (Table 4).

Chloride not removed in the extraction procedure was assumed to be adsorbed on clay particles. According to Grim (1968), this is possible only at low pH. Based on measurements made on selected samples during the tests, pH ranged from 6.0 to 8.0. Thus, adsorption should not be significant. A mineralogic source would release chloride slowly, but is not expected in these

Table 3. Results of flushing test; each sample was shaken with fresh deionized water five times.

Sample No.		Specific Conductance (micromhos)				
		Run 1[1]	Run 2[2]	Run 3[3]	Run 4[4]	Run 5[5]
Sand	1	35	35	35	35	40
	3	42	--	35	40	40
	5	45	48	30	35	40
	7	35	30	35	40	40
	9	65	25	25	40	38
	11	38	--	--	35	35
	13	72	32	--	48	42
	15	45	45	35	40	40
Mud	2	150	210	80	88	70
	4	355	100	85	85	70
	6	138	130	130	145	120
	8	170	145	142	148	--
	10	125	145	125	122	105
	12	200	100	--	160	--
	14	150	125	125	115	--

[1] All samples shaken 2 hrs 36 min.

[2] Sands 1-15 and muds 2, 4 shaken 1 hr 32 min; muds 6-14 shaken 2 hrs 7 min.

[3] Sands 1-15 and muds 2, 4 shaken 2 hrs 7 min; muds 6-14 shaken 5 hrs.

[4] Sands 1-9 shaken 2 hrs 10 min; sands 11-15 and muds 2-14 shaken 5 hrs

[5] Sands 1-15 and muds 2, 4 shaken 5 hrs; muds 6-14 shaken 5 hrs 30 min.

-- = not measured

Table 4. Background chloride concentrations in extracts of selected flushed samples. Chloride determined by colorimetric titration in all cases.

Initial Chloride		Final (Background) Chloride		
Sample No.	Cl in extract (mg/L)	Sample No.	Total shaking time	Cl in extract (mg/L)
Sand 16 (Table 5)	4.20	Sand 1	13 hrs 25 min	2.88
		15	16 hrs 15 min	2.88
Mud 4 (Table 7)	10.63	Mud 1	16 hrs 15 min	4.29
		6A	20 hrs 13 min	4.53
		6B	20 hrs 13 min	3.63
		6C	20 hrs 13 min	3.71
		Deionized water plus indicator used for titration	none	1.65

samples. The reason for a background chloride value thus remains uncertain.

It is not clear from Tables 3 and 4 whether one flushing dissolves all of the soluble salts present, and thus a stable minimum conductance is attained, or whether repeated flushing would permit withdrawal of additional ions from the finer soil-particle surfaces. Further work should include the measurement of chloride content in extract after each flushing run.

Optimum Shaking Time

Inasmuch as projects often involve several hundred samples, the less time spent in each step of the chloride analysis the better. Tests were therefore conducted to determine the minimum shaking time necessary to achieve a maximum chloride content in the extract.

Procedure

The relationship between chloride in extract and shaking time was examined by means of three tests. The first involved shaking different samples for different periods of time. The other two involved reshaking each sample for additional periods of time.

In the first test a total of 32 soil samples was used. These included 15 samples of sand and 15 samples of mud which had been used in the flushing test and two unflushed samples to serve as blanks. Samples from the flushing test were oven dried at 105°C overnight. Next 10 ml of 500 ppm chloride solution were added to all but three of the dried samples (mud 1, 6; sand 15), which were to serve as flushed blanks. Each of the 32 samples was weighed immediately and then allowed to dry overnight in the oven at 105°C. The dried samples were weighed, the balance was tared, 60-100 ml of deionized water was added, and the sample was reweighed.

Samples were then shaken for a period of 1, 3, 5.75, 7, and 8 hrs. Three samples of each texture group were removed from the shaker after each interval. In other words, the first three samples of each texture were shaken for 1 hr, whereas, the last four were shaken for 8 hrs. After settling, a known volume of extract was removed from each sample by pipette and titrated to measure chloride content.

The second shaking test involved 10 sand samples to which a known amount of each of three standard chloride solutions (low = 31.8 ppm Cl, medium = 305.8 ppm Cl, high = 5,517.7 ppm Cl) had been added. After approximately 100 ml of deionized water were added to each, they were shaken for periods of 2, 4, 8, and 24 hrs. Between each shaking interval, the samples were allowed to settle overnight and an aliquot of extract was decanted into a 2-oz jar. Chloride content of the aliquot was measured by the electrode method.

The third test involved 5 mud samples to which no chloride had been added. The same shaking times used in the second test were employed. Chloride content of aliquots was measured by titration because concentrations were near the detection limits of the electrode.

Results and Discussion

Data pertinent to the three shaking tests are given in

Tables 5, 6, and 7. Each lists the data necessary to calculate chloride content of the artificial or natural soil water initially in the samples. Note that Table 5 lists a single chloride value for each sample, whereas, Tables 6 and 7 give four separate chloride values for each sample. Graphical depictions of the change in chloride content with increased shaking time for tests 2 and 3 are given in Figures 1 and 2.

Table 5 shows that for both texture groups the average chloride concentrations in soil water are similar. This suggests that there is little change with shaking time. Tests 2 and 3 (Tables 6 and 7) provide a better idea of the relationship between chloride extracted and shaking time because samples were repeatedly reshaken and reanalyzed. Both Figures 1 and 2 show that the chloride values generally increase to a maximum after 4-8 hrs of shaking, then generally remain constant or decrease. An optimum shaking time of 8 hrs, regardless of texture, is suggested by the data.

Comparison of chloride values for the flushed and unflushed blanks in Table 5 suggests that the flushing reduced background chloride content of the mud samples but not of the sand samples.

A further test like tests 2 and 3, but involving more samples and more time intervals, would provide additional information. Such a test would be quite time-consuming, however, because samples must be allowed to settle between shaking intervals. Also, the soil-sample size and the amount of deionized water added must be such that numerous aliquots may be removed and chloride concentrations are high enough to be detected.

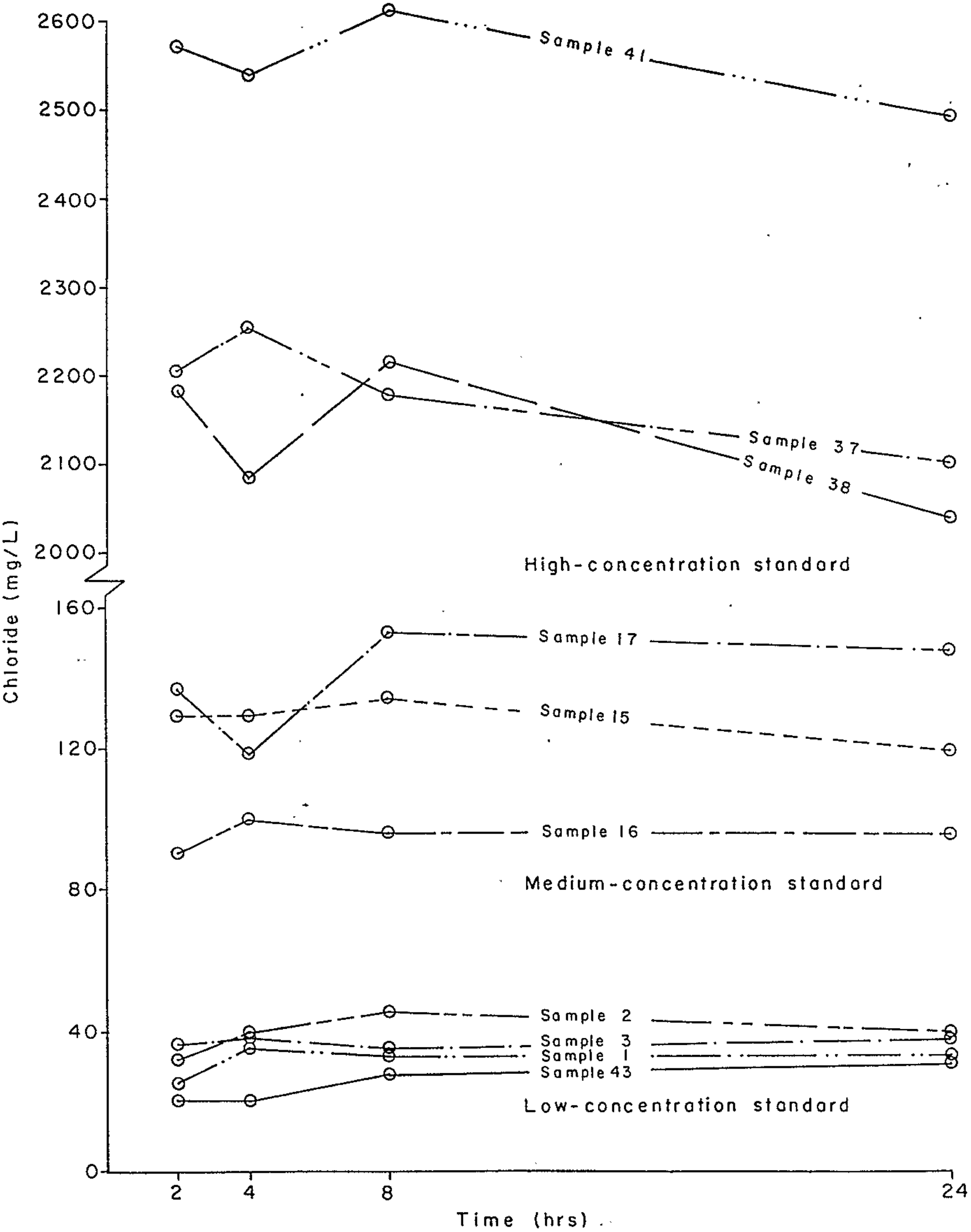

Figure 1. Chloride in soil water versus shaking time for test 2 (sand samples).

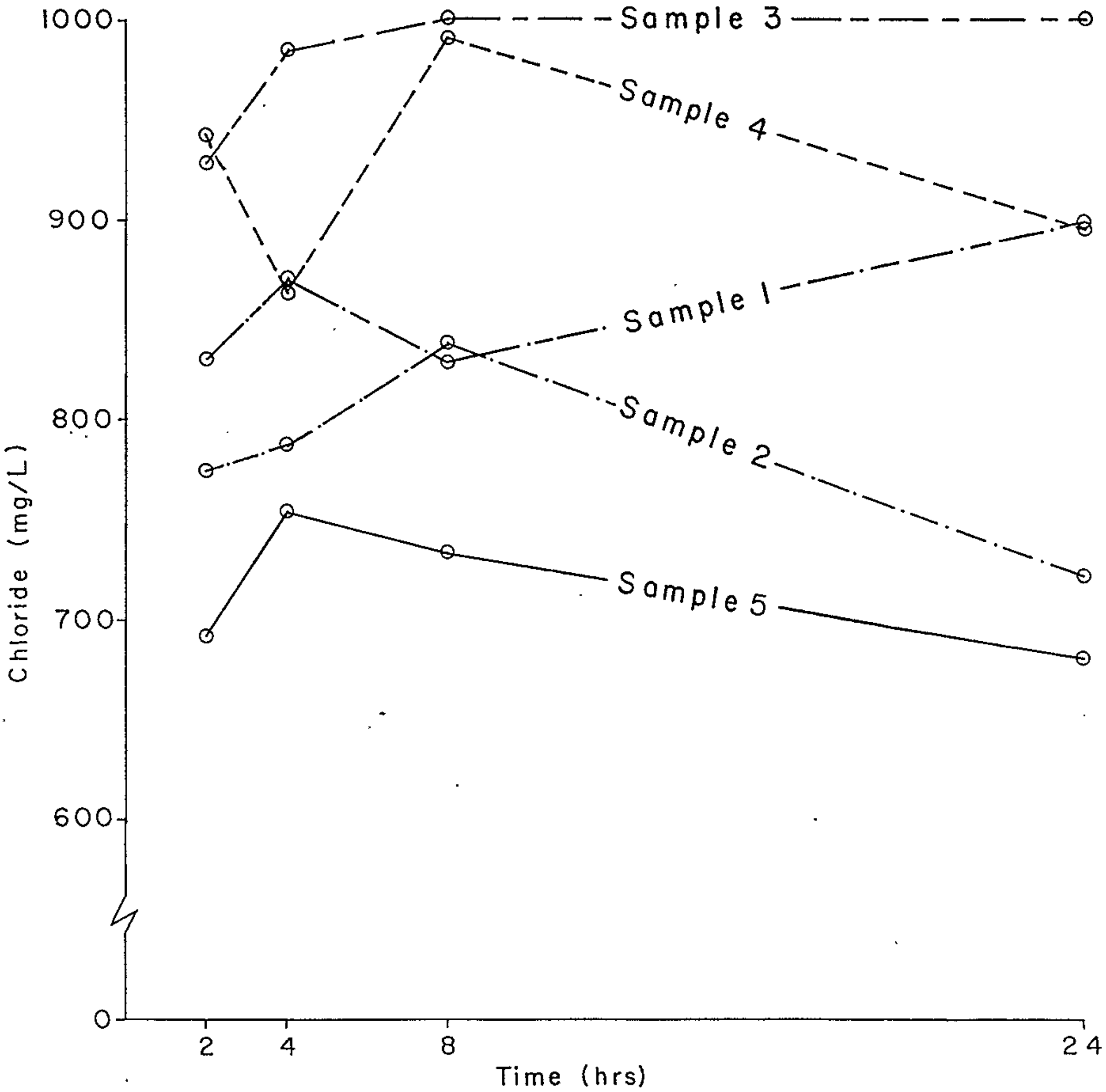

Figure 2. Chloride in soilwater versus shaking time for test 3 (mud samples).

Table 5. Results of shaking test 1: 500 ppm Cl solution added to 32 samples from flushing test (16 sand, 16 mud) prior to shaking for various times (one shaking period each). Clsw = soil water chloride.

Sample No.		Moisture content (g/g)	Dry wt. soil (g)	Wt. water added (g)	Cl in extract (mg/L)	Cl in soil water (mg/L)	Shaking time (hrs)	Average Clsw for shaking time (mg/L)
SAND	1	0.26	38.95	104.09	44.02	457.04	1	462.73
	2	0.22	45.69	74.14	63.31	467.05	1	
	3	0.24	41.18	82.27	56.55	464.09	1	
	4	0.29	35.26	76.78	60.18	459.77	3	458.66
	5	0.24	41.32	76.78	65.95	502.99	3	
	6	0.20	49.09	76.39	54.41	413.22	3	
	7	0.24	41.99	87.11	52.92	458.84	5.75	472.65
	8	0.24	42.34	89.81	52.76	469.88	5.75	
	9	0.25	39.44	83.65	58.69	489.22	5.75	
	10	0.23	43.94	66.03	73.36	483.58	7	491.23
	11	0.23	43.54	66.22	77.82	513.98	7	
	12	0.20	51.64	73.67	65.12	476.14	7	
	13	0.21	46.93	70.53	70.89	497.85	8	422.96
	14	0.25	39.89	68.29	51.11	348.07	8	
	15	0.20	49.72	71.72	4.12	29.43	8[1]	
	16	0.20	50.58	81.70	4.20	33.22	8[2]	
MUD	1	0.78	12.82	83.19	5.44	45.08	1[1]	514.83
	2	0.84	2.01	77.52	66.77	514.33	1	
	3	1.01	10.04	81.49	63.81	515.34	1	
	4	0.71	14.18	85.91	61.83	528.78	3	533.82
	5	0.78	12.87	85.56	63.48	538.87	3	
	6	0.46	22.09	80.72	6.26	50.26	3[1]	
	7	0.39	26.11	79.05	71.72	563.69	5.75	563.68
	8	0.39	25.83	84.72	64.30	540.54	5.75	
	9	0.44	22.70	75.70	77.82	586.82	5.75	
	10	0.48	20.84	78.33	48.71	379.27	7	458.74
	11	0.40	25.16	88.21	53.86	470.49	7	
	12	0.45	22.17	89.23	59.35	526.47	7	
	13	0.32	31.09	82.12	64.06	525.72	8	510.11
	14	0.46	21.89	74.39	67.65	498.30	8	
	15	0.40	25.10	71.96	70.98	506.31	8	
	16	0.37	33.72	86.13	18.63	130.36	8[2]	

[1] flushed blank (no chloride added)
[2] unflushed blank (no chloride added)

Table 6. Results of shaking test 2: ten sand samples, four shaking periods for each.

Sample No.	Shaking time (hrs)	Moisture content (g/g)	Dry wt. soil (g/g)	Wt. Water added (g)	Cl in extract (mg/L)	Cl in soil water (mg/L)	Avg. Clsw for sample (mg/L)
1	2	0.20	49.95	100.31	2.55	25.59	32.24
1	4	0.20	49.95	100.31	3.70	37.14	
1	8	0.20	49.95	100.31	3.30	33.12	
1	24	0.20	49.95	100.31	3.30	33.12	
2	2	0.19	53.15	102.03	3.20	32.87	39.16
2	4	0.19	53.15	102.03	3.85	39.55	
2	8	0.19	53.15	102.03	4.40	45.20	
2	24	0.19	53.15	102.03	3.80	39.04	
3	2	0.22	46.06	99.20	3.75	37.45	37.70
3	4	0.22	46.06	99.20	3.95	39.45	
3	8	0.22	46.06	99.20	3.55	35.46	
3	24	0.22	46.06	99.20	3.85	38.45	
15	2	0.19	51.82	99.02	13.00	129.87	128.62
15	4	0.19	51.82	99.02	13.00	129.87	
15	8	0.19	51.82	99.02	13.50	134.86	
15	24	0.19	51.82	99.02	12.00	119.88	
16	2	0.22	45.96	98.66	9.20	91.66	96.40
16	4	0.22	45.96	98.66	10.20	101.63	
16	8	0.22	45.96	98.66	9.70	96.65	
16	24	0.22	45.96	98.66	9.60	95.65	
17	2	0.21	48.39	109.28	12.50	137.26	139.45
17	4	0.21	48.39	109.28	10.80	118.59	
17	8	0.21	48.39	109.28	14.00	153.73	
17	24	0.21	48.39	109.28	13.50	148.24	
37	2	0.22	45.85	101.80	215.00	2208.10	2187.55
37	4	0.22	45.85	101.80	220.00	2259.45	
37	8	0.22	45.85	101.80	212.00	2177.28	
37	24	0.22	45.85	101.80	205.00	2105.39	
38	2	0.24	41.81	96.22	225.00	2188.51	2135.01
38	4	0.24	41.81	96.22	215.00	2091.24	
38	8	0.24	41.81	96.22	228.00	2217.69	
38	24	0.24	41.81	96.22	210.00	2042.61	
41	2	0.19	51.39	96.85	265.00	2572.20	2555.73
41	4	0.19	51.39	96.85	260.00	2540.47	
41	8	0.19	51.39	96.85	268.00	2618.64	
41	24	0.19	51.39	96.85	255.00	2491.62	
43	2	0.22	44.78	109.09	2.05	22.54	25.70
43	4	0.22	44.78	109.09	1.90	20.89	
43	8	0.22	44.78	109.09	2.60	28.59	
43	24	0.22	44.78	109.09	2.80	30.78	

Table 7. Results of shaking test 3: five unflushed mud samples, four shaking periods each.

Sample no.	Moist (g/g)	Dry wt. soil (g)	Wt. water added (g)	Cl in extract (mg/L)	Clsw (mg/L)	Shaking time (hrs)	Avg. Clsw for samples (mg/L)
1	0.06	20.13	113.56	8.39	831.27	2	858.97
1	0.06	20.13	113.56	8.82	872.86	4	
1	0.06	20.13	113.56	8.39	831.27	8	
1	0.06	20.13	113.56	9.09	900.49	24	
2	0.06	22.63	114.97	8.39	774.58	2	781.02
2	0.06	22.63	114.97	8.53	787.50	4	
2	0.06	22.63	114.97	9.09	839.08	8	
2	0.06	22.63	114.97	7.83	722.91	24	
3	0.06	17.33	99.18	9.09	929.22	2	979.29
3	0.06	17.33	99.18	9.65	986.44	4	
3	0.06	17.33	99.18	9.79	1000.75	8	
3	0.06	17.33	99.18	9.79	1000.75	24	
4	0.05	20.25	101.33	10.07	942.38	2	925.17
4	0.05	20.25	101.33	9.23	863.80	4	
4	0.05	20.25	101.33	10.63	994.68	8	
4	0.05	20.25	101.33	9.62	899.82	24	
5	0.06	25.04	105.47	9.23	692.87	2	716.51
5	0.06	25.04	105.47	10.07	755.90	4	
5	0.06	25.04	105.47	9.79	734.89	8	
5	0.06	25.04	105.47	9.09	682.37	24	

SOIL-WATER-CHLORIDE DETERMINATION

Chloride content of extract solutions may be measured by colorimetric titration or using a specific-ion electrode. The electrode method is more rapid and thus the most desirable when analyzing a large number of samples. The accuracy and precision of determining soil-water chloride by both of these methods were evaluated. Additionally, the optimum amount of 5 M $NaNO_3$ ionic strength adjustor (ISA) to use in the electrode method was examined.

Procedure

This test involved forty-three samples of sand. Natural chloride was flushed from thirty-nine of the samples for 6 hrs. After these samples had settled, the supernatant (extract) was decanted. The natural or background chloride of five of these extracts was determined by titration. Both the flushed and unflushed samples were then dried in the oven. Next, 10 ml of a standard chloride solution (low, medium, or high concentration) were added to all but two of the samples so that the following four groups resulted.

1. Low-Concentration-Standard Group
   31.8 ppm Cl solution was added to:
   samples 1-13 (flushed)
   sample 14 (unflushed)

2. Medium-Concentration-Standard Group
   305.8 ppm Cl solution was added to:
   samples 15-27 (flushed)
   sample 28 (unflushed)

3. High-Concentration-Standard Group
   5,517.7 ppm Cl solution was added to:
   samples 29-38 and 40-41 (flushed)
   sample 39 (unflushed)

4. Blanks
   no Cl was added to:
   sample 42 (flushed)
   sample 43 (unflushed).

Each sample was then weighed, dried, and reweighed to measure moisture content. Next, a known weight of deionized water was added to each sample and they were shaken in two groups. The majority of samples were shaken for 6 hours, whereas, samples 12-14, 26-28, 39-41, and 43 were shaken continuously for 24 hours.

After settling, an aliquot (usually 20 ml) of the supernatant from each sample was removed by pipette to a 2-oz jar. A known volume of ISA was then added to each (0.4 ml per 20 ml aliquot). Removal of extract was spaced over 20 days.

The chloride concentration of each aliquot was measured three separate times by electrode. Electrode readings were sequential. That is, for each group of extract samples to be analyzed during any one day, the first readings were taken in succession, then the second readings, and so on. All three readings for any one sample were taken on the same day, however. The electrode was recalibrated with standard chloride solutions after every two hours of continuous use and the jars were kept tightly closed at all times. The chloride content of each aliquot was determined by titration after all electrode readings on it were completed.

Next, approximately 20 ml of extract were decanted from the remaining liquid and approximately 0.3-0.4 ml of ISA was added to each. Chloride concentrations in these decanted samples were then measured by electrode. As a result, there are five values for chloride-in-extract for each sample: three determined by electrode from the pipetted aliquot, one determined by titration, and one determined by electrode from the decanted aliquot.

Results and Discussion

Table 8 contains background chloride-in-extract values. Results of the accuracy and precision tests are presented in Tables 9-12.

The averages of all five chloride-in-extract values (column 4, Table 10) were used to calculate the chloride-in-soil-water (CLsw) values. These data are presented in Table 11. Examination of this table provides a rough estimate of the accuracy of the chloride method. If one assumes that the CLsw values of samples 42 and 43 (Table 10) are representative of the background CLsw of all of the samples, an average background CLsw for all of the sand samples can be assumed at 23.1 mg/L. This number can be combined with the amount of chloride in the solution added to obtain an "actual" chloride value. Thus, the relative error for each observed CLsw value can be calculated from the following relationship:

Relative error = Observed CLsw - Actual CLsw /Actual CLsw.

For example, since the "actual" CLsw of samples 1-14 equals 31.8 mg/L plus 23.1 mg/L, or 54.9 mg/L, the relative error of sample 1 equals:

$$54.50 - 54.90 / 54.90 = .00073 \text{ or } 0.73\%.$$

Based on calculations like this, the average percent relative error for samples 1-14 equals 15.05%. For samples 15-28

Table 8. Background chloride-in-extract values; determined by titration of extracts from flushed samples.

Sample no.	Chloride conc. (mg/L)
1	1.08
10	1.35
20	2.16
30	1.08
40	1.35

Table 9. Comparison of chloride-in-extract values. Readings 1-4 made on same aliquot; reading 5 made on a new aliquot.

Sample no.	Electrode—exact ratio[1]			Titration (mg/L)	Electrode—approx. ratio[2] (mg/L)	Settling time (days)
	Reading 1	Reading 2 (mg/L)	Reading 3	Reading 4	Reading 5	
1	4.30	6.90	7.20	5.60	5.50	1
2	5.20	7.80	7.80	5.74	6.50	1
3	5.70	7.80	7.20	5.60	6.80	1
4	7.10	8.10	8.40	6.16	8.00	1
5	6.50	7.90	7.80	6.04	7.10	1
6	6.70	7.50	6.90	7.00	8.00	5
7	7.40	7.30	7.40	6.30	8.30	5
8	8.00	8.10	8.10	6.30	10.20	5
9	10.50	10.60	10.40	7.80	10.50	7
10	9.80	8.20	8.10	7.00	9.60	7
11	5.40	6.00	6.50	5.74	5.50	20
12	7.60	7.30	8.20	7.30	8.10	0.17 (4 hrs)
13	9.60	8.10	8.20	8.10	8.90	4
14	9.80	8.80	8.90	7.80	9.80	6
15	33.50	38.50	38.00	38.80	45.50	1
16	31.00	34.00	34.00	35.50	40.00	1
17	31.50	33.00	35.50	35.30	40.00	1
18	32.00	38.00	36.00	38.50	39.00	1
19	38.50	40.00	40.00	39.50	42.00	1
20	51.00	46.00	48.00	42.00	44.50	5
21	50.00	46.50	46.50	43.20	43.00	5
22	40.50	37.00	47.50	34.40	35.50	5
23	36.50	35.00	35.50	39.90	38.00	20
24	39.00	37.00	38.00	39.20	41.00	7
25	46.00	44.00	42.00	40.30	40.00	7
26	35.00	36.50	34.50	38.60	38.00	0.17 (4 hrs)
27	35.00	39.00	39.00	35.40	41.00	6
28	39.00	44.00	43.00	38.10	40.00	4
29	805.00	860.00	800.00	655.00	—	1
30	775.00	840.00	790.00	635.00	610.00	1
31	905.00	960.00	900.00	759.00	660.00	1
32	920.00	945.00	900.00	727.00	710.00	1
33	860.00	855.00	805.00	648.00	660.00	1
34	935.00	915.00	870.00	727.00	720.00	5
35	790.00	800.00	840.00	612.00	600.00	5
36	920.00	940.00	900.00	727.00	700.00	5
37	680.00	685.00	680.00	729.00	780.00	7
38	680.00	690.00	680.00	693.00	705.00	12
39	915.00	855.00	880.00	710.00	680.00	0.17 (4 hrs)
40	760.00	705.00	725.00	586.00	590.00	4
41	880.00	820.00	830.00	674.00	705.00	5
42	2.50	2.60	2.60	3.20	2.30	1
43	2.40	2.60	2.75	2.80	2.65	4

[1] exact ratio of ionic strength adjustor to sample (0.4 ml ISA/20 ml extract)
[2] approximate ratio of ionic strength adjustor to sample (0.3-0.4 ml ISA/aliquot)
— = not measured

Table 10. Means of chloride-in-extract values; all values in mg/L.

Sample no.	Electrode (exact ratio)[1]	Electrode & titrat. (exact ratio)[2]	Electrode only[3]	All 5 values[4]	Mean of Means	Std. dev.	Std. dev. as % of mean
1	6.13	6.00	5.98	5.90	6.002	0.084	1.40
2	6.93	6.63	6.82	6.61	6.750	0.135	2.00
3	6.90	6.58	6.88	6.62	6.743	0.146	2.16
4	7.87	7.44	7.90	7.55	7.690	0.198	2.57
5	7.40	7.06	7.33	7.07	7.213	0.152	2.11
6	7.03	7.03	7.28	7.22	7.138	0.111	1.55
7	7.37	7.10	7.60	7.34	7.352	0.177	2.41
8	8.07	7.63	8.60	8.14	8.108	0.346	4.27
9	10.50	9.83	10.50	9.96	10.196	0.307	3.01
10	8.70	8.28	8.93	8.54	8.610	0.237	2.75
11	5.97	5.91	5.85	5.83	5.889	0.054	0.92
12	7.70	7.60	7.80	7.70	7.700	0.071	0.92
13	8.63	8.50	8.70	8.58	8.603	0.073	0.85
14	9.17	8.83	9.33	9.02	9.084	0.184	2.03
15	36.67	37.20	38.88	38.86	37.900	0.985	2.60
16	33.00	33.63	34.75	34.90	34.069	0.790	2.32
17	33.33	33.83	35.00	35.06	34.305	0.746	2.17
18	35.33	36.13	36.25	36.70	36.102	0.493	1.37
19	39.50	39.50	40.13	40.00	39.781	0.285	0.72
20	48.33	46.75	47.38	46.30	47.190	0.763	1.62
21	47.67	46.55	46.50	45.84	46.639	0.656	1.41
22	41.67	39.85	40.13	38.98	40.155	0.969	2.41
23	35.67	36.72	36.25	36.98	36.405	0.501	1.38
24	38.00	38.30	38.75	38.84	38.473	0.341	0.89
25	44.00	43.08	43.00	42.46	43.134	0.554	1.28
26	35.33	36.15	36.00	36.52	36.001	0.429	1.19
27	37.67	37.10	38.50	37.88	37.787	0.501	1.33
28	42.00	41.03	41.50	40.82	41.336	0.456	1.10
29	821.67	780.00	—	—	—	—	—
30	801.67	760.00	753.75	730.00	761.354	25.826	3.39
31	921.67	881.00	856.25	836.80	873.929	31.702	3.63
32	921.67	873.00	868.75	840.40	875.954	29.216	3.33
33	840.00	792.00	795.00	765.60	798.150	26.733	3.35
34	906.67	861.75	860.00	833.40	865.454	26.313	3.04
35	810.00	760.50	757.50	728.40	764.100	29.316	3.84
36	920.00	871.75	865.00	837.40	873.537	29.752	3.41
37	681.67	693.50	706.25	710.80	698.054	11.390	1.63
38	683.33	685.75	688.75	689.60	686.858	2.487	0.36
39	883.33	840.00	832.50	808.00	840.958	27.177	3.23
40	730.00	694.00	695.00	673.20	698.050	20.396	2.92
41	843.33	801.00	808.75	781.80	808.721	22.262	2.75
42	2.57	2.73	2.50	2.64	2.608	0.084	3.22
43	2.58	2.64	2.60	2.64	2.615	0.024	0.92

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[1] mean of first three columns in Table 9

[2] mean of first four columns in Table 9

[3] mean of first three and fifth column in Table 9

[4] mean of all five columns in Table 9

— = not determined

Table 11. Chloride-in-soil-water values, all methods.

Sample no.	Moisture Content (gm/gm)	Dry wt. soil (gm)	Wt. Water added (gm)	Cl in extract[1] (mg/L)	Cl in soil water (mg/L)[2]
1	0.20	49.95	92.85	5.90	54.50
2	0.19	53.29	81.50	6.61	53.32
3	0.22	46.20	87.49	6.62	57.67
4	0.21	49.33	73.05	7.55	54.20
5	0.20	50.01	93.69	7.07	65.70
6	0.22	41.03	88.01	7.22	68.89
7	0.21	48.33	75.10	7.34	54.56
8	0.24	42.27	81.47	8.14	65.76
9	0.20	49.85	71.94	9.96	71.10
10	0.20	49.03	78.65	8.54	66.96
11	0.22	46.91	83.08	5.83	47.85
12	0.24	42.81	79.07	7.70	60.22
13	0.23	44.45	83.41	8.58	70.92
14	0.21	47.81	82.67	9.02	72.55
15	0.19	51.93	77.29	38.86	301.21
16	0.22	46.06	84.34	34.90	294.09
17	0.21	48.54	86.72	35.06	304.21
18	0.19	51.75	83.44	36.70	305.62
19	0.20	50.63	76.18	40.00	303.99
20	0.21	47.65	73.43	46.30	340.16
21	0.21	48.74	72.79	45.84	332.86
22	0.24	41.90	94.40	38.98	366.81
23	0.21	48.90	73.74	36.98	271.92
24	0.24	41.65	79.79	38.84	310.15
25	0.19	53.84	81.90	42.46	347.42
26	0.21	48.62	83.45	36.52	304.57
27	0.21	47.81	89.32	37.88	339.35
28	0.23	43.70	80.89	40.82	322.96
29	0.19	51.80	81.69	780.00	6316.37
30	0.21	48.34	84.05	730.00	6050.65
31	0.19	52.49	72.89	836.80	6052.42
32	0.20	51.36	74.15	840.40	6188.37
33	0.21	47.49	81.98	765.60	6215.17
34	0.20	51.11	74.01	833.40	6125.21
35	0.19	53.07	89.03	728.40	6422.26
36	0.19	52.90	73.75	837.40	6166.16
37	0.22	46.00	73.00	710.80	5140.94
38	0.24	41.95	78.55	689.60	5403.66
39	0.20	50.03	75.83	808.00	5998.64
40	0.23	43.25	92.08	673.20	6160.85
41	0.20	51.52	78.32	781.80	6075.77
42	0.23	42.14	85.84	2.64	22.93
43	0.22	45.00	88.46	2.64	23.26

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[1] from fourth column in Table 10

[2] soil water is that added to samples

Table 12. Chloride-in-soil-water values, titration only.

Sample no.	Moisture Content (gm/gm)	Dry wt. soil (gm)	Wt. Water added (gm)	Cl in extract (mg/L)	Cl in soil water (mg/L)
29	0.19	51.80	81.69	655.00	5304.13
30	0.21	48.34	84.05	635.00	5263.23
31	0.19	52.49	72.89	759.00	5489.71
32	0.20	51.36	74.15	727.00	5353.34
33	0.21	47.49	81.98	648.00	5260.49
34	0.20	51.11	74.01	727.00	5343.20
35	0.19	53.07	89.03	612.00	5395.97
36	0.19	52.90	73.75	727.00	5353.23
37	0.22	46.00	73.00	729.00	5272.58
38	0.24	41.95	78.55	693.00	5430.30
39	0.20	50.03	75.83	710.00	5271.08
40	0.23	43.25	92.08	586.00	5362.84
41	0.20	51.52	78.32	674.00	5238.00

it is 7.03%; and for samples 29-41 it is 9.90%.

An examination of the results for the high-chloride-standard (Table 9) reveals a discrepancy between the electrode values obtained on 7 Nov. 84 (samples 29-36, 39-41) and the corresponding titration and approximate ratio (0.3-0.4 ml ISA/decanted aliquot) values for each sample. All three exact ratio (0.4 ml ISA/20 ml extract) electrode readings are noticeably higher than the other two values. It is believed that this is due to improper calibration of the electrode system when this group of readings was taken. Approximate ratio readings taken for samples 30, 31, 39, and 40 later the same day (after recalibration) are generally much closer to the corresponding titration values. The electrode readings for samples 37 and 38, taken on 13 Nov. 84, are further evidence of this. The precision of the chloride-in-extract values for these two samples, as measured by the last column of Table 10, is better than that of the rest of the high range samples. Also, an estimate of average relative error using CLsw values from just these two samples is 4.85%. Finally, Table 11 lists the CLsw values of samples 29-41, calculated using titration values only. The average relative error calculated from these results is only 3.74%.

The five values of chloride-in-extract for each sample are listed on Table 9. Extract volumes did not permit evaluation of precision of the titration method. In order to examine the precision of the electrode method, average Cl in extract values were calculated for each sample four different ways. These four means are tabulated in Table 10, along with their collective mean and standard deviation. Note that a fifth value for sample number 29 was not measured (Table 9). Consequently, no mean and standard deviation are given for this sample in Table 10. The last column of this table lists the standard deviation as a percent of the mean given in the fifth column. In this way, the variations in extract values determined by the three methods (electrode - exact ISA ratio, titration, electrode - approximate ISA ratio) described above can be compared. The average percent standard deviation is 2.06% for the low-chloride samples (1-14), 1.44% for the medium-chloride samples (15-28), and 2.91% for the high-chloride samples (29-43).

The data at hand suggest that the most precise CLsw estimates are attained when the chloride concentration of the extract is above 10 ppm. In conclusion, the electrode method is acceptable for the determination of extract chloride, provided that care is taken to ensure that the electrode system is operating and calibrated properly. The accuracy of the extraction procedure, as calculated in the manner described above, is not great. However, when the endproduct (an estimate of ground-water recharge) is considered, a great deal of accuracy is not required. This is because the yearly recharge rates over areas for which the chloride method is applicable are so small that a 15 or 20 percent change is not significant.

Also, no significant difference in extract chloride values was noted between electrode readings on aliquots with exact ISA/sample ratios and those without exact ratios.

In the future, routine analyses of large groups of samples should be conducted as follows:

- determine moisture content as previously described
- shake samples mechanically for 8 hours
- measure chloride-in-extract by the electrode method using decanted (rather than pipetted) aliquots

A better way of estimating the accuracy of soil-water-chloride determinations would be to calculate the background chloride in soil water for each sample, then add a known amount of standard chloride solution to each. This could not be done with the samples listed on Table 8 because, unfortunately, the weight of deionized water added during flushing was not recorded, hence background CLsw values could not be calculated.

Finally, it should be noted that this test was designed to allow only an indirect evaluation of the accuracy of the two chloride-in-extract determination procedures by comparing results from the same aliquot. Because accuracy of the methods is well documented (Franson, 1976), it was decided that a more direct evaluation was not needed. Accuracy is assured as long as the established procedures are followed.

EFFECTS OF EVAPORATION

When large numbers of samples are being analyzed, the time interval between shaking a sample and measuring the chloride content of its extract can be quite lengthy. Evaporation of the extract during this time results in an anomalously high chloride content. Two steps were therefore taken to assess evaporation potential in the laboratory. First, temperature and humidity were measured over a 4-wk period. Second, chloride content of a sample set was monitored over a period of up to 20 days.

Procedure

Laboratory environment was assessed by means of a recording hygrothermograph. Temperature and humidity variations were monitored continuously from 18 September through 19 October, 1984.

The timing of measurements for the chloride-content tests described above was designed so that effects of evaporation might be evaluated. Aliquots of sample extracts were removed after samples had been sitting in the lab for periods of 4 hrs to 20 days. Most, however, were removed after samples had been sitting only 1-7 days.

Results and Discussion

Hygrothermograph strip charts show temperature and relative humidity are fairly constant in the lab, at least for the short period monitored. Temperature remained between 70° and 78°F. Humidity varied betwen 40% and 60%. Evaporation potential was thus slightly variable but moderate throughout the test period.

Actual evaporation was probably minimal because jars were kept tightly sealed. No visual decrease in volume of extracts was observed.

The right hand column of Table 10 gives the length of time the extract had been sitting before chloride content was measured. No trend toward increase in chloride with time is indicated. Evaporation does not appear to be a hazard, in spite of the lack of a constant laboratory environment. Settling time (time since removal of a sample from the shaker) is apparently not a factor in chloride content, as long as jars are tightly covered.

Any further tests should involve repeated analyses at regular time intervals. Evaporation potential may be further documented by recording losses from both open and closed sample jars over a long time period. Hygrothermograph data for a similar period in the summer would also be useful.

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