Stream quality measurements along a livestock wintering operation
by Glenn Hagfeldt

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Agricultural Engineering
Montana State University

Abstract:
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The location of the test site was the Holmstrom Ranch located northwest of White Sulphur Springs, Montana. Through the winter of 1970-1971 there were 1100 head of sheep, 85 hogs, 185 cows, and 243 head of calves wintered along the creek.

Four water sampling stations were set up along the creek, three in the wintering area and a fourth approximately four miles upstream. Periodically samples were taken and the nitrate and chloride ion concentrations were recorded using a specific ion meter. Conductivity, sample temperature, stream flow, and weather conditions were also recorded. The testing indicated the concentrations of nitrate and chloride ion were very small, much less than the upper limits allowed by the United States Public Health Service. The readings were also consistently the same during the project. Because the levels were so low, the actual concentrations could not be determined using the equipment and techniques available. Averaging all the readings taken over the project period (April 1 to May 18) did indicate that both nitrate and chloride ion decreased slightly along the wintering area. It was felt that more testing was needed to determine if these paramenters did actually decrease, or if this was a result of the testing methods used.

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STREAM QUALITY MEASUREMENTS ALONG A LIVESTOCK WINTERING OPERATION

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STREAM QUALITY MEASUREMENTS ALONG A LIVESTOCK WINTERING OPERATION

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ABSTRACT

Although many studies have been undertaken to see what the pollutional effects of large concentrations of animals in feedlots are, very little research has been done relative to livestock wintering operations. Many states, including Montana, still utilize a summer range with confinement during the winter months. With the current emphasis on protection of the environment it was felt that research was needed to determine what the pollutional effects, if any, of these wintering operations might be.

In many cases livestock wintering operations are located near streams because of the protection from wind usually found near streams, and for ease in getting the animals to water. When the waste actually enters the environment where it could affect human lives, then it becomes important to know where the waste goes. In the case of livestock concentrated along streams the two major concerns are a buildup of some constituents of animal wastes, such as nitrates, to potentially harmful levels, and the possibility of disease transmission through the wastes.

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Four water sampling stations were set up along the creek, three in the wintering area and a fourth approximately four miles upstream. Periodically samples were taken and the nitrate and chloride ion concentrations were recorded using a specific ion meter. Conductivity, sample temperature, stream flow, and weather conditions were also recorded. The testing indicated the concentrations of nitrate and chloride ion were very small, much less than the upper limits allowed by the United States Public Health Service. The readings were also consistently the same during the project. Because the levels were so low, the actual concentrations could not be determined using the equipment and techniques available. Averaging all the readings taken over the project period (April 1 to May 18) did indicate that both nitrate and chloride ion decreased slightly along the wintering area. It was felt that more testing was needed to determine if these paramenters did actually decrease, or if this was a result of the testing methods used.

INTRODUCTION

Public concern for the protection and wise management of our environment has increased within the last few years. Many areas of our economy which have been ignored over the years are now being re-evaluated.

Cattle feedlots have been increasingly under attack over the last several years. Many states, including Montana, have been attempting to formulate regulations in order to control the pollution caused by the confinement of animals, yet be equitable enough to allow the rancher to continue his business without undue restrictions.

One of the questions that arises is how to consider wintering operations. Montana is a state with large amounts of rangeland and harsh winters. Many ranchers confine their animals throughout the winter in order to protect them from the weather and for convenience of feeding while the ground is covered with snow. In the case of breeding stock, this confinement may extend well into the springtime runoff period, until all animals have given birth to their young.

Working under the direction of Dr. C. M. Milne, with funding through the Montana Agricultural Experiment Station, an attempt was made to develop a program which would help determine if animal wintering operations located along streams are polluters, and if so under what conditions the pollution occurs. To begin the project it was decided to sample the water as it moved through the wintering area for evidence of animal activity. If the animal wastes were getting into the stream

in quantity, it was felt that changes in the concentration of certain constituents of the water sample would be found.

REVIEW of LITERATURE

Animal Confinement Pollution

The project's purpose was to find what effect, if any, animal wintering operations along a stream has on stream quality. Very little work has been done regarding pollution from wintering operations, and in order to give some background to the problem, the wintering operation can be considered as a semi-yearly feedlot operation. Studies on feedlots within the last few years have been conducted which will shed some light on what might be expected from wintering operations.

The confined wintering operation represents a pollution potential. Whereas domestic sewage reaches the environment in a continuous flow, wastes from confined animal units reach the environment in quantity intermittently. Although the waste comes from a single source, the results are two different wastes. First, there is the solids build up; secondly, there is the runoff that can occur over the confining area, and enter the stream. In colder regions, the potential for stream degradation is highest during periods of spring snow-melt and runoff, and during periods of rain in early spring and fall.

Wintering area location has usually been unfavorable to stream quality. The Honorable Bill Clayton of the Texas House of Representatives said, "In the not too distant past, feedlots were, by design,

situated in such a manner that wastes were allowed to run off into nearby draws or other natural drainage features. The only thought in mind was the ease in the removal and disposal of waste material." (22, p. 6)

Unfortunately, the criteria for wintering operations and feed lots are very much the same. In general, they are located close to water sources and in areas where the terrain gives good drainage and brush gives protection from the wind.

The actual volume, strength, and rate of delivery of wastes from the wintering area depends on several variables. The topographic, meteorologic, and geologic conditions effect the rate and strength of delivery of the wastes. It has also been shown that the moisture content of the manure, temperature, nature of the surface, and animal density have an effect on delivery. (14, p. 7) This would indicate that the wintering operation becomes a polluter only during periods of heavy run-off, when the wastes find their way into the water course before sufficient biodegradation has taken place.

One indication of the degree of pollution has been the feedlots' association with fish kills. The organic material from the animal wastes lowers the oxygen level of the stream to a point where most life cannot survive. Table I shows the percentage of fish kills reportedly caused by feedlots in the state of Kansas. (14, p. 10)

Table I - Fish-kills reported in Kansas 1960-1968.

KANSAS						
	Total Number Fish Kills		Total Fish Killed (mil)		% Fish Kills Attributed to Feed-lots	No. Commercial Feedlots January 1
Year	All Causes	Feed-lots	All Causes	Feed-lots		
1960	No	Report				58,000
61	4	1	No	Report		88,000
62	1	0	0.005	0	0	99,000
63	9	2	0.14	0.12	89	150,000
64	26	16	1.35	1.12	82	183,000
65	6	5	0.57	0.57	99	200,000
66	23	16	1.2	1.0	90	260,000
67	29	18	1.0	1.0	94	311,000
68	16	3	0.4	.03	7	338,000

There is no information on fish kills caused by wintering operations. This is probably because the animal densities do not approach those found in feedlots, and the tremendous shock loading required to deplete the oxygen level does not occur.

Waste Characteristics

The physical, chemical, and biological characteristics of animal wastes are difficult to determine. Animal wastes are affected by the physiology of the animal. The type of feed and environment also play a part in determining waste characteristics. Table II lists some of the parameters of animal waste for several different animals. (13, p. 12)

Table II - Suggested values for manure defecation rates per 1,000 lb. liveweight in confinement animal production.

Items	Units	Dairy Cattle	Beef Cattle	Poultry Hens	Pigs	Sheep
Raw manure (WM) ..	lb./day	88	-	59	50	37
Total solids (TS).	lb./day	9	-	17.4	7.2	8.4
	% WM	10	-	30	14.4	22.7
Volatile solids (VS)	lb./day	7.2	-	12.9	5.9	6.9
	% TS	80	80	74	82	82
BOD	lb./day	1.7	-	4.4	2.1	0.7
	lb./day VS	0.2333	0.252	0.338	0.363	0.101
BOD/COD	%	16	-	28	33	-
Nitrogen	% TS	4	9.8	11.5	5.6	-
P_2O_5	% TS	1.1	-	-	2.5	-
K	% TS	1.7	-	-	1.4	-

The percent of solids present in the waste is dependent primarily on animal type and the type and amount of feed used. Whereas municipal and industrial sewage is primarily water with some solids, feedlot wastes are characterized as solids containing some water. Although animal excrement contains a high degree of moisture, the dilution is far below the ratio of domestic sewage dilutions. This causes some problems when the attempt is made to run the traditional tests on the wastes. The BOD, COD, and suspended solids tests were developed for use with the highly liquefied domestic sewages. The waste slurries from the feedlots are highly concentrated and must be diluted before the traditional tests can be run.

After the BOD, COD, and the amount of suspended solids of the waste

are known, their value is further diminished because the wastes tested on the feedlot surface bear little resemblance to what actually finds its way into the water course.

"The feces, urine, and feed deposited on the lot undergo continuing physical, chemical, and biological change. The extent of such changes is variable from one location to another and from time to time at the same location. Natural drying may be an important factor at one location and time but not at another. Biological activity may result in considerable waste stabilization at one time, but not at another. The biological decomposition may proceed under either aerobic or anaerobic conditions, or both at different times at locations on the same feedlot." (5, p. 3)

F. B. Morrison, in his book Feeds and Feeding states, "The feces of farm animals consists chiefly of undigested food that has never really been within the body proper. This undigested food is mostly cellulose fibers, which has escaped bacterial action. A portion of the other nutrients usually escape digestion . . .

In addition to undigested food, the feces also contain residue from the digestive fluids, waste mineral matter, worn-out cells from the intestinal linings, mucus, and bacteria. They may also contain such foreign matter as dirt consumed along with the food.

Nearly all of the nitrogenous waste, resulting from the breakdown of protein material in the body, is excreted in the urine through the kidneys.

A great variety of other end-products of metabolism are likewise eliminated by the kidneys through the urine. Much of the mineral matter is excreted in the urine. However, calcium, magnesium, iron, and phosphorus are voided chiefly in the feces." (15)

The undigested material and bacterial cells account for 20-30% of the solid excrement, and this contains half or more of the nitrogen. Because animal wastes are so concentrated and heterogenous, a representative sample is very hard to obtain. (12, p. 28)

The Livestock Digestive System

The digestive system of the animal plays an important role in the waste characteristics. Non-ruminants such as swine, are called simple-stomached animals. The wastes produced by non-ruminants are similar to that of a human, with relatively small amounts of excreta produced for the amount of food consumed. (12, p. 24) The ruminants, which include cattle, sheep, and goats have a compartmented stomach. The stomach is made up of four different areas and this compartmentization allows the animal to effectively utilize the cellulose fibers of the feed, which the simpler stomached animals cannot do. With non-ruminants (simple-stomached) animals, micro-organisms seem to have only a minor role in the digestive system, whereas in the ruminants, a symbiotic relationship is formed "with micro-organisms ingested with the feed by providing a first-stomach compartment, the paunch or rumen, which is simply a large fermentation vessel . . . which results in the growth of enormous numbers

of micro-organisms, ten billion per ml of fluid." (13, p. 9)

Although the ruminant is able to handle the cellulosic feeds, the feed also contains many compounds, such as lignins, which are not digested. The net result is that the ruminant has high amounts of wastes produced per pound of feed consumed. (12, p. 25)

Because of the many differences in digestive systems and type of feed, "one must be cautious in assuming that data accumulated with one species of animals will be applicable to other species." Care must also be taken in assuming that studies made with human wastes will apply to the wastes of animals. (12, p. 26)

Disease Transmission

The high amount of micro-organisms in the ruminants stomach brings up the question of diseases and their transmission to humans from animal wastes. In Farm Animal Waste Management, edited by J. Ronald Miner, it states that livestock wastes are a potential source of infectious agents of disease that may affect animals and man by way of water and insects and, sometimes by air. Even though there have been relatively few cases where water borne diseases have been traced to animals, a few cases have occurred, and with the increase in outdoor and water-related recreation in the United States, the opportunities for exposure have been greatly increased. (13, p. 6)

Coliform bacteria can be used as indicators of contamination. The coliform group is technically defined as those aerobic and facultative

anaerobic, non-spore forming, Gram-negative, rod-shaped bacteria that ferment lactose (milk sugar) with the production at 35°C. of gas within 48 hours. (7, p. 32-28) Because coliform bacteria originate in soil and vegetation as well as the intestinal tract of warm blooded animals, the Gram stain test is an indicator of the source of the coliform.

Fair, Geyer, and Okun, in Water Purification and Wastewater Treatment and Disposal, list why the coliform bacteria do indicate contamination.

"1.) When sewage is examined for coliform organisms, about half of the lactose fermenters are found to belong to the species originating in fecal matter. Because human feces are the principal source of enteric pathogens, the finding of coliforms offers significant evidence of danger. The rate of their destruction or death, are substantially parallel to the respective rate for pathogenic intestinal bacteria.

2.) The number of coliform organisms in human feces is estimated to be between 10^{11} and 10^{13} per capita daily . . . The current U. S. Public Health Service Standards for drinking water supplied to interstate carriers set a limit of no more than one coliform organism in 100 ml or 40 coliform per gallon . . ." (7, p. 32-28)

The above statements indicate that the large numbers of coliform found in human wastes are good indicators of potential contamination from pathogenic enteric bacteria. "Whether this is so in like measure

for other disease species - the virus of infectious hepatitas for instance - remains unproved." (7,p. 32-28)

Temperature Effects on Bio-activity

Almost all bio-chemical reactions take place between the temperature range of 0-60°C. It is generally assumed that these reactions with organic matter roughly follow the Vant Hoff rule of doubling their rate for every increase of 10°C. This would indicate that waste matter from feedlots would not only accumulate during the colder periods, but also that biological activity would be at a minimum.

Standards for Water Quality

Table III is a summary of the U. S. Public Health Service Drinking Water Standards. The table includes suggested limits for some parameters, and an upper limit for rejection in some cases. (20, p. 33)

Ion-selective Electrodes and Their History

Many of the new ion-selective electrodes which have been developed within the last few years are an outgrowth of the older glass pH and sodium electrodes. Table IV gives a listing of the different electrodes currently available, and some of their properties. (8, p. 1) There are several reasons why the specific-ion electrode is ideal for water pollution monitoring. First, the electrode covers a wide range of concentration in a single instrument. Referring to Table IV, the range of magnitude of detection varies from 1 to 10^{-5} Molar (a molar contains

Table III - U. S. Public Health Service Drinking Water Standards, 1962.

Characteristic	Suggested Limit For Should Not Be Exceeded	Cause For Rejection
Physical		
Color	15 units	
Taste	Unobjectionable	
Threshold odor number	3	
Turbicity	5 units	
Chemical	mg/l	mg/l
Alkyl benzene sulfonate	0.5	
Arsenic	0.01	0.05
Barium		1.0
Cadmium		0.01
Chloride	250	
Chromium (hexavalent)		0.05
Copper	1	
Carbon chloroform extract	0.2	
Cyanide	0.01	0.2
Fluoride	0.7-1.2	1.4-2.4
Iron	0.3	
Lead		0.05
Manganese	0.05	
Nitrate	45	
Phenols	0.0001	
Selenium		0.01
Silver		0.05
Sulfate	250	
Total dissolved solids	500	
Zinc	5	

Table IV - Electrodes for water analyses.

Ion	Activity Range (M)	pH Range
calcium	10^{0}-10^{-5}	5.5-11
water hardness (divalent cation)	10^{0}-10^{-8}	5.5-11
nitrate	10^{-1}-10^{-5}	2-12
chloride	10^{-1}-10^{-5}	2-11
chloride	10^{0}-$5x10^{-5}$	0-14
cyanide	10^{-2}-10^{-4}	0-14
fluoride	10^{0}-10^{-6}	0-8.5
sulfide	10^{0}-10^{-17}	0-14

one mole of solute per liter of solution) for the calcium electrode to 1 to 10^{-17} for the sulfide electrode. Also, the response time for the electrode is within the range of several minutes at the longest, giving quick results. Little or no pre-treatment of the sample is required, making it an excellent instrument for field work. Samples as small as 15 ml can be tested, and the composition of the sample is not significantly altered from testing. Additional information regarding this type of instrument is contained in the Appendix.

STATEMENT OF PROBLEM

General Approach

If animal wintering operations are polluters, it would be desirable to develop methods that could detect this pollution. With most confined animal operations, the most concern is when these wastes enter a stream in concentrations high enough to affect human life. The best approach to the problem seemed to be to sample the stream flow near the wintering operation for constituents that might indicate animal activity.

Area Location

The area chosen was the Holmstrom Ranch owned by Robert Weitz, located approximately six miles northwest of White Sulphur Springs, Montana. Figure 1 is a map showing the location of the Holmstrom Ranch.

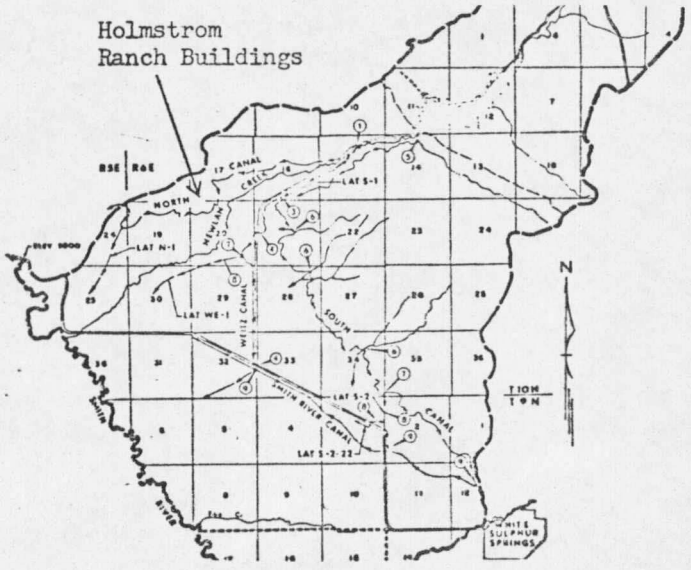

Figure 1 - Location of Holmstrom Ranch northwest of White Sulphur Springs, Montana.

This area was chosen for the study for several reasons. The Holmstrom Ranch was representative of a typical rangeland cattle-sheep operation in Montana, and the animals were wintered in a fairly restricted area along Newlan Creek.

Area Description

Figure 3 is a sketch of the sampling area and the Holmstrom Ranch as Newlan Creek passes through it.

Several of the pens, shown in Figure 2, were fairly steep, and drain right into the creek.

Figure 2 - Location of pens near station three.

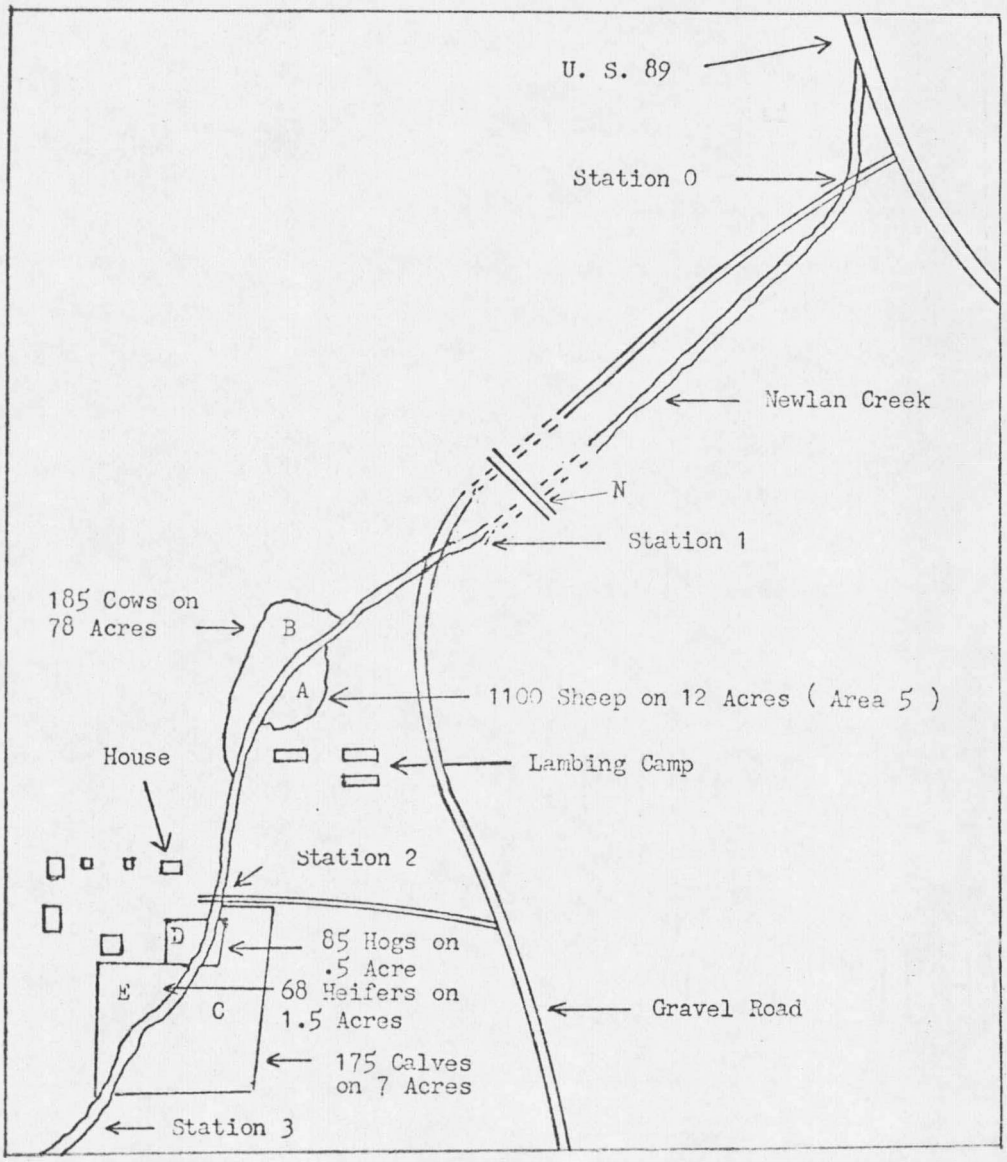

Figure 3- Sketch of Holmstrom Ranch showing wintering areas and sampling stations. Not to scale.

Stations zero, one, two, and three are the locations of the four sampling stations. Originally only three stations were used, and the fourth station, zero, was started on May 4, because it was felt that a station farther upstream would be necessary to see what changes in concentrations of nitrates and chlorides occurred naturally along the stream, and if the changes along the ranch were higher than the changes that occurred naturally.

Figure 3 also shows the wintering area locations (A through E) and gives the approximate acreages and number of animals wintered in each area. Table V lists the animal densities for each feeding area. Table VI gives the approximate distance in river miles between stations.

Table V - Type of animal and animal densities for wintering areas shown in Figure 3.

		Animal Densities	
Area Designation	Type of Animal	Area	Density ($ft.^2$/animal)
A	Sheep	12 Acres	476
B	Cows	78 Acres	18,500
C	Calves	7 Acres	1,745
D	Hogs	.5 Acres	257
E	Heifer calves	1.5 Acres	960

Table VI - Distance between sampling stations, river miles.

Station	Distance
0	
	3.8
N	
	1.2
1	
	2.1
2	
	.25
3	

The feed used consisted of about 1100 tons of Timothy-Alsike clover mixture and Alfalfa. The feed was supplemented with oats and cake. Some of the feed was ground.

Figure 4 shows sampling station zero which was located farthest upstream, about 100 feet from Highway 89.

Figure 4 - Photo of culvert at sampling station zero.

Figure 5 is a photo of the bridge where current meter readings were taken to calibrate the concrete control structure at station one for stream flow measurements. The location of this bridge is designated as N on Figure 3.

Figure 5 - Photo of section of stream where current meter was used to determine flow rate.

Figure 6 shows the concrete control structure located at station one. The opening on the right carries the main river channel, and was calibrated to give a stage-discharge relationship. The opening on the left carries irrigation water down a ditch to fields south of the house. This irrigation system caused some problems because it was not known how much of the water found its way back into the main stream or where it found its way back.

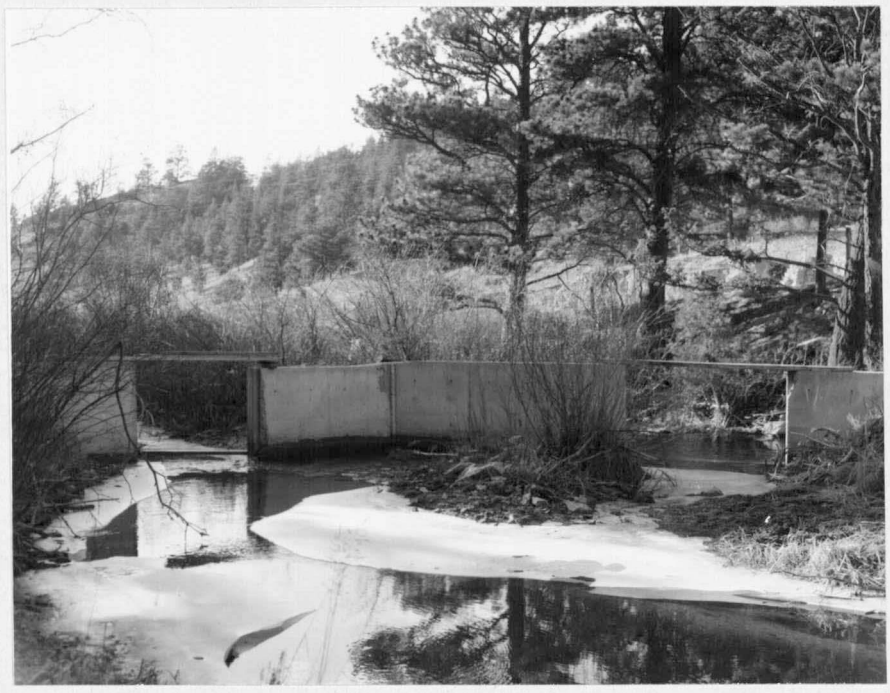

Figure 6 - Photo of concrete control structure located at station one.

Figure 7 - Photo showing the lambing area.

Figure 7, designated as area 5 on Figure 3, is a picture of the lambing facilities. The whole area drains into the creek.

Figure 8 - Photo of sampling station two.

Figure 8 shows sampling station two. This is located where the bridge crosses the river leading to the house. Sampling area three can be seen in Figure 2 (page 14), and is located just below the bushes that appear in the left hand corner of the photo.

Newlan Creek

Newlan Creek runs in a southwesterly direction into the Smith River, which is a tributary of the Missouri River. The creek drains an area of 44.8 square miles, and has an average annual runoff of 9.53 cfs. (15) It is an erratic stream, and records indicate that the flow can vary

from one cfs to over 200 cfs. It is essentially a mountain stream fed by snow-melt runoff. The Holmstrom Ranch is located about fifteen miles from the source, and the area down to the ranch does have some cattle activity, primarily summer range with very little winter feeding, but not as concentrated in area as at the Holmstrom Ranch.

DESCRIPTION OF EQUIPMENT

To begin the project, it was decided to measure nitrates, chlorides, conductivity, and temperature. Nitrates are one of the products of animal wastes that can readily affect humans if present in concentrations that are too high. Large amounts of nitrates can cause nitrate cyanosis in infants, a poisoning of the blood which deprives organs and tissues of oxygen. Nitrates are also thought to be partly responsible for the widespread occurrence of goiter in some areas. Chlorides were chosen because they are a relatively stable ion, and are a good indicator of animal activity. Conductivity and temperature measurements were needed to correlate ion activity to ion concentration. Following is a description of the equipment selected.

Orion Equipment

The Model 401 Specific Ion Meter with nitrate and chloride sensing electrodes was selected to measure the nitrates and chlorides. Figure 9 shows the meter with the electrodes attached, setting in a test sample. (19, p. 4)

Orion nitrate and chloride standardizing solution, numbers 92-07-06 and 94-17-06 respectively, were used as standards of comparison.

Figure 10 is a schematic diagram of the meter-electrode set up. (21, p. 59) The ion selective electrode is defined as an indicator or measuring electrode with a relatively high degree of specificity for a single ion or a class of ions. (10, p. 349) The selective membrane is

permeable only to a specific ion that is being measured. The internal

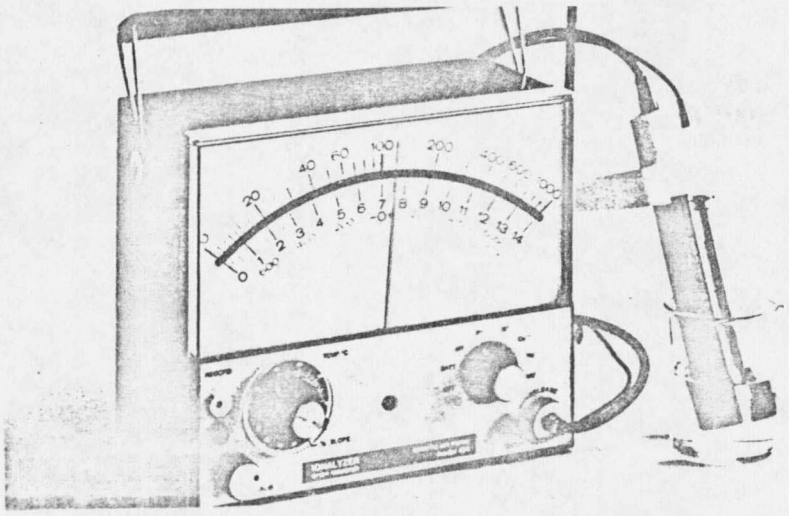

Figure 9 - Orion specific ion meter and electrodes.

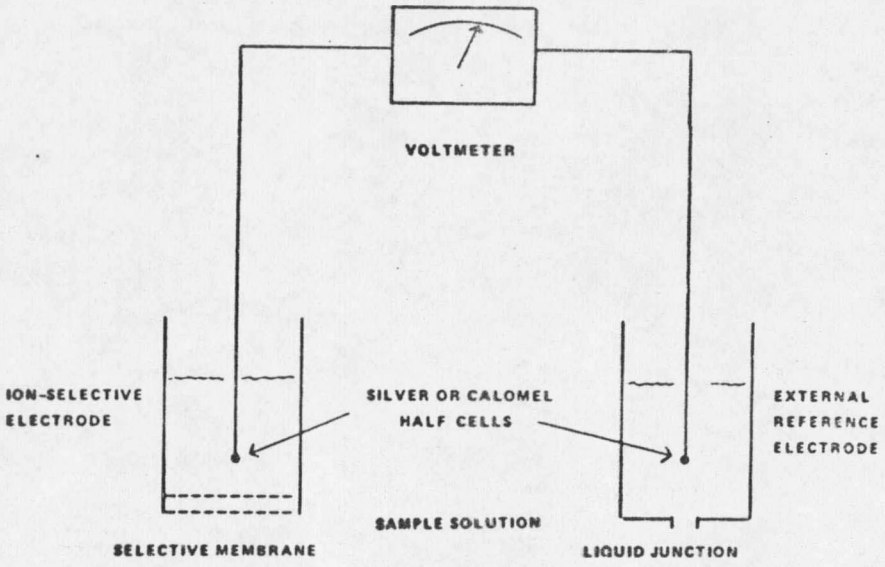

Figure 10 - Schematic diagram of the apparatus used in ion-selective electrode measurement.

solution in the electrode contains a fixed level of activity of the ion that the selective membrane allows to pass through. As the electrode is put into the solution being tested, there is a momentary flux of ions toward the solution (internal or sample) containing the lowest level of activity. The ions carry a charge, and as an equilibrium is established, a potential is set up across the membrane exactly equal to that required to prevent further movement of ions. The task then becomes measuring this change in potential across the membrane. This is accomplished by:

1) Contacting the inner solution with an internal reference electrode.

2) Contacting the sample by means of a second (external reference electrode) by means of a salt bridge.

a voltmeter is placed between the two reference electrodes and the potential can then be measured. (21, p. 58)

See the appendix for a more complete discussion of the theory of measurement with specific ion meters, and the errors involved in measurement.

Conductivity Measurements

Conductivity measurements were made with a Barnstead Model PM-70CB conductivity bridge and a Beckman No. 3997-P conductivity cell with a cell constant K = 1.00. This model is a direct digital read-out device. It is battery operated, and can be used to give quick and direct read-outs of conductivity in the field. It has a range of 0.1 micromhos to

0.12 mhos. (2, p. 8)

Miscellaneous Equipment

A thermometer was required for water temperature measurements. Assorted beakers and flasks were required, and two Burets were used in the preparation of standards. A data sheet was prepared for use in the field. Flow measurements were made by calibrating the concrete control structure at station one with a Gurley current meter.

EXPERIMENTAL PROCEDURE

Field Measurements

The testing stations were located as explained in the section on area location. The technique of measurement used was to grab sample the water at each station. Typically three readings were taken with each electrode and recorded in the field. The conductivity of the sample was also recorded at the same time. The temperature of the water was noted, the time, and the rate of stream flow was observed, along with the weather conditions. If all the equipment was working properly, testing at the four stations could be completed in about one and one-half hours.

The measurements were taken as readings using the millivolt scale. It was found that when using the F^- scale for direct readouts, the meter was much too erratic, and had to be continuously calibrated. Meter calibration curves were made using Orion recommended standards for nitrates and chlorides. The average of the three field samples was then used to determine activity of the samples by comparison to the standards.

Samples were tested intermittently from April 1 to May 18. The Orion ion-selective meter unit began to respond poorly during May, and had to be sent in for repairs. No data was collected after May 18.

DATA

The parameters measured were nitrate concentration, chloride concentration, temperature, conductivity, and stream flow. This data is presented in its raw form in the appendix.

Figure 11 shows a plot of nitrate ion electrode meter reading against temperature. Figure 12 shows the relationship between nitrate ion electrode meter reading and data date reading, where the data dates are the same as those found in the raw data in the appendix and reflect the change in nitrate ion activity as a function of time throughout the project.

Figures 13 and 14 give the same information for chlorides, 13 being a function of temperature and 14 being a function of time.

Because a decrease in the meter reading implies an increase in the concentration of the ion being measured, the ordinate on the plots of nitrate and chloride ion concentration against sample date (Figures 12 and 14) has been reversed to show an increase in concentration as moving up the ordinate. The concentrations could not directly be plotted because the readings the instrument gave indicated that the ions were present in concentrations that were below the range of the calibration charts, so Figures 12 and 14 only indicate the direction of change of the concentration of the ions from each sampling period.

Figure 15 is a plot of conductivity for the four stations against time, where the data date again refers to the related date given in the appendix. The conductivity readings are all standardized to 25°C.

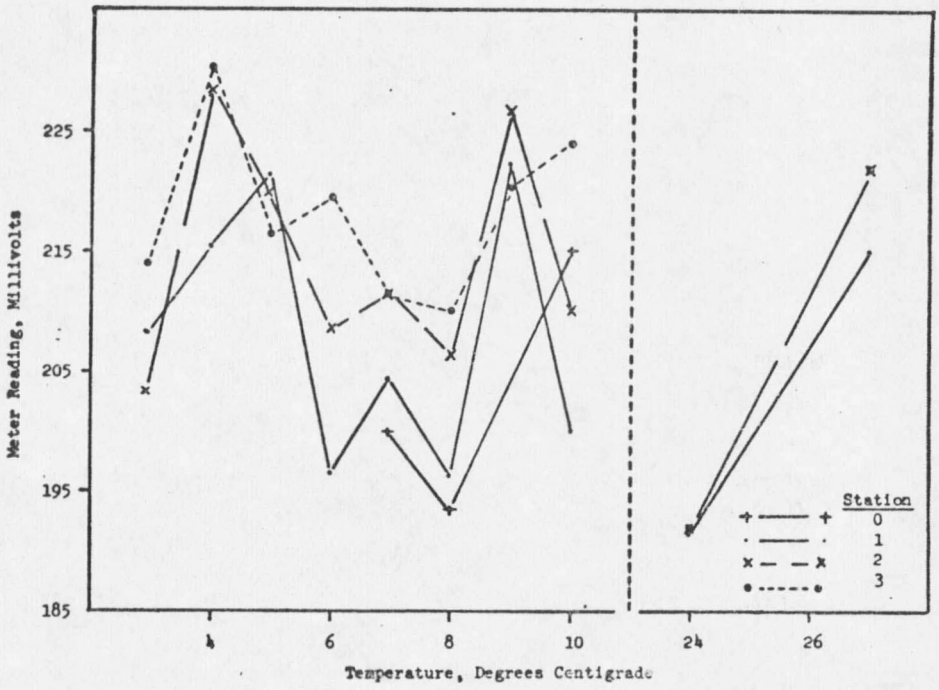

Figure 11 - Nitrate electrode meter reading versus sample temperature.

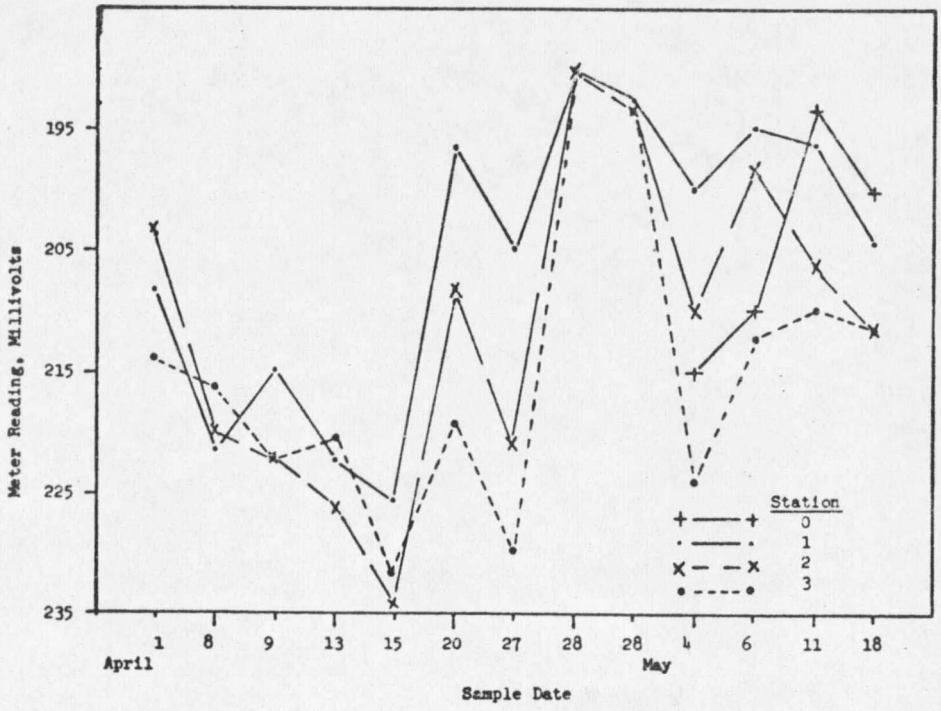

Figure 12 - Nitrate electrode meter reading versus sample date.

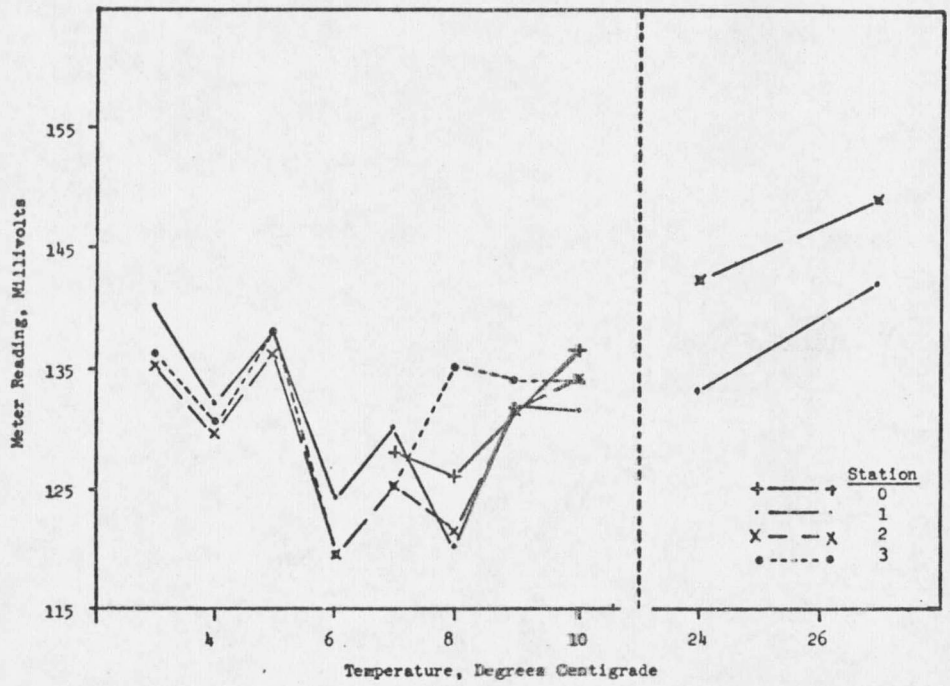

Figure 13 - Chloride electrode meter reading versus sample temperature.

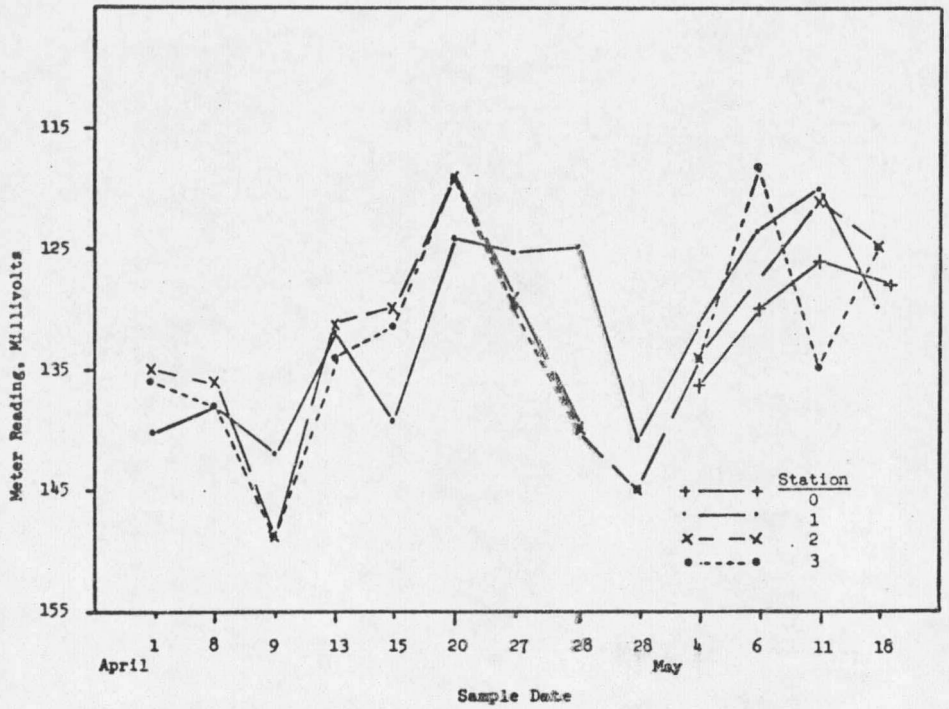

Figure 14 - Chloride electrode meter reading versus sample date.

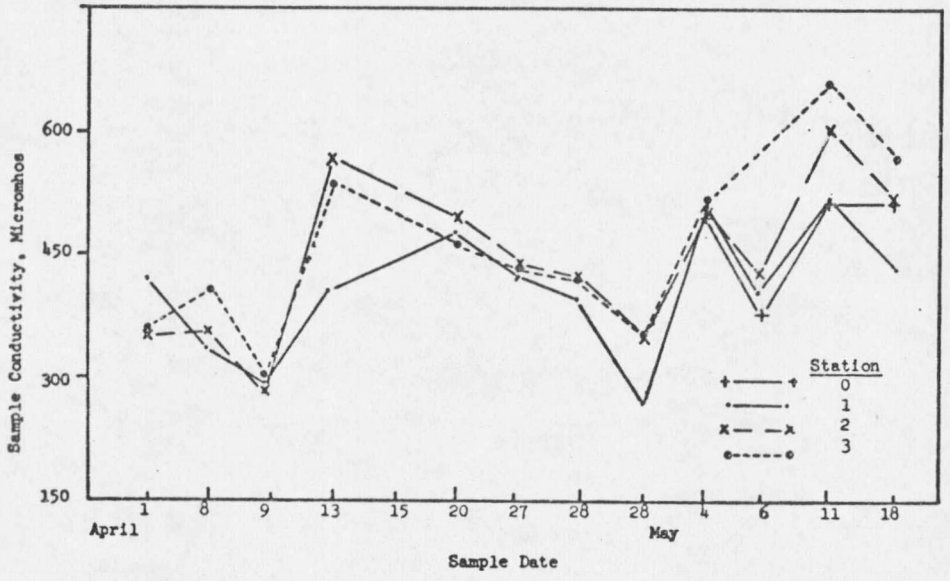

Figure 15 - Sample conductivity versus sample date for the four stations.

Figures 16 and 17 are plots of nitrate and chloride ion activity against meter reading in millivolts. They were obtained by averaging the readings obtained from the Orion standard solutions over a period of time. The charts indicate that an increase in millivolt reading for either the nitrate or chloride electrode implies a decrease in the concentration of that ion being tested.

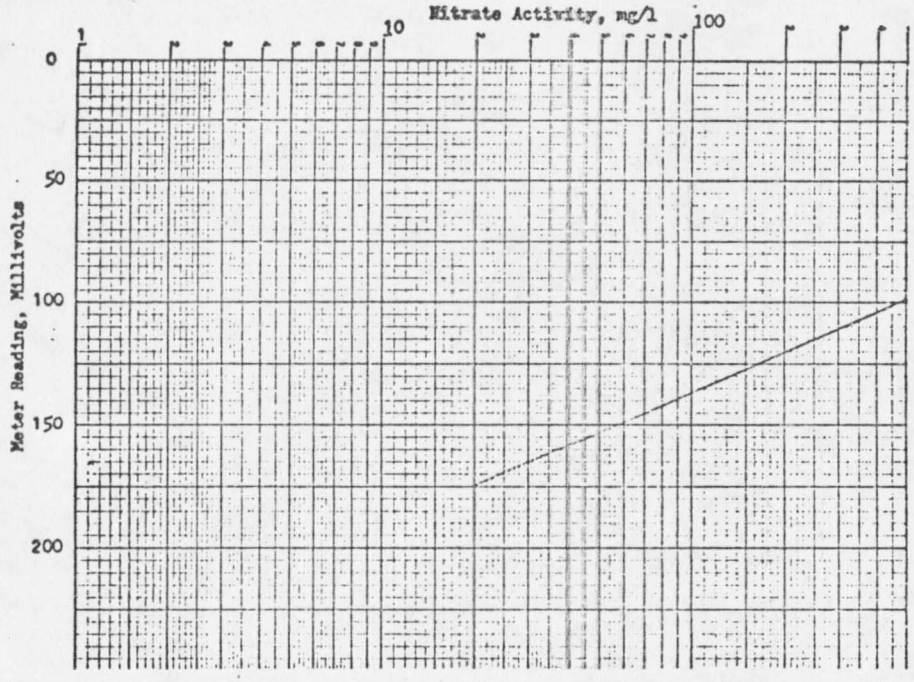

Figure 16 - Nitrate electrode meter reading versus nitrate activity.

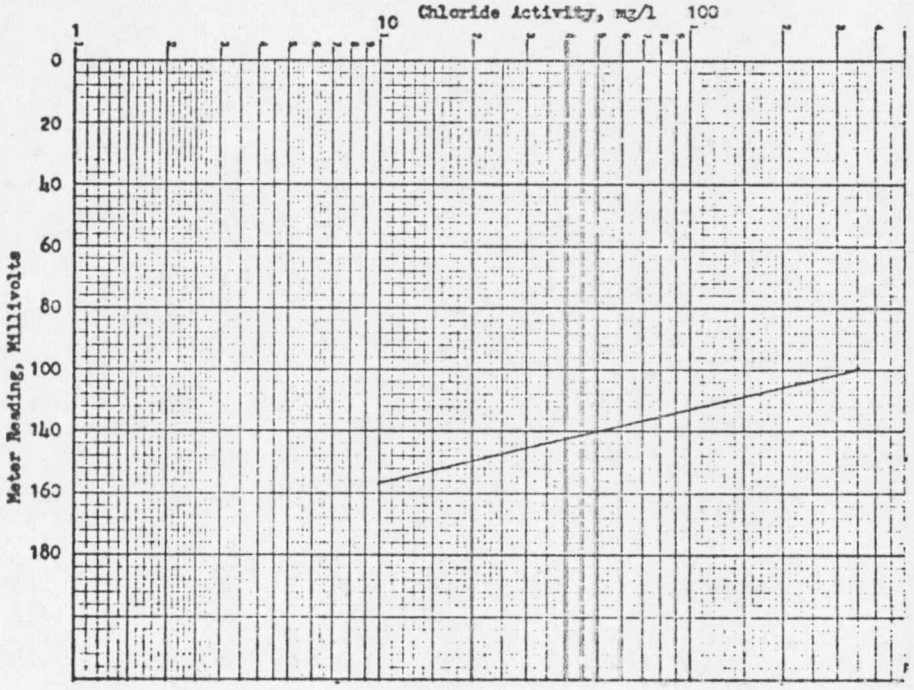

Figure 17 - Chloride electrode meter reading versus chloride activity.

Figure 18 shows the relationship between head-discharge for the concrete control structure, and was used to estimate the flow of the stream at the time of the readings.

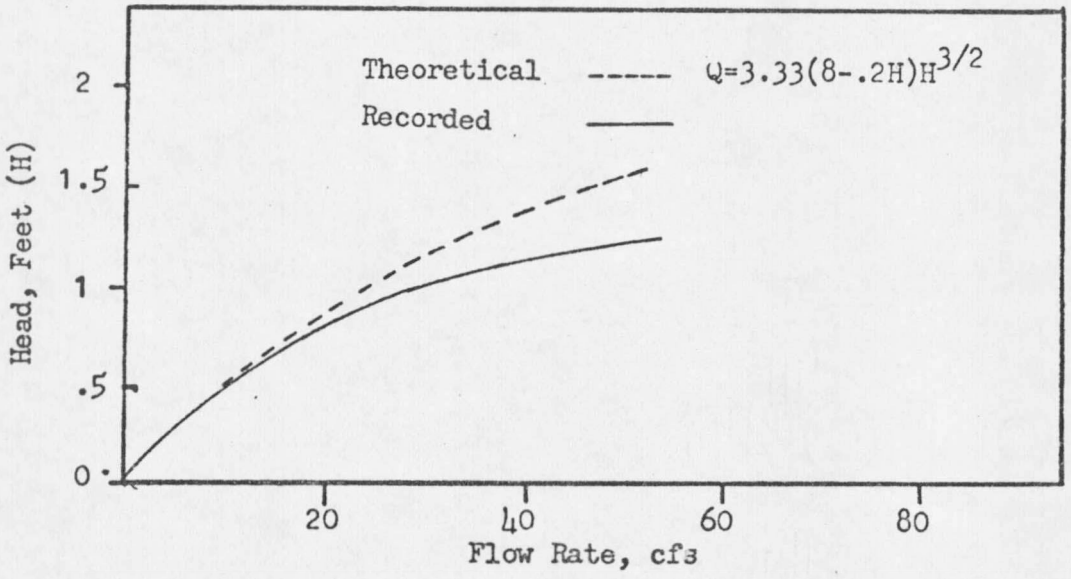

Figure 18 - Calibration curves for concrete control structure located at station one.

Table VII shows the results of water samples brought back on May 18, and tested by the Montana State University Agricultural Experiment Station. The samples were brought back and frozen before testing, except for sample number 3H, which contained a special nitrate preservative.

Table VII - Results of water samples from Newlan Creek tested at the Montana State University Agricultural Experiment Station.

Sample Number	NO_3-N ppm	Conductivity mmhos	Conductivity ppm	pH	meq/L Bicarbonates	meq/L Chlorides	ppm
0	.027	380	241	7.2	.015	.01	.35
1	.04	360	229	7.4	.045	.008	.28
2	.13	490	313	7.6	.015	.009	.315
3H	.27	530	338	8.0	.075	.008	.28
3	.13	540	345	7.9	.045	.006	.21

Sample Number	PPM IN SAMPLE Sulfates	Calcium	Magnesium	Potassium	Sodium
0	459	36.6	22.7	1.0	1.67
1	385	29.7	23.5	1.39	2.22
2	845	44.4	30.8	4.27	4.66
3H	918	52.4	30.8	4.77	5.22
3	845	52.4	30.8	4.77	5.22

Table VIII lists the results of water samples collected approximately four miles west of Bozeman. Samples one and two were taken directly from potholes in the corner of a lot where about fifty head of cows were confined, and sample three from a clear running stream adjacent to the lot. These samples were taken to see what readings were obtained when concentrated animal wastes were encountered.

Table VIII - Results of samples taken four miles west of Bozeman, Montana.

Sample Number	NO_3^- Meter Reading	NO_3^- Apparent Concentration	Cl^- Meter Reading	Cl^- Apparent Concentration
1	79 millivolts	900 mg/l	68 millivolts	2000 mg/l
2	97 "	540 mg/l	73 "	1500 mg/l
3	190 "	13 mg/l	140 "	50 mg/l

INTERPRETATION OF DATA

Figures 11, 12, 13, and 14 on pages 28 through 29 indicate that no significant pattern in the data exists. The readings for data dates April 28, are lower and higher than average for nitrates and chlorides respectively, but these are lab checks on samples brought back from the field, and reflect not only differences in temperature, but also a lapse in time where the samples had a chance to change. This would indicate that samples cannot be brought into the lab, and the field results duplicated. As temperature increases, the Nernst factor $\frac{RT}{F}$ increases, (see appendix, page 51) and the overall emf given by the Nernst equation should decrease. Figures 11 and 13, pages 28 and 29, tend to show this decrease up until about 8°C, then both start to show an increase in millivolt readings for nitrates and chlorides. This may reflect some chemical change in the water, where more ions become complexed, or other interferences become more prominent.

An interesting result shows up in Table IX, where all the readings are averaged over the time period of the project.

Table IX - Summary of date collected from April to May 18, on Newlan Creek

Station	N^0	Cl	N^1	Cl	N^2	Cl	N^3	Cl
Maximum	215	136.3	225.6	142	236	149	231.3	149
Minimum	193.3	126.3	190	120.3	190	119.3	190	119.3
Average	204.5	130.2	205.6	131.8	211.3	132.3	214.9	133.5

Both nitrate and chloride millivolt readings increase as the stations go downstream from 204.5 to 214.9 millivolts for nitrates, and from 130.2 to 133.5 millivolts for chlorides, implying a decrease in concentration. The most significant decreases in nitrates occur between stations one and three, with the decreases in chlorides fairly uniform throughout the sampling area. A decrease in nitrates and chlorides is unexpected. This pattern of change could also be a reflection of the method of testing, where the stations were always checked in a given order. Further testing in a random manner would show if this is a constant pattern, or just a result of testing methods. If further testing continues to show this pattern, then this indicates that sampling over a period of time would sense the changes in concentrations as the river moves through the wintering area.

Figure 15, page 30, showing the change in conductivity with respect to time, follows a pattern similar to that established by the nitrate readings on page 28. Some of the readings were questionable because the instrument was affected by the direct sunlight striking the conductivity cell. The instrument was not shaded in any was, and the type of day, whether it was cloudy or sunny did affect the performance of the meter.

The results of the lab tests shown in Table VII, page 34, using the calibration curve on page 32, and a typical reading of 210 millivolts for nitrates would indicate that nitrates were present in only very small amounts, much less than the recommended limit of forty-five mg/l, set by the United States Public Health Service. Taking a typical reading for

chlorides of 130 millivolts would give a reading of sixty mg/l on the chloride activity chart. This is significantly higher than the .35 to .021 mg/l reported in Table VII. The discrepancies can probably be explained by considering the high amount of sulfates encountered, ranging form 385 to 918 parts per million. (See Table VII, page 34) This is one of the ions that interferes with chloride reading. Figure 19 is a plot showing the theoretical response of the electrode to various concentrations of SO_4^- ion.

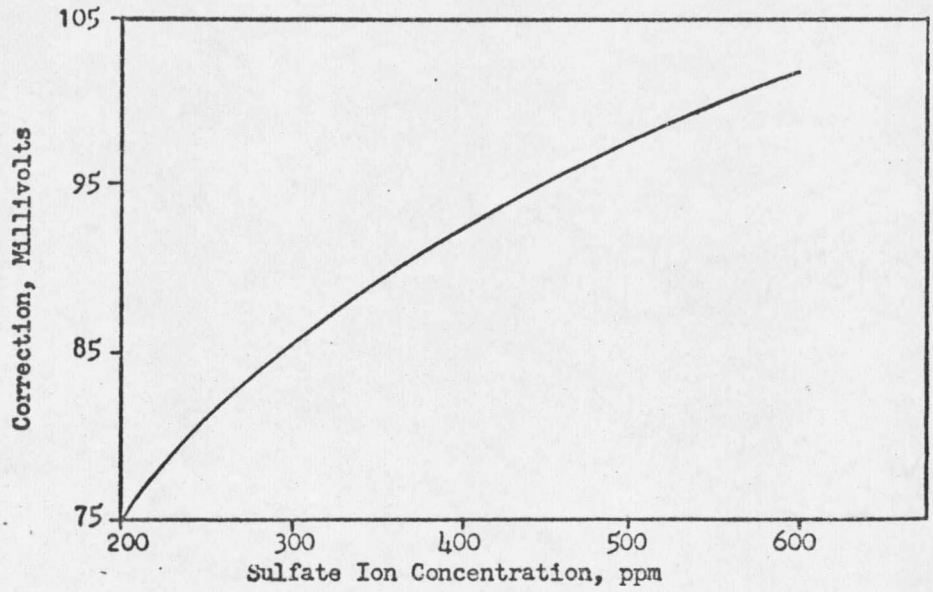

Figure 19 - Theoretical response of specific ion meter to sulfate ion.

Once sulfate concentration is known, the correction in millivolts to be subtracted from the constant E_0 can be made, giving a new reading. For the chloride electrode, the constant term is about 205 millivolts.

A typical activity for sulfates might be 250 ppm, giving a correction of 80 millivolts on Figure 19. Subtracting this from E_0 = 205 gives a reading of 125 millivolts for the meter. This shows that a false reading for the level of chlorides is obtained due to sulfate interference, and the actual level for chlorides is probably very small.

Table VIII, page 35 shows the results taken from a lot where fifty head of cattle were confined. Samples one and two were taken from potholes in the lot where concentrated wastes had accumulated after a heavy rainstorm. Sample three was taken from a small stream across the road. Samples one and two give a significantly lower millivolt reading then sample three. This lower reading indicates higher concentrations of nitrates and chlorides in the cattle wastes. The nitrate readings from the potholes are about 70 times as concentrated as the readings from the small stream, and the chloride readings are about 35 times as concentrated.

SUMMARY

The objective of the project was to begin to develop the instrumentation and techniques necessary to determine if animal wintering operations located along streams are polluters. This was done by trying to detect changes in the water quality that would indicate that animal wastes were getting into the stream. Specifically, nitrate and chloride ion activity, conductivity, water termperature, and stream flow were recorded intermittently from April 1 to May 18 during the snow runoff period. The site of the study was the Holmstrom Ranch located on Newlan Creek, near White Sulphur Springs, Montana. The ranch wintering area is involved with approximately two river miles, and included 1100 head of sheep, 85 hogs, 185 head of cattle, and 243 head of calves through the winter of 1970-71. Four sampling stations were established along the creek involving a distance of seven river miles. Samples taken were grab samples, and three measurements were taken at each station. The three readings were averaged.

CONCLUSIONS

Both nitrates and chlorides did show a slight decrease through the wintering area over a long time average. Although a decrease did show up, all levels of concentration recorded were far below the upper limit allowed by the U. S. Public Health Service. The testing done to date indicates that there is no serious pollution caused by wintering operations. The extremely low concentrations encountered made estimates of the exact amounts of nitrates and chlorides impossible using the present instrumentation and techniques. The results also only represent a fraction of the amount of flow moving through the area and do not represent unusual conditions, such as after periods of rainfall. Additional testing is needed to determine if there are any times the concentration of nitrates and chlorides does become high.

RECOMMENDATIONS FOR FURTHER STUDY

1) The study should be continued for another year, and expanded. The number of tests should be increased to include pH, coliform, and some form of BOD measurement. Coliform bacteria, as explained in the introduction, is a good indicator of wastes getting into the stream. In addition to running BOD tests, the use of a dissolved oxygen meter might be considered. There are dissolved oxygen meters available which are designed for field use, and might be a good addition to the BOD measurement.

2) Consideration should be given to locating another site for study. The Holmstrom Ranch is an excellent choice as far as its involvement with the river and number of animals, but the distance involved (over 100 miles) from the University to the project site is a handicap. This limits readings to once or at most twice a week, and makes it impossible to catch unusual conditions, such as immediately after a rain. If a closer suitable site cannot be found, there is the alternative of hiring someone at White Sulphur Springs to take the necessary measurements. The instruments could be left there, and the only travelling involved would be to periodically collect the data and service the instruments.

3) The two culverts located downstream from station one, and under the roadway should be calibrated for flow measurements, instead of using the concrete control structure. Much time was spent in trying to find a way that flow could be easily determined, and the net result was only a

few good measurements towards the end of the project. Measurements within a reasonable amount of accuracy could probably be obtained using the culverts. The concrete control structure could then serve as a check.

4) Some type of carrying box should be built. Much time was spent in taking out and putting away instruments. A well-organized equipment box would eliminate this loss of time. It should also include some provision for shading the conductivity cell from direct sunlight during use. The equipment box should be built so the instruments receive as little jarring during transportation as possible. Some of the trouble with the equipment may have been due to rough riding during transportation.

5) More samples should be brought into the lab for analysis. Preferably samples should be brought in every two weeks for lab testing. Not only can this be used to compare with the meter readings but it also gives some indication of the interferences that are present.

6) Elimination of interferences should be looked into. It appears that the sulfate ion may be causing incorrect readings with the chloride electrode. Possibly Orion has some equipment or procedures that would eliminate this interference.

7) The sampling stations should be checked randomly. The time of day and sequence in which the stations are checked should be varied in order to eliminate errors that may be due to following the same procedures each time.

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- APPENDIX -

APPENDIX A

Tabulation of Raw Data

Station 0

Date	NO_3^- (Millivolts)	Cl^- (Millivolts)	Conductivity* (Micromhos)	Water Temp. (°C)	Stream Flow (cfs)
5/4	215	136.3	503	10	42
5/6	210	130	386	—	—
5/11	193.3	126.3	364	8	26
5/18	200	128.3	336	7	25
Ave	204.5	130.2	397		

*Standardized to 25°C.

Station 1

	Date	NO_3^- (Millivolts)	Cl^- (Millivolts)	Conductivity* (Micromhos)	Water Temp. (°C)	Stream Flow (cfs)	Comments
(1)	4/1	208.3	140	430	3½		
	4/6	—	—	—	9		
(2)	4/8	221.6	138	340	5		
(3)	4/9	215	142	296	27		Lab rerun of samples 4/8
(4)	4/13	222.3	132	417	9		
(5)	4/15	225.6	139.3	165	4	33	
(6)	4/20	196.6	124.3	486	6	25	
(7)	4/27	205	125.3	433	4		
(8)	4/28	190	125	413	24		Lab run samples 4/27
(9)	4/28	192.5	141	286	24		Lab run samples 4/15
(10)	5/4	200	131.3	520	10	42	
(11)	5/6	195	124.3	422	—		
(12)	5/11	196.3	120.3	366	8	26	
(13)	5/18	204.3	130	284	7	25	

*Standardized to 25° C

Station 2

Date	NO_3^- (Millivolts)	Cl^- (Millivolts)	Conductivity* (Micromhos)	Water Temp. (°C)	Stream Flow (cfs)	Comments
(1) 4/1	203.3	136	358	3½		
(2) 4/6	----	---	---	9		
(3) 4/8	220	136	369	5		
(4) 4/9	222	149	289	27		Lab run samples 4/8
(5) 4/13	226.6	131.3	575	9		
(6) 4/15	236	130	165	4	33	
(7) 4/20	208.3	119.3	505	6	25	
(8) 4/27	221	129.3	445	4		
(9) 4/28	190	140	128	24		Lab run samples 4/27
(10) 4/28	193.5	145	352	24		Lab run samples 4/15
(11) 5/4	210	134	517	10	42	
(12) 5/6	198.3	124.3	436			
(13) 5/11	206.3	121.3	427	8	26	
(14) 5/18	211.6	125	341	7	25	

*Standardized to 25°C.

Station 3

Date	NO_3^- (Millivolts)	Cl^- (Millivolts)	Conductivity* (Micromhos)	Water Temp. (°C)	Stream Flow (cfs)	Comments
(1) 4/1	214.0	136	376	3½		
(2) 4/6	----	---	---	9		
(3) 4/8	216.3	138	416	5		
(4) 4/9	222	149	306	27		
(5) 4/13	220.3	134	546	9		
(6) 4/15	231.3	131.3	165	4	33	
(7) 4/20	219.3	119.3	477	6	25	
(8) 4/27	230	130	442	4		
(9) 4/28	190	140	427	24		
(10) 4/28	193.5	145	354	24		
(11) 5/4	224	134	525	10	42	
(12) 5/6	212.3	118.6	300	---		
(13) 5/11	210	135	465	8	26	
(14) 5/18	211.6	125	373	7	25	

*Standardized to 25°C.

APPENDIX B

Specific Ion Electrodes Theory of Operation

The theoretical potential between two solutions can be predicted by the Nernst equation

$$E = E_0 + \frac{2.3RT}{ZF} \log \gamma A$$

where E is total potential in millivolts.

E_0 is a potential developed which is dependent on the ion activity of the inner solution, the choice of reference electrode and a small potential due to the salt bridge contact point.

R - universal gas constant, 8.314×10^7 ergs g-mole $^{\circ}K$

T - temperature of solution, $^{\circ}$Kelvin

Z - number of transferred electrons (the ions charge including sign)

F - Faraday constant, 96,487 Coulombs/g-mole

γ - activity coefficient, relating activity and concentration

A - activity of the ion being measured

The quantity $\frac{RT}{F}$ is called the Nernst factor, and takes on a value of 59.16 millivolts at 25°C.

In the introduction, several reasons were given for choosing the specific ion meter. One advantage that was mentioned was the wide range of concentrations that could be measured. This wide range also limits the precision. Ross and Frant state that "precision is ultimately limited to somewhere around 2% for monovalent ions and about twice that for divalent ions. This has never bothered anyone doing pH measurements,

and I suspect that for most water pollution problems if the ultimate 2% figure could be reached many people would be very happy." (8, p.1)

One of the so-called disadvantages of the electrode is that it measures ion activity rather than concentration. Ion activity is the "thermodynamically effective ion-concentration, in the same way that one speaks of the activity of the hydrogen ion in pH measurements." (8, p. 1) For example, if a .1 M acetic acid solution and a .1 M HCl solution are measured, the pH turns out to be around 3.15 and 1.02 respectively, while both solutions have a hydrogen ion concentration which should give a pH of 1. The reason for this is because ion activity and ion concentration are not the same. There are two factors which cause the difference between activity and concentration.

1) The total ionic strength of the solution affects the "activity coefficient." Figure 20 illustrates how the coefficient varies with total ionic strength for fluorides.

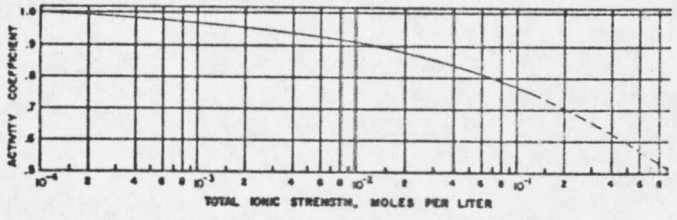

Figure 20 - Variation of activity coefficient with total ionic strength for fluorides.

2) The formation of complexes also effect activity. The electrode responds only to free ions, and not those that are tied up in complexes

with other ions. (8, p. 1)

Although ion activity is a better parameter than ion concentration in many cases (activity gives a measure of the chemical effectiveness of an ion), currently water pollution monitoring is usually reported as concentration of a certain ion. Most regulations for the limits on different constituents are given in terms of concentration, rather than ion activity. The relationship between activity and concentration is as follows:

$A = \gamma C$ where

A = ion activity

C = ion concentration

γ = activity coefficient

In order to determine the ion activity coefficient Orion suggests using sample conductivity. Table X shows the relationship between sample conductivity and total ionic strength.

Table X - Sample conductivity versus ionic strength at 25°C.

Conductivity (micromhos)	Ionic Strength (moles per liter)
10	1.1×10^{-4}
50	5.7×10^{-4}
100	1.2×10^{-3}
500	6.2×10^{-2}
1000	1.3×10^{-2}
5000	7.1×10^{-2}

Once the total ionic strength is determined, Figures 21 and 22 can be used to determine the activity coefficient for nitrates and chlorides respectively. (18, p. 11, 19, 21)

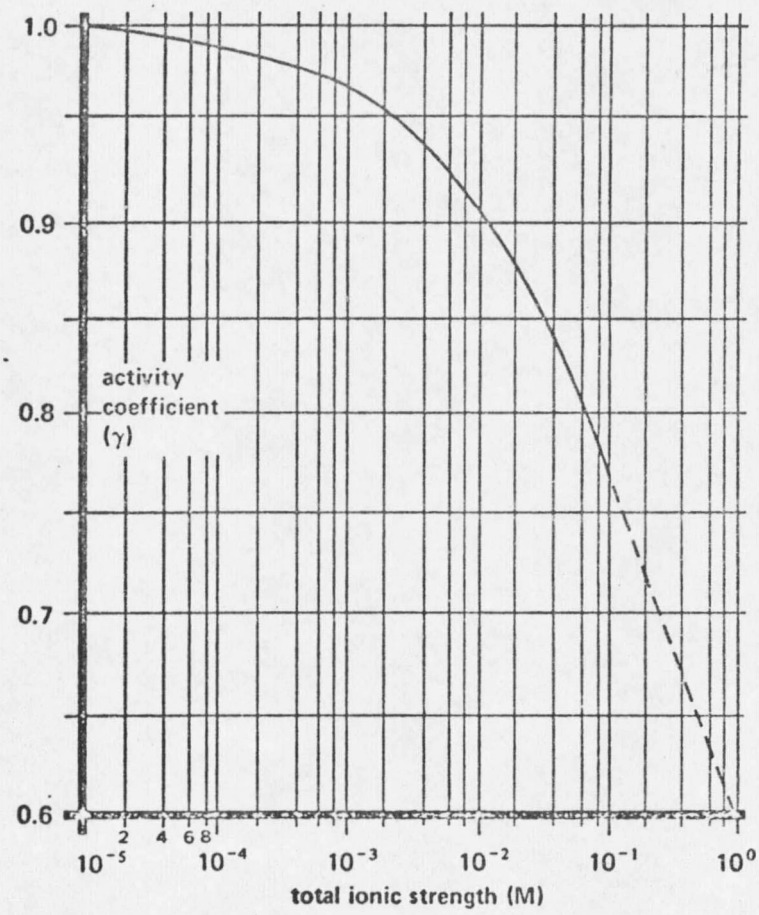

Figure 21 - Ionic activity coefficient of nitrate ion versus total ionic strength in pure sodium nitrate solutions.

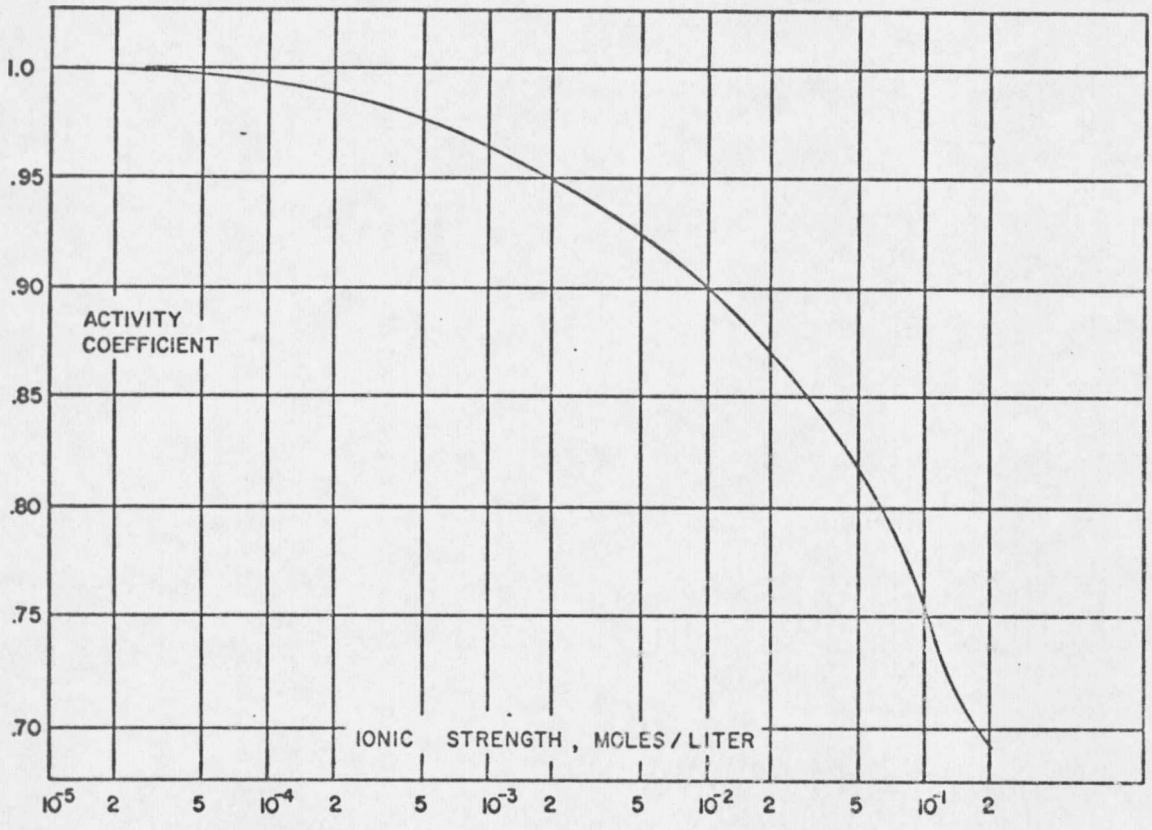

Figure 22 - Ionic activity coefficient of Cl^- as a function of total ionic strength in pure NaCl solutions.

The specific ion meter, as with other analytical techinques, is subject to interferences. Interferences can be broken down into two categories, electrode and method interferences. Some species of ions are measured along with the ion of interest. This is electrode interference. Its effect can be subtracted out of the Nernst equation by knowing the "selectivity constant" for the interfering ion. In the case of the nitrate and chloride electrodes, the Nernst equation becomes:

$$E = E_0 - 2.3 \frac{RT}{F} \log (A + KiCi)$$

All quantities are as previously defined (see page 51) and Ki is the selectivity constant of the interfering ion and Ci is the activity of the interfering ion. Table XI and XII are lists of interfering ions and their selectivity constants for the nitrates and chlorides electrodes. (18, p. 14, 17, 19)

Table XI - Approximate Orion selectivity constants for the nitrate electrode.

Interfering Ions	K_x	Interfering Ions	K_x
ClO_4^-	10^3	Cl^-	4×10^{-3}
I^-	20	OAc^-	4×10^{-4}
ClO_3^-	2	$CO_3^=$	2×10^{-4}
Br^-	1.3×10^{-1}	$PO_4^=$	1×10^{-4}
HS^-	4×10^{-2}	F^-	6×10^{-5}
NO_2^-	4×10^{-2}	$H_2PO_4^-$	5×10^{-5}
CN^-	1×10^{-2}	$SO_4^=$	3×10^{-5}
HCO_3^-	9×10^{-3}	$HPO_4^=$	3×10^{-5}

Table XII - Approximate Orion selectivity constants for the chloride electrode.

Interfering Ions	k_i
ClO_4^-	32
I^-	17
NO_3^-	4.2
Br^-	1.6
OH^-	1.0
OAc^-	0.32
HCO_3^-	0.19
SO_4^-	0.14
F^-	0.10

The effect of the interfering ion can then be subtracted out, once the level of activity of the interfering ion is known.

The other type of interference, method interference, is caused by species that mask the ion being measured so that the electrode cannot detect its presence. This type of interference can be partially eliminated by the choice of technique used in sampling.

There are several areas for sources of error, besides interferences, that can occur with specific ion electrodes. They include:

1) Errors in the measuring electrode.

2) Errors in the reference electrode.

3) Errors in the measuring system (meter unit)

4) Errors caused by temperature changes

5) Solution errors

A relationship exists between the error in reading (emf) and the corresponding error in concentration. This can be found by differentiating the Nernst equation with respect to concentration.

$$E = E_0 + \frac{2.3\ RT}{FZ} \log C$$

$$\frac{dE}{dc} = 0 + \frac{59.16}{Z} d \log C$$

$$d \log C = \frac{1}{C} \log_{10} C = \frac{1}{C} (.43407)$$

$$\frac{dE}{dc} = \frac{59.16}{Z} (.43407) \frac{1}{C}$$

Taking it as a finite derivative:

$$\frac{\Delta E}{\Delta C} = \frac{25.68}{Z} \frac{1}{C}$$

$$\Delta E = \frac{(.2568)\ 100}{Z} \frac{1}{C} \Delta C$$

$$\Delta E = \frac{(.2568)\ (100\ \Delta C)}{(Z)\qquad (C)}$$

Let $(\frac{100\ \Delta C}{C})$ = Relative Error, RE, in concentration. Then $\Delta E = \frac{(.2568)}{Z} RE$.

Figure 23 is a plot of ΔE vs. RE for monovalent (Z = 1) and divalent (Z = 2) electrodes. (6, p. 356)

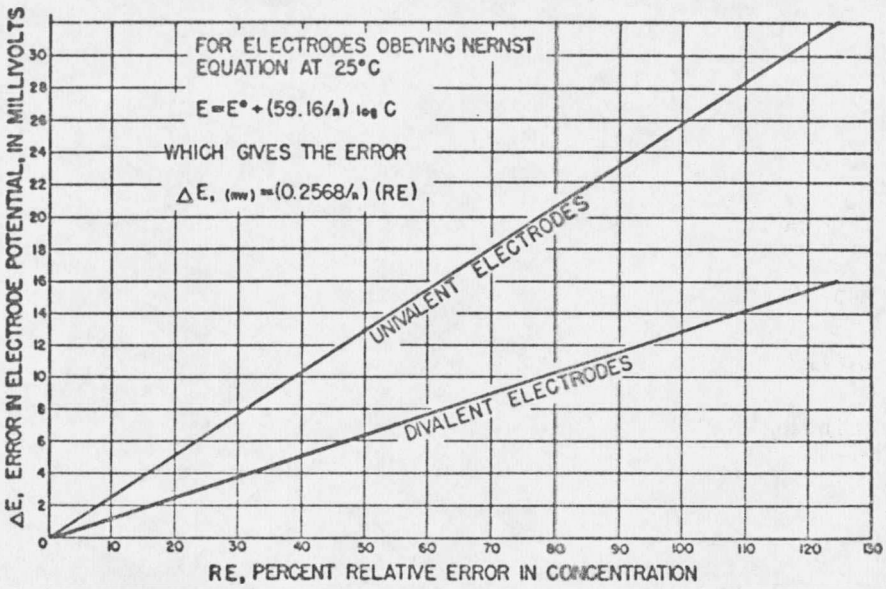

Figure 23 - Theoretical error in potential as a function of relative error in concentration.

The error due to temperature changes can also be found by differentiating the Nernst equation with respect to temperature.

$$E = E_0 + \frac{RT}{FZ} \log \Delta A$$

$$\frac{dE}{dT} = \frac{dE}{dT}0 + \frac{R}{FZ} \log \Delta A + \frac{RT}{FZ} d \frac{\log \Delta A}{dT}$$

(1) (2) (3)

Term one, $\frac{dE}{dT}0$, is a characteristic of the electrodes and their filling solutions. Term two, $\frac{R}{FZ} \log \Delta A$, is a temperature coefficient slope term for the Nernst equation. Truman S. Light, in Industrial Analysis and Control With Ion-Selective Electrodes states, "A frequently occurring

error in using pH or ion selective meters is caused when it is assumed that this (term) is the only cause for variation of observed emf's with temperature." The third term, $\frac{RT}{FZ} d \frac{\log \Delta A}{dT}$, is called the "solution temperature coefficient term," and reflects how the ions activity is changed due to temperature differences. Light goes on to state that, "The establishment of reference and materials, solutions and the temperature coefficients for ion-selective electrodes largely remains to be done." (6, p. 355) This leaves the user in a slight dillema. The best that can be done is to recognize that changes in temperature does introduce sources of error, including changes in the solution being measured, and changes in the instrument itself.