AN EMPIRICAL ESTIMATE OF THE RELATIVE MOBILITIES OF THE COMMON ROCK-FORMING ELEMENTS

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(1953)

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF
SCIENCE
as the
Massachusetts Institute of Technology

March, 1956

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Department of Geology and Geophysics
March 19, 1956

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Rec'd (Geol.) Aug. 23, 1956

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ABSTRACT

Relative mobility may be defined as the comparative rates at which elements, in ionic and/or colloidal form, move in the surface waters. Numerical values, or, empirical estimates, for the relative mobility may be calculated by comparing the composition of stream or river water residues with the composition of the rocks forming the drainage basins.

The above comparison was applied and empirical estimates of the relative mobility of the common rock-forming elements were calculated for three areas in the Connecticut Valley region of New England. The rocks forming the drainage basins in these areas are; Littleton schist, Oliverian granite, and Black Mountain leucogranodiorite. The order of decreasing mobility in these areas was; Mg, Ca, Na, K, Si, Fe, and Al. This order is believed to be the result of the differing solubilities of the minerals forming the rocks of the drainage basins. This order is different, particularly with regard to Mg and Ca, than the order for the general estimates as calculated by Smyth and Polynov. In view of this difference, it is suggested that the general estimates may be in error.

An Appendix, which contains the spectrochemical and chemical methods used in analysing the rocks and waters, is included as a possible aid to future investigators.

AN EMPIRICAL ESTIMATE OF THE RELATIVE MOBILITIES OF THE COMMON ROCK-FORMING ELEMENTS

INTRODUCTION

Mobility, as defined by Hawkes (10), is the ease and speed with which materials move in the surficial environment. If follows from this definition that relative mobility is a measure of the comparative rates at which the different materials move in the surficial environment. Thus, the definition is a general one and applies to all types of materials and transporting agents. In view of this generality, it seems desirable to modify the definition so that it is more specific and applies more directly to this report.

Most materials, in the surficial environment, are carried by surface waters and, to varying degrees, reach the end-points of water transport. Thus, nearly all the common elements of the lithosphere can be found in sea waters. Also, the materials transported by the waters are in the form of; coarse and fine particles, colloidal suspensions, and ions. As this report is concerned with the relative mobility of the elements in the highest state of dispersion (colloidal suspension and/or ionic solution), it is desirable to specify this in the definition.

Therefore, taking into account the above modifications,

RELATIVE MOBILITY MAY BE DEFINED AS THE COMPARATIVE RATES AT WHICH ELEMENTS, IN IONIC AND/OR COLLOIDAL FORM, MOVE IN THE SURFACE WATERS.

FACTORS AFFECTING THE MOBILITY

THE PERCENTAGE COMPOSITION OF THE DISSOLVED ELEMENTS IN STREAM OR RIVER WATER RESIDUES (1) IS DIFFERENT FROM THE PERCENTAGE COMPOSITION OF THE SAME ELEMENTS IN THE ROCKS OF THE DRAINAGE BASIN. IF THE PERCENTAGE COMPOSITIONS WERE THE SAME IN THE RESIDUE AS IN THE ROCK THEN THE RELATIVE MOBILITIES OF THE COMMON ROCK-FORMING ELEMENTS WOULD BE UNITY AND THE TERM MEANINGLESS. THAT THERE IS A DIFFERENCE IS DUE TO MANY FACTORS. CHIEF AMONG WHICH IS THE SOLUBILITY OF THE INDIVIDUAL MINERALS FORMING THE ROCKS OF THE DRAINAGE BASIN.

SOLUBILITY

MANY STUDIES HAVE BEEN MADE, PARTICULARLY IN THE PERIOD FROM 1850 TO 1900, ON THE SOLUBILITY OF MINERALS UNDER THE ACTION

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(1) BY RESIDUE IS MEANT THE SOLIDS OBTAINED BY EVAPORATING FILTERED STREAM OR RIVER WATERS.

of pure and carbonated waters. As far back as 1848, the Rogers brothers, W.B. and R.E. (19), tested a variety of minerals and found that some, particularly the ferro-magnesians, were partially decomposed and dissolved by the action of carbonated waters. Later work by Johnstone (11), Clarke (5), Steiger (22), Cushman (7), Leith and Mead (13), Stevens (23), and many others confirmed these earlier observations by the Rogers brothers.

Goldich's Stability Series

In 1938, Goldich (9), established an order of stability or, more correctly, an order of relative solubility for the common igneous rock-forming minerals which he called the mineral-stability series. This order is shown in Table 1, below. It is divided because, as a group, the mafic minerals are less resistant to the weathering processes than the salic minerals.

The similarity with Bowen's reaction series is striking. Goldich's stability series does not imply, of course, that the different minerals will invert one into the other on weathering. It does imply, however, that, under ordinary conditions of temperature and pressure, the last-formed minerals of igneous rocks are more resistant to weathering processes than those formed at an earlier stage of crystallization. He suggests that the differential between equilibrium

Table 1/ Goldich's Stability Series

Olivine
Calcic plagioclase
Augite
Calci-alkalic plagioclase
Hornblende Alkali-calcic plagioclase
Alkalic plagioclase
Biotite
Potash feldspar
Muscovite
Quartz

conditions at the time of formation and those existing at the surface today governs this order of stability. Later work by Pettijohn (16) adds both support and minerals to Goldich's stability series.

Other Factors

But solubility, although major, is not the only factor affecting the mobility of the elements. Once in solution, the elements are at the mercy of many other factors. The other factors include; the effects of changing pH, adsorption, absorption, coprecipitation, oxidation, reduction, formation of complex ions, and the action of biological processes. Besides these are many physical factors, such as, texture, grain size, and fractures, common to the rock itself. Thus, the mobility of the elements is not a function of the solubility alone but is the result of the action of a complex

SERIES OF VARIABLES WHICH TEND TO MODIFY, TO VARYING DEGREES, THE MOBILITY OF THE INDIVIDUAL ELEMENTS. IT REMAINS TO BE SHOWN IN A QUANTITATIVE MANNER, THE FINAL RESULT, OR, THE OVERALL EFFECT, OF THESE VARIABLES ON THE ROCK-FORMING ELEMENTS. IN OTHER WORDS, TO ESTABLISH, EMPIRICALLY, THE RELATIVE MOBILITY OF THE COMMON ROCK-FORMING ELEMENTS.

EMPIRICAL ESTIMATES OF THE RELATIVE MOBILITY

EMPIRICAL ESTIMATES OF THE RELATIVE MOBILITY ARE USUALLY OBTAINED BY ONE OR BOTH OF THE FOLLOWING METHODS. THE FIRST METHOD INVOLVES THE ANALYSIS OF FRESH ROCK AND THE CORRESPONDING RESIDUUM. BY COMPARING THESE ANALYSES THE RELATIVE GAIN- OR LOSS OF EACH CONSTITUENT CAN BE CALCULATED. THOSE ELEMENTS SHOWING A GAIN IN THE RESIDUUM WOULD BE RELATIVELY IMMOBILE AS COMPARED WITH THOSE SHOWING A LOSS. THE SECOND METHOD AND THE ONE USED IN THIS THESIS INVOLVES THE ANALYSIS OF STREAM AND/OR RIVER WATER AND THE FRESH ROCK OF THE DRAINAGE BASIN. BY COMPARING THE PERCENT OF EACH ELEMENT IN THE WATER RESIDUE WITH THE PERCENT OF THE CORRESPONDING ELEMENTS IN THE ROCK, AN ORDER OF RELATIVE MOBILITY FOR THE ROCK-FORMING ELEMENTS CAN BE CALCULATED.

TWO PREVIOUS INVESTIGATORS, SMYTH (20) AND POLYNOV (17), HAVE USED THE LATTER METHOD TO SHOW THE GENERAL RELATIVE MOBILITY OF THE ROCK-FORMING ELEMENTS. SMYTH APPLIES IT TO THE SURFACE OF THE EARTH AS A WHOLE, WHEREAS, POLYNOV APPLIES IT TO IGNEOUS ROCKS IN GENERAL. BOTH INVESTIGATORS BASE THEIR ESTIMATES ON PUBLISHED ANALYSES OF ROCKS AND RESIDUES. THEIR ESTIMATES ARE CONSIDERED IMPORTANT ENOUGH TO WARRANT FURTHER DESCRIPTION BELOW.

General Estimate

Smyth's Estimate

Smyth considered, as a unit, the entire mass of the crust acted upon by rain waters. Thus, by taking the overall average composition of crustal rocks and comparing it with the overall average composition of water residues, he was able to calculate an order of mobility for the common rock-forming elements.

In his calculations he used Clarke's estimate for the average composition of the crustal rocks. Clarke's estimate represents the average composition of a shell 10 miles thick of which probably 95% consists of igneous rocks. Since drainage waters act on surface rocks that are 75% sedimentary, it was necessary to take this into account in arriving at a reasonable approximation for the composition of surface rocks. Thus Smyth combined sedimentary with igneous rocks in the ratios of three to one to obtain his approximation. These weighted averages, together with the average composition of river water, are given in columns 1 and 11 of Table 2, below. The values for the relative mobility (2), column 111, are obtained by dividing the elements in column 11 by the

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(2) Smyth refers to these values as relative solubility; relative mobility is the more suitable term.

CORRESPONDING ELEMENTS IN COLUMN I. IT SHOULD BE POINTED OUT THAT THE FIGURES IN COLUMNS I AND II REPRESENT THE ACTUAL PERCENTAGE OF EACH CONSTITUENT, AS THE ELEMENT, RECALCULATED TO 100%. THIS PROCEDURE IS FOLLOWED THROUGHOUT IN ORDER THAT THE RELATIVE MOBILITIES, AS CALCULATED BY THE DIFFERENT INVESTIGATORS, MAY BE READILY COMPARED.

TABLE 2/ SMYTH'S ESTIMATE OF THE RELATIVE MOBILITY

ELEMENT	I SURFACE ROCKS *	II WATER RESIDUES *	III RELATIVE MOBILITY (II/I)
CA	7.91	52.63	6.65
NA	2.62	16.51	6.31
MG	3.63	8.79	2.42
K	4.95	3.95	0.79
SI	57.70	14.06	0.24
(AL, FE)	23.19	4.06	0.17
	100.00	100.00	1.00

* RECALCULATED TO EQUAL 100%.

THUS THE FIGURES IN COLUMN III GIVE SOME IDEA OF THE RELATIVE RATES AT WHICH THE VARIOUS ELEMENTS TRAVEL. ASSUMING THE ACCURACY OF THE FIGURES USED IN COLUMNS I AND II, IT FOLLOWS THAT: CA AND NA APPEAR TO MOVE AT ROUGHLY THE SAME RATE; MG ABOUT ONE-THIRD THIS RATE; K ABOUT ONE-NINTH

THIS RATE; SI ABOUT ONE-THIRTIETH THIS RATE; AND AL AND FE TOGETHER, ABOUT ONE-SIXTIETH THIS RATE. TAKING THE ELEMENTS IN GROUPS IT CAN BE SAID THAT THE ALKALIS AND ALKALINE EARTH ELEMENTS ARE MORE MOBILE THAN THE MORE ABUNDANT ROCK-FORMING CONSTITUENTS SI, AL, AND FE.

THE RELATIVE MOBILITIES, AS EXPRESSED ABOVE, GIVE SOME INDICATION OF THE GENERAL TREND. IT IS DESIRABLE TO COMPARE THIS GENERAL TREND WITH A MORE SPECIFIC ONE, AS CALCULATED INDEPENDENTLY BY POLYNOV, FOR IGNEOUS ROCKS AND THEIR DRAINAGE BASINS.

POLYNOV'S ESTIMATE

POLYNOV CONSIDERED, AS A UNIT, THE TOTAL MASS OF SURFACE IGNEOUS ROCKS ACTED UPON BY RAIN WATERS. THUS, TO OBTAIN HIS ORDER OF RELATIVE MOBILITIES, HE COMPARED THE AVERAGE COMPOSITION OF IGNEOUS ROCKS WITH THE AVERAGE COMPOSITION OF WATER RESIDUES WHICH DRAIN AREAS OF IGNEOUS ROCKS.

IN HIS CALCULATIONS HE USED FERSMAN'S AVERAGE FOR THE COMPOSITION OF IGNEOUS ROCKS. THE AVERAGE COMPOSITION OF WATER RESIDUES WAS OBTAINED FROM CLARKE (6) AND REPRESENTS THE AVERAGE OF 30 ANALYSES OF WATERS BELIEVED TO DRAIN ONLY IGNEOUS AREAS. THESE AVERAGES ARE SHOWN IN TABLE 3, COLUMNS IV AND V. COLUMN VI IS POLYNOV'S ESTIMATE OF THE RELATIVE MOBILITY OF THE COMMON ROCK-FORMING ELEMENTS.

TABLE 3/ POLYNOV'S ESTIMATE OF THE RELATIVE MOBILITY

ELEMENT	IV IGNEOUS ROCKS *	V WATER RESIDUES *	VI RELATIVE MOBILITY (V/IV)
CA	6.94	36.64	5.27
NA	5.72	23.56	4.12
MG	4.06	12.16	2.99
K	4.95	10.91	2.20
SI	53.00	14.88	0.28
AL	15.55	1.16	0.075
FE	9.78	0.69	0.071
	100.00	100.00	1.00

* RECALCULATED TO EQUAL 100%.

THE SIMILARITY BETWEEN POLYNOV'S FIGURES, COLUMN VI, AND SMYTH'S, COLUMN III, IS STRIKING. BOTH THE ORDER AND MAGNITUDE ARE ROUGHLY THE SAME. ONE NOTABLE EXCEPTION IS THE RELATIVE INCREASE IN THE MOBILITY OF K IN AREAS OF IGNEOUS ROCKS. THIS IS PROBABLY THE RESULT OF THE GREATER RESISTANCE TO WEATHERING OF THE K-BEARING CLAY MINERALS IN SEDIMENTARY ROCKS AS COMPARED WITH K-BEARING MINERALS IN IGNEOUS ROCKS.

Discussion of Smyth's and Polynov's Estimates

By comparing the composition of the water residues with the composition of the rocks comprising the drainage basins, as done by Smyth and Polynov, a general estimate of the relative mobility can be calculated. Whether these estimates are valid or not depends, to a large extent, on the assumptions used in their calculations. The major assumptions, by both investigators, involves the composition of the rocks of the drainage basins.

Smyth, in his estimate of the composition of surface rocks, combines sedimentary with igneous rocks in the ratios of three to one. Limestones, dolomites, sandstones, and shales are the predominant rock types included under the classification of sedimentary rocks. Each of these rock types contains minerals having widely different solubilities so that the proportions of each rock type used in computing an average composition for the sedimentary rocks is of critical importance. If the limestone and/or dolomite contents are over-estimated then high relative mobilities for the Ca and Mg can be expected. The high relative mobilities would be further enlarged by the greater solubility of the minerals in the limestones and dolomites as compared with those in the sandstones and shales.

The proper weighting for the different rock types is equally important in Polynov's estimate for areas underlain

BY IGNEOUS ROCKS. THE AVERAGE COMPOSITION OF IGNEOUS ROCKS REPRESENTS THE WEIGHTED AVERAGE OF FELSIC ROCKS, WHICH CONTAIN RELATIVELY INSOLUBLE MINERALS, AND MAFIC ROCKS, WHICH CONTAIN RELATIVELY SOLUBLE MINERALS. THUS, HIGH OR LOW MOBILITIES COULD RESULT FROM IMPROPER WEIGHTING OF THE VARIOUS ROCK TYPES. THESE ANOMALIES WOULD BE DEFINITELY ENLARGED BY THE FACT THAT THE ROCK TYPES, AS A UNIT, HAVE DIFFERENT SOLUBILITIES.

TAKING INTO ACCOUNT THE ABOVE ASSUMPTION, PLUS THE ASSUMPTION THAT THE STREAM WATERS DO ACTUALLY DRAIN THE AREAS IN WHICH THE ROCKS HAVE THE COMPOSITION AS STATED, IT MAY BE SAID THAT THE ABOVE ESTIMATES OF THE RELATIVE MOBILITIES EXPRESS ONLY A GENERAL RELATION. PETROLOGIC, CLIMATIC, AND TOPOGRAPHIC VARIABLES ARE NECESSARILY ABSORBED IN THE GENERAL AVERAGES USED BY SMYTH AND POLYNOV. THE WRITER BELIEVES THAT THE ASSUMPTIONS USED IN THE ABOVE CALCULATIONS CAN BE AVOIDED, OR DEFINITELY MINIMIZED, BY CONSIDERING THE RELATIVE MOBILITY IN A SPECIFIC AREA. WITH THIS IN MIND, THREE AREAS IN THE CONNECTICUT VALLEY REGION OF NEW HAMPSHIRE AND VERMONT WERE ANALYSED AND THE RELATIVE MOBILITIES OF THE COMMON ROCK-FORMING ELEMENTS CALCULATED. THE ANALYTICAL DATA PLUS THE CALCULATIONS WILL BE DESCRIBED IN CONSIDERABLE DETAIL IN THE NEXT SECTION.

SPECIFIC ESTIMATE

IT FOLLOWS FROM THE ABOVE WORK OF SMYTH AND POLYNOV THAT A SPECIFIC ESTIMATE OF THE RELATIVE MOBILITY CAN BY OBTAINED BY COMPARING THE COMPOSITION OF THE ROCK IN ONE LOCAL AREA WITH THE COMPOSITION OF THE WATER RESIDUES OBTAINED FROM THIS AREA. UNLIKE THE ABOVE GENERAL ESTIMATE, HOWEVER, THE SPECIFIC ESTIMATE CAN BE MORE CLOSELY CONTROLLED. AN AREA OF HOMOGENEOUS ROCK, SUCH AS A SMALL IGNEOUS STOCK, CAN BE SAMPLED AND, BY VISUAL INSPECTION, ONE CAN BE REASONABLY ASSURED THAT THE STREAM'S DRAINAGE BASIN IS CONFINED TO THIS AREA OF SAMPLED ROCK.

BEFORE DISCUSSING THE RESULTS IT SEEMS BOTH DESIRABLE AND APPROPRIATE TO DESCRIBE THE AREAS SAMPLED, AND THE ANALYTICAL DATA USED IN CALCULATING THE RELATIVE MOBILITIES.

LOCATION AND DESCRIPTION OF SAMPLED AREAS.

OF CRITICAL IMPORTANCE WAS THE SELECTION OF AN AREA IN WHICH A STREAM FLOWED OVER A ROCK OF UNIFORM COMPOSITION. HIGH RELIEF COMBINED WITH A MINIMUM OF GLACIAL OVERBURDEN WERE ALSO DESIRABLE FEATURES. PROFESSOR MACDONALD PROVED HELPFUL IN SUGGESTING POSSIBLE AREAS TO SAMPLE AND, GUIDED BY HIS SUGGESTIONS, THREE AREAS - TWO IN NEW HAMPSHIRE AND ONE IN VERMONT - WERE CHOSEN (FIG. 1). UPON PERSONAL

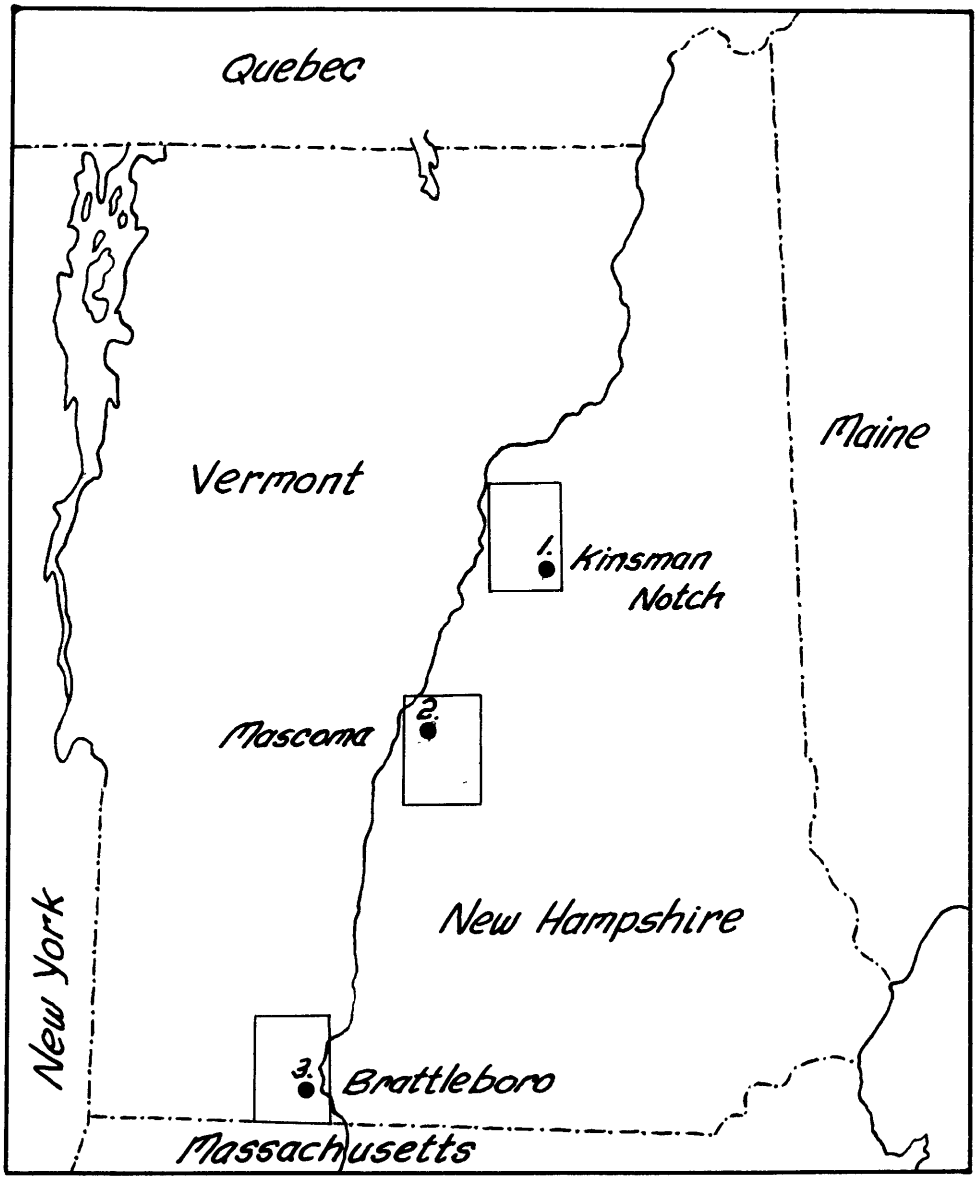

Figure 1. – Location of Sampled Areas

INSPECTION OF THESE AREAS IT WAS FOUND THAT THE ROCK WAS UNIFORM IN COMPOSITION AND THE STREAM'S DRAINAGE BASIN WAS CONFINED TO THIS AREA OF HOMOGENEOUS ROCK.

SAMPLE 1-AB: LITTLETON SCHIST, KINSMAN NOTCH, NEW HAMPSHIRE

SAMPLES WERE COLLECTED FROM BEAVER BROOK WHICH DRAINS THE NORTHEAST SLOPE OF MT. BLUE (ELEVATION = 4530 FT.) ABOUT 3/4 OF A MILE WEST OF KINSMAN NOTCH, NEW HAMPSHIRE. ACCORDING TO BILLINGS (2), THE ROCKS OF THIS AREA CONSIST OF MICA SCHIST, QUARTZ-MICA-SCHIST, GARNET SCHIST, STAUROLITE-SILLIMANITE SCHIST AND SILLIMANITE SCHIST. ROCK SAMPLES WERE TAKEN ALONG THE BROOK FOR CONSIDERABLE DISTANCE AND, ALTHOUGH THERE APPEAR TO BE MANY DIFFERENT ROCK TYPES INVOLVED, THIS METHOD OF SAMPLING AND THE SIMILARITY OF THE MEMBERS OF THE METAMORPHIC ROCK SEQUENCE WOULD TEND TO CANCEL THIS APPARENT INHOMOGENEITY.

SAMPLE 2-AB: OLIVERIAN GRANITE, MASCOMA, NEW HAMPSHIRE.

SAMPLES WERE COLLECTED FROM A SMALL STREAM LOCATED ON THE EAST SLOPE OF MOOSE MOUNTAIN (APPROXIMATE ELEVATION = 2000 FT.) ABOUT 1/4 OF A MILE NORTH OF GROSS NEIGHBORHOOD SCHOOL, NEW HAMPSHIRE. ACCORDING TO CHAPMAN (3), THE OVERALL COMPOSITION OF THIS GROUP OF ROCKS RANGES FROM QUARTZ DIORITE TO GRANITE. MAJOR MINERALS ARE QUARTZ, MICROCLINE, OLIGOCLASE, AND BIOTITE. MINOR ACCESSORIES ARE MUSCOVITE, EPIDOTE, SPHENE, MAGNETITE, ZIRCON, APATITE, AND SERICITE. THE ROCKS FROM

AROUND GROSS NEIGHBORHOOD SCHOOL ARE CONSISTENTLY PINK GRANITES AND, THEREFORE, THE REQUIREMENT OF ROCK HOMOGENEITY IS SATISFIED.

SAMPLE 3-AB: BLACK MOUNTAIN GRANITE, BRATTLEBORO, VERMONT.

SAMPLES WERE COLLECTED FROM A SMALL SPRING ENTERING THE ABANDONED PRESBREY-LELAND COMPANY QUARRY. THE QUARRY IS LOCATED ON THE WEST SLOPE OF BLACK MOUNTAIN (APPROXIMATE ELEVATION = 1300 FT.) ABOUT 5½ MILES NORTHEAST OF BRATTLEBORO, VERMONT. THE ROCK TYPE, ACCORDING TO CHURCH (4), IS A LEUCOGRANODIORITE. MAJOR MINERALS ARE QUARTZ, MICROCLINE, ALBITE-OLIGOCLASE, MUSCOVITE, AND BIOTITE. MINOR ACCESSORIES ARE ORTHOCLASE, MAGNETITE, GARNET, AND EPIDOTE. WITH REGARD TO THE UNIFORMITY OF THE ROCK, CHURCH SAYS:

> "PLOT OF TRAVERSES SHOWED A HIGH DEGREE OF UNIFORMITY THROUGHOUT THE ENTIRE AREA EXCEPT FOR A SLIGHTLY HIGHER PERCENTAGE OF BIOTITE IN THE SOUTHERN PART OF THE IGNEOUS MASS."

SAMPLING PROCEDURE.

CHIP SAMPLES OF RELATIVELY FRESH ROCK WERE TAKEN FOR SOME DISTANCE UPSTREAM FROM WHERE THE WATER SAMPLES WERE COLLECTED. SIX TO EIGHT LITRE WATER SAMPLES WERE COLLECTED NEAR THE BASE OF THE SLOPE AND STORED IN POLYETHYLENE CONTAINERS. TEMPERATURE AND pH WERE MEASURED AT THE TIME OF COLLECTION. TABLE 4 SUMMARIZES THE DATA obtained for temperature, pH, and salinity of the water samples.

Table 4 - Location, Temperature, pH, and Salinity of Water Samples.

Sample No.	Location	Temperature °C	pH	Salinity Mg/litre
1-A	Kinsman Notch, N.H.	2.0	5.4	10.9
2-A	Mascoma, N.H.	6.0	6.1	20.6
3-A	Brattleboro, Vt.	9.0	5.6	15.2

Analytical Data

(a) For Waters: A combination of wet chemical and flame photometric methods were used to determine the concentrations of the various elements in the stream waters. The methods used were those recommended by 'Standard Methods' (21). A complete description of each method, together with the results obtained, are given in the Appendix. The figures for the concentration of each element are given in Table 5.

TABLE 5/ CONCENTRATION OF ELEMENTS IN STREAM SAMPLES.

ELEMENT	CONCENTRATION * (% BY WHT.)		
	1-A	2-A	3-A
MG	29.44	15.09	12.80
CA	25.37	42.64	27.61
NA	11.30	17.35	22.33
K	7.44	3.03	3.19
SI	23.99	21.49	32.62
FE	0.39	0.26	0.25
AL	2.07	0.14	1.20
	100.00	100.00	100.00

* RECALCULATED TO EQUAL 100%.

(B) FOR ROCKS: THE MUTUAL STANDARD METHOD, AS OUTLINED BY DENNEN AND FOWLER (8), WAS USED IN THE ANALYSIS OF THE ROCK SAMPLES. A DESCRIPTION OF THE METHOD, TOGETHER WITH THE RESULTS OBTAINED, IS GIVEN IN THE APPENDIX. FIGURES FOR THE CONCENTRATIONS OF THE VARIOUS ELEMENTS IN THE ROCKS OF THE DRAINAGE BASINS ARE GIVEN IN TABLE 6.

TABLE 6/ CONCENTRATION OF ELEMENTS IN ROCK SAMPLES.

ELEMENT	CONCENTRATION *		
	1-B	2-B	3-B
MG	1.90	0.42	0.26
CA	4.54	2.36	2.15
NA	2.31	4.04	3.94
K	8.39	5.10	6.04
SI	64.70	73.20	72.20
FE	6.24	2.61	2.07
AL	11.25	12.10	13.24
MN	0.09	0.06	0.04
TI	0.58	0.11	0.06
	100.00	100.00	100.00

* RECALCULATED TO EQUAL 100%.

CALCULATION OF THE RELATIVE MOBILITY

THE RELATIVE MOBILITIES OF THE COMMON ROCK-FORMING ELEMENTS IN THE CONNECTICUT VALLEY REGION ARE SHOWN IN TABLE 7, COLUMNS VII, VIII, AND IX. THE NUMBERS 1,2,3, REFER TO THE SAMPLE LOCATIONS; (1) KINSMAN NOTCH, (2) MASCOMA, AND (3) BRATTLEBORO. THE LETTERS, A AND B,

REFER TO THE CONCENTRATION OF THE ELEMENTS IN (A) WATER RESIDUES AND (B) ROCKS. THE FIGURES FOR RELATIVE MOBILITY ARE THUS OBTAINED FROM THE RATIOS A/B.

TABLE 7/ RELATIVE MOBILITY OF THE ELEMENTS IN THE CONNECTICUT VALLEY REGION.

ELEMENT	RELATIVE MOBILITY		
	VII 1(A/B)	VIII 2(A/B)	IX 3(A/B)
MG	15.48	35.90	69.50
CA	5.58	18.01	12.82
NA	4.89	4.29	5.67
K	0.88	0.59	0.52
SI	0.37	0.29	0.45
FE	0.06	0.09	0.12
AL	0.18	0.01	0.09

THUS THE ORDER OF MOBILITY FOR THE COMMON ROCK-FORMING ELEMENTS IS THE SAME FOR AREAS CONTAINING A SCHIST, A GRANITE, AND A LEUCOGRANODIORITE. THE MAGNITUDE VARIES SLIGHTLY, PARTICULARLY WITH REGARD TO THE MOST MOBILE CONSTITUENTS - CA AND MG. BEFORE DISCUSSING THE ORDER AND MAGNITUDE OF THE RELATIVE MOBILITIES IN THE CONNECTICUT VALLEY REGION, IT IS INSTRUCTIVE TO CONSIDER SMYTH'S ESTIMATE OF THE RELATIVE

MOBILITIES IN THE PIKES PEAK AREA OF COLORADO.

SMYTH CONSIDERED, AS A UNIT, THE AREA OF THE PIKES PEAK GRANITE THAT WAS DRAINED BY THE CACHE A LA POUDRE RIVER. IN HIS CALCULATIONS HE USED THE PUBLISHED ANALYSES FOR THE CONCENTRATIONS OF THE ELEMENTS IN THE ROCK AND WATER. ASSUMING THE HOMOGENEITY OF THE PIKES PEAK GRANITE AND THE FACT THAT THE CACHE A LA POUDRE RIVER, IN ITS UPPER COURSE, DOES ACTUALLY DRAIN ONLY THE PIKES PEAK GRANITE, THEN THE ESTIMATE OF RELATIVE MOBILITIES, AS SHOWN IN TABLE 8, COLUMN XII, MAY BE CONSIDERED A SPECIFIC ONE.

TABLE 8/ RELATIVE MOBILITY OF THE ELEMENTS IN THE PIKES PEAK AREA.

ELEMENT	X PIKES PEAK GRANITE *	XI CACHE A LA POUDRE RIVER *	XII RELATIVE MOBILITY XI/X
MG	0.08	6.92	86.60
CA	1.03	35.21	34.40
NA	4.51	25.23	5.61
K	9.64	6.44	0.67
SI	68.52	25.62	0.37
(AL, FE)	16.22	0.58	0.03
	100.00	100.00	1.00

* RECALCULATED TO EQUAL 100%.

The order and magnitude of mobilities in the Pikes Peak area are roughly the same as those in the Connecticut Valley region. This similarity, in itself, is remarkable. The order of mobility as found for the two widely separated areas is believed to be the direct result of the differing solubilities of the minerals forming the rocks of the drainage basins. Thus, referring to Goldich's stability series the Mg-bearing minerals are more soluble than the Ca-bearing feldspars, which in turn are more soluble than the Na-bearing feldspars, and so on.

Discussion of Specific and General Estimates

Smyth's and Polynov's general estimates together with the writer's specific estimates for the relative mobilities are shown in Figure 2. Plotted in this way, the relative mobilities may be readily compared.

The specific estimates of the relative mobilities differs both in order and magnitude, from the general estimates. With regard to the order of mobility, the most striking difference is the pronounced increase in the relative mobilities of Ca and Mg in the specific estimates. And, in fact, Mg has now taken the place of Ca as the most mobile constituent. The order of mobility for the remaining elements, with the exception of Al, remains unchanged.

With regard to the magnitude of the mobilities, both Ca and Mg show a marked increase in mobility when calculated for a specific area. Al also shows marked changes. The fluctuations in the magnitude of the relative mobilities may indicate the degree to which some of the elements are affected by variations in local conditions of petrology, climate, and topography. If this be true then it may be said that Ca, Mg, and Al are sensitive to changes in local conditions, as reflected in the relative mobilities, whereas, Na, K, Si, and Fe are insensitive to local variations and the magnitude of the mobilities remains fairly constant.

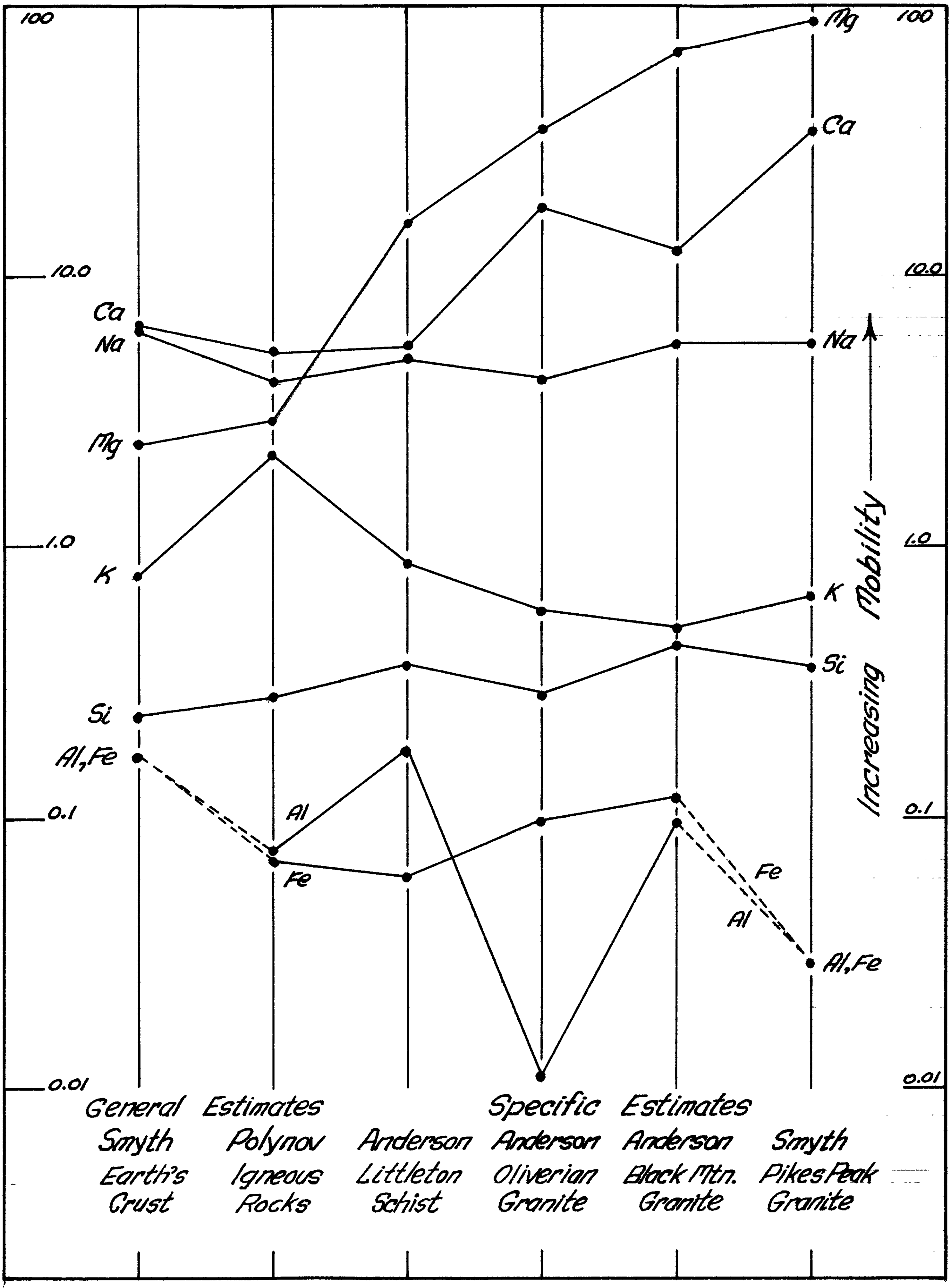

Figure 2. - Comparison of the Relative Mobilities for General and Specific Estimates.

CONCLUSIONS

The comparative rates at which elements, in ionic and/or colloidal form, move in the surface waters are given numerical values by comparing the composition of the water residues with the composition of the rocks forming the drainage basins. The resulting numerical values express the relative rates at which the different elements travel in stream waters.

Applying the above principle to three areas in the Connecticut Valley region, the relative mobilities were calculated. For areas containing a schist, a granite, and a leucogranodiorite, the order of decreasing mobility is; Mg, Ca, Na, K, Si, Fe, and Al. This same order was calculated, by Smyth, for a granite area in the Pikes Peak area of Colorado. Considered in groups it can be said that the alkaline earth and alkali elements are more mobile than Si which in turn is more mobile than Fe and Al. It is believed that the order of mobility as calculated is a reflection of the differing solubilities of the minerals forming the rocks of the drainage basins.

The order of decreasing mobility, as calculated by Smyth and Polynov, is Ca, Na, Mg, K, Si, and (Al, Fe). This order is considered to be the order for the surface of the earth as a whole (Smyth) and for igneous rocks in general (Polynov). The calculation of the relative

MOBILITY FOR A SPECIFIC AREA NECESSARILY AVOIDS THE SWEEPING ASSUMPTION REGARDING THE COMPOSITION OF THE ROCKS IN THE DRAINAGE BASINS AND THE ASSUMPTION THAT THE STREAM WATERS DO ACTUALLY DRAIN THE AREAS IN WHICH THE ROCKS HAVE THE COMPOSITION AS STATED. IN VIEW OF THESE SWEEPING ASSUMPTIONS, AND IN VIEW OF THE FACT THAT THREE SPECIFIC AREAS IN NEW ENGLAND AND ONE IN COLORADO YIELDED ORDERS AND MAGNITUDES OF MOBILITY THAT WERE ROUGHLY THE SAME, IT IS POSSIBLE THAT THE GENERAL ESTIMATES, AS CALCULATED BY SMYTH AND POLYNOV, MAY BE IN ERROR. THIS POSSIBILITY CAN BE SUPPORTED OR REFUTED BY FURTHER ANALYSES OF SPECIFIC AREAS AND ROCK TYPES.

THE DETERMINATION OF THE RELATIVE MOBILITIES OF THE MAJOR ROCK-FORMING ELEMENTS IS THE FIRST STEP IN THE BETTER UNDERSTANDING OF DISPERSION PATTERNS OF THE ORE MINERALS AROUND POTENTIAL ORE DEPOSITS. LATERITE AND BAUXITE DEPOSITS OWE THEIR FORMATION TO THE RELATIVE IMMOBILITY OF FE AND AL IN TROPICAL CLIMATES. WITH REGARD TO THE MINOR ELEMENTS, PB IS CONSIDERED TO BE ONE OF THE IMMOBILE ELEMENTS. IF A HIGH CONCENTRATION OF PB IS FOUND IN THE RESIDUUM THEN THE PLACE TO LOOK FOR THE SOURCE OF THIS PB IS DIRECTLY BELOW THE ANOMALY. IN VIEW OF THIS PRACTICAL APPLICATION, IT IS DESIRABLE TO ESTABLISH AN ORDER OF MOBILITY FOR BOTH THE MAJOR AND THE MINOR ELEMENTS. IT IS HOPED THAT, WITH THE DEVELOPMENT OF MORE SENSITIVE TECHNIQUES FOR THE ANALYSIS OF MINOR ELEMENTS IN STREAM WATERS, SUCH AN ORDER WILL BE ESTABLISHED IN THE NEAR FUTURE.

ACKNOWLEDGEMENTS

Sincere thanks are due Dr. H.E. Hawkes who suggested the problem as a possible line of research. His enthusiasm, suggestions, and constructive criticism guided the writer, both materially and mentally, throughout the thesis investigation.

Many thanks are due Dr. W.H. Dennen and Dr. H.W. Pinson for their assistance in the analytical methods used in this thesis.

To all others who contributed, in one way or the other, the writer offers his sincerest thanks and appreciation.

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APPENDIX

SPECTROCHEMICAL AND CHEMICAL METHODS OF ANALYSIS

SPECTROCHEMICAL METHODS OF ANALYSIS

(A) MUTUAL STANDARD METHOD FOR ROCK ANALYSIS

Mutual standard method, as outlined by Dennen and Fowler (8), provides an easy, rapid, and accurate method for silicate rock analysis. The reader is referred to the above work for a good description of the principles involved in mutual standardization. Herein will be described the operating procedure, measurements, and calculations leading up to the determination of the various elements in the silicate rocks.

Operating Procedure

Preparation of Samples and Standards

The samples were reduced, by crushing and fine grinding, to -100 mesh and ignited at about 800°C to determine the loss on ignition. Samples were then mixed 1:1 with carbon powder and loaded into 1/8 inch carbon electrodes having a diameter of 1 mm and a depth of 4 mm. The approximate weight of sample per electrode was 8 milligrams.

Standard mixtures of G-1 and W-1, in varying proportions, were prepared as above. The proportions of G-1 and W-1 used, together with the weighted averages of the majors (as % oxide) and minors (as ppm element), are given in Table 9.

Table 9/ Standards

(a) Major elements - % oxide

	S-1*	S-2	S-3	S-4
SiO_2	72.45	68.46	62.46	52.50
TiO_2	0.25	0.41	0.65	1.05
Al_2O_3	14.30	14.47	14.73	15.15
Total Fe as Fe_2O_3	1.90	3.74	6.50	11.10
MnO	0.025	0.054	0.098	0.17
MgO	0.45	1.69	3.55	6.65
CaO	1.35	3.27	6.15	10.95
Na_2O	3.35	3.10	2.73	2.10
K_2O	5.45	4.49	3.05	0.65

(b) Minor elements ppm element

	S-1*	S-2	S-3	S-4
Cu	11	31	60	110
Co	4	10	20	36
Ni	5	22	47	90
Pb	27	23	17	7

* S-1 G-1 S-3 G-1 W-1 (1:1)

S-2 G-1 W-1 (4:1) S-4 W-1

Instrument Setup

Instrument settings are summarized in Table 10.

Table 10/ Instrument Settings

Optics	- quartz
Wavelength range	- 2650 - 4100 angstroms
External optics	- short focus (convergence at slit)
Focus	- 2.0
Inclined screw	- 11
Slit height	- 10.5 mm
Slit width	- 0.06 mm
Sector steps	- 7
Amperage	- 6 amp.
Excitation	- anode

Arcing Procedure

A total of 4 plates were run and each plate contained seven spectra. The block system was used in order to have some checks between plates. The arcing outline is shown in Table 11, where S-1, S-2, S-3, S-4 are standards and A-1, A-2, A-3 are unknowns.

Table 11/ Arcing Outline

Plate 1	Plate 2	Plate 3	Plate 4
S-1	S-1	S-2	S-3
S-1	S-2	S-3	S-4
S-1	S-2	S-3	S-4
A-1	S-2	S-3	S-4
A-1	A-2	A-2	S-1
A-1	A-2	A-3	A-3
A-2	A-2	A-3	A-1

The samples were excited at the anode and burned to completion (90 sec.) at 6 amperes. Seven sector steps transmitting 1/2 to 1/128 of the incident light provided sufficient selection of line intensities.

Photographic Process

Eastman 103-0 photographic plates were used as they are more sensitive to the minor elements. Each plate was developed in a fresh batch of D-19 developer. This procedure was followed in order to avoid any irregularities that may be introduced by using progressively weakened developer. Also, the time saved is considerable.

Measurements and Calculations

Calibration Curves

Five calibration curves (Al,Ca,Fe,Zr,K) were drawn for each plate. Each curve was used for calculating the relative intensity of the following elements:

Al	for	Al,Mg,Mn
Ca	for	Ca,Pb,Ti,Si
Fe	for	Fe, Cu,Na
Zr	for	Zr, Co,Ni
K	for	K

Calibration curves for background were also made and fitted to the line calibration curves. Background deflection readings were made along with each line reading

AND, AFTER CONVERTING TO RELATIVE INTENSITY, WERE SUBTRACTED FROM THE VALUES FOR LINE INTENSITY. THUS, BACKGROUND VARIATIONS, BOTH WITHIN AND BETWEEN PLATES, WERE CORRECTED AND A GOOD CORRELATION BETWEEN PLATES WAS POSSIBLE.

WORKING CURVES

A PLOT (WORKING CURVE) OF INTENSITY RATIO VERSUS CONCENTRATION RATIO OF THE STANDARDS WAS USED TO COMPUTE THE CONCENTRATION RATIOS OF THE UNKNOWNS. A LINE SHIFT OF THE WORKING CURVE FOR CA, FE, AND K NECESSITATED THE DRAWING OF TWO CURVES FOR THESE ELEMENTS; ONE FOR PLATES 1, 2, 3, AND ANOTHER FOR PLATE 4.

THE MINOR ELEMENT CONCENTRATIONS WERE OBTAINED FROM A WORKING CURVE BASED ON VALUES OF CONCENTRATION VERSES INTENSITY FOR THE STANDARDS.

RESULTS

THE CONCENTRATIONS OF THE MAJOR AND MINOR ELEMENTS ARE GIVEN IN TABLE 12. NO CHEMICAL ANALYSES WERE AVAILABLE FOR COMPARISON, HOWEVER, THE PRECISION WAS EXCELLENT, AND, ON THE BASIS OF THIS HIGH PRECISION, IT IS BELIEVED THAT THE ACCURACY IS GOOD ALSO.

TABLE 12/ CONCENTRATION OF UNKNOWNS

(A) MAJOR ELEMENTS - % OXIDE

	A-1	A-2	A-3
SiO_2	70.6	76.7	77.2
TiO_2	0.521	0.104	0.057
Al_2O_3	11.20	11.68	12.87
TOTAL FE AS Fe_2O_3	4.73	1.85	1.53
MnO	0.062	0.043	0.028
MgO	1.68	0.37	0.21
CaO	3.38	1.70	1.52
Na_2O	1.66	2.69	2.69
K_2O	5.34	3.14	3.69
TOTAL	99.173	98.832	99.792

(B) MINOR ELEMENTS - PPM ELEMENT

CU	15	31	16
CO	16	4	4
NI	47	9	14
PB	5	21	10

(B) ADDITION METHOD FOR WATER ANALYSIS

It was thought the optical spectrograph could be used to advantage in analysing the water residues. Besides being a fast method of analysis, it would also allow the detection of some elements which are below the sensitivity limits for chemical methods. With this in mind, a spectrographic method, involving the addition of a standard granite (G-1) in varying proportions to the dried water residues, was tried. The results of this method, however, proved unsatisfactory and had to be discarded. The possibility that this method can be modified to give good results still exists and for that reason a brief description, together with suggestions, is included.

Following Ahrens' (1) principle for the addition method, a standard granite (G-1) was added, in varying proportions, to the unknown water residue. Separate addition (or dilution) plots of intensity versus concentration for the various elements were prepared and extended to intersect the concentration axis. The point of intersection of the extended line and the concentration axis was taken to represent the concentration of the particular element in the water residue. The concentrations obtained in this way were compared with those obtained by chemical methods. Agreement was poor and in view of the known reliability of the chemical

RESULTS, THE SPECTROGRAPHIC ANALYSES WERE DISCARDED.

THE CHIEF CAUSE OF THE FAILURE OF THE METHOD IS-BELIEVED TO BE DUE TO A MATRIX DIFFERENCE. THE STANDARD GRANITE CONSISTS OF MOSTLY SILICATES, WHEREAS THE WATER RESIDUE CONSISTS OF CARBONATES, SULPHATES, AND CHLORIDES. ALSO, THE RELATIVE PROPORTIONS OF THE ELEMENTS IN THE STANDARD GRANITE ARE DIFFERENT FROM THE PROPORTIONS IN THE WATER RESIDUE. TO ELIMINATE THIS MATRIX DIFFERENCE IT IS RECOMMENDED THAT A SYNTHETIC RESIDUE, APPROXIMATING THE COMPOSITION OF THE WATER RESIDUE, BE USED AS THE ADDITION STANDARD. A SYNTHETIC RESIDUE SIMILAR TO KLEINKOPF'S (12) MIGHT BE APPROPRIATE. IT CONSISTED OF THE FOLLOWING: 50% $CaCO_3$, 15% $CaSO_4 \cdot 2H_2O$, 13% SiO_2, 10% $MgCO_3$, 10% $NaCl$, 1% Al_2O_3, AND 1% Fe_2O_3. THUS, THE ADDITION METHOD, AS APPLIED TO WATER RESIDUES, MERITS FURTHER TESTING AND THE ABOVE SUGGESTIONS ARE OFFERED AS A BASE FOR FUTURE INVESTIGATORS.

CHEMICAL METHODS OF ANALYSIS

A COMBINATION OF WET CHEMICAL AND FLAME PHOTOMETRIC METHODS WERE USED TO DETERMINE THE CONCENTRATIONS OF THE VARIOUS ELEMENTS IN THE STREAM WATERS. THE METHODS USED WERE THOSE RECOMMENDED BY 'STANDARD METHODS' (21). A COMPLETE DESCRIPTION OF EACH METHOD, TOGETHER WITH THE RESULTS OBTAINED, ARE GIVEN IN THE FOLLOWING SECTION.

THE TIME INVOLVED IN CHEMICAL ANALYSES IS CONSIDERABLE. IT IS, NEVERTHELESS, TIME WELL SPENT IF RELIABILITY IN THE MEASUREMENTS IS DESIRED. IN THE DISCUSSION OF THE METHOD THE PRECISION AND ACCURACY ARE CONSIDERED TOGETHER. THE PRECISION, IN EVERY CASE, WAS GOOD. WITH REGARD TO THE ACCURACY OF THE METHOD THE WRITER DEPENDS ON THE STATEMENT OF THE ACCURACY AS DETERMINED BY A COOPERATIVE ARRANGEMENT BETWEEN DIFFERENT LABORATORIES.

SODIUM AND POTASSIUM - FLAME PHOTOMETER

The flame photometric method, according to 'Standard Methods', is probably the best method for determining the concentration of sodium and potassium in natural waters. It is more sensitive, more rapid, and generally more accurate than other methods. Once the analyst has become familiar with the instrument and has prepared all the necessary standards, unknown samples can be run quickly and with confidence.

Principle

The ease with which the spectra of the alkali metals, sodium, potassium, and lithium, are excited in an acetylene flame provides the basis of the flame tests for these elements. A solution containing the metals is sprayed into an acetylene flame and excitation takes place. A monochromatic device isolates the desired spectral line and a phototube potentiometer circuit measures the intensity of the light. The light emitted is approximately proportional to the concentration of the element.

Apparatus

Flame Photometer: Perkin-Elmer or any other suitable photometer.

Regulating valves for air and acetylene.

REAGENTS

Contamination from glassware can be avoided by storing standards in polyethylene bottles. Cleaning mixtures, soap cleansers, dust, corks, filter paper, and perspiration, may contribute sodium and potassium and due care should be taken wherever possible to avoid such contamination.

Reagents consist of standard stock solutions of sodium, potassium, and lithium. These are prepared as follows:

(1) Standard sodium solution: Dissolve 2.542 g dried sodium chloride in distilled water and dilute to 1 litre. 1 ml contains 1.0 mg sodium.

(2) Standard potassium solution: Dissolve 1.907 g dried potassium chloride in distilled water and dilute to 1 litre. 1 ml contains 1.0 mg potassium.

(3) Standard lithium solution: Dissolve 6.102 g dried lithium chloride in distilled water and dilute to 1 litre. 1 ml contains 1.0 mg lithium.

PROCEDURE

The internal standard procedure, using 20 ppm. lithium as the internal standard, was used in the analysis. Air and acetylene were set at 10 and 5 psi, respectively.

For the actual operating procedure, the reader is referred to the instruction manual that accompanies the instrument.

The instrument is quite sensitive to; variations in line voltage, movement of people in the laboratory, opening of laboratory doors, and cigarette smoke. Analyses should be done either late at night or on weekends when these disturbing factors are at a minimum.

Sodium

Data

A series of standards were prepared from the standard stock solution and a calibration curve (Fig. 3) of scale reading versus concentration was plotted. The data used in plotting the calibration curve are summarized below in Table 13.

Table 13/ Data Used in Calibration Plot for Sodium

Standards Concentration (ppm)		Scale Readings			Scale Reading Average
Na	Li	Trial 1	Trial 2	Trial 3	
5.0	20.0	100.0	100.0	100.0	100.0
2.5	20.0	47.5	47.5	47.0	47.3
1.0	20.0	19.3	20.0	20.0	19.7

The scale readings and corresponding concentrations of the unknowns are shown in Table 14. Samples 1, 2, and 3 are from locations described in the body of the report.

Fig 3.-Calibration Curve for Sodium using 20 ppm of Lithium as Internal Standard

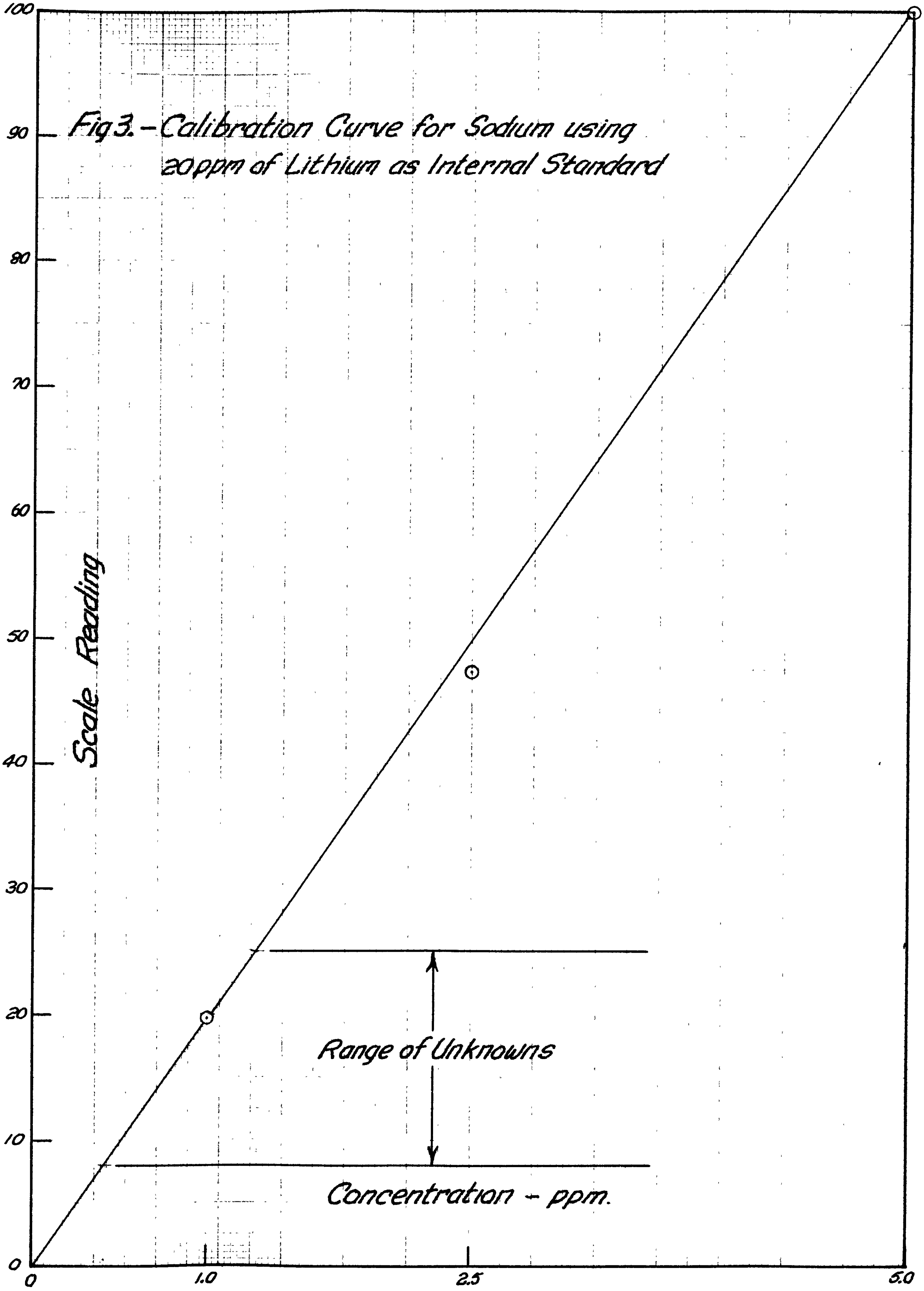

TABLE 14/ CONCENTRATION OF SODIUM IN UNKNOWNS

SAMPLE	SCALE READING			CONCENTRATION (PPM)			CONC. AVERAGE (PPM)
	TRIAL 1	TRIAL 2	TRIAL 3	TRIAL 1	TRIAL 2	TRIAL 3	
1	8.5	8.0	8.5	0.42	0.40	0.42	0.41
2	20.8	20.5	20.0	1.05	1.03	1.00	1.03
3	25.2	24.0	27.0	1.26	1.19	1.34	1.26

DISCUSSION

THE PRECISION AND ACCURACY FOR THIS METHOD ARE GOOD. IN THE ABSENCE OF INTERFERING SUBSTANCES, WHICH ARE NOT EXPECTED IN WATERS OF SUCH LOW SALINITY, THE PRECISION AND ACCURACY FOR SAMPLES 1, 2, AND 3 ARE 2.4%, 1.9%, AND 6.3%, RESPECTIVELY.

POTASSIUM

DATA

A SERIES OF STANDARDS WERE PREPARED FROM THE STANDARD STOCK SOLUTION AND A CALIBRATION CURVE (FIG. 4) OF SCALE READING VERSUS CONCENTRATION WAS PLOTTED. THE DATA USED IN PLOTTING THE CALIBRATION CURVE ARE SUMMARIZED BELOW IN TABLE 15.

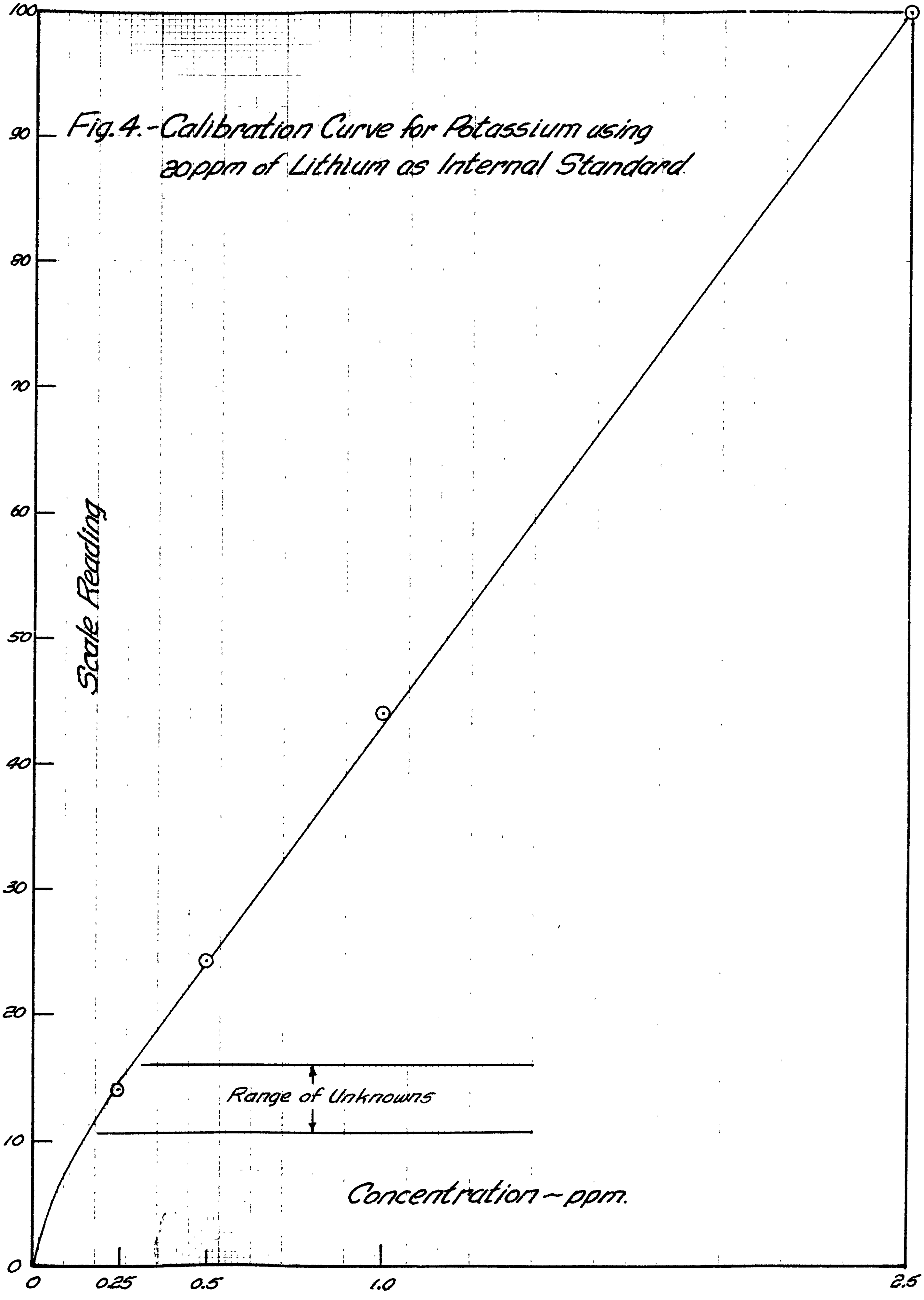

Fig.4.-Calibration Curve for Potassium using 20ppm of Lithium as Internal Standard

TABLE 15/ DATA USED IN CALIBRATION PLOT FOR POTASSIUM

STANDARDS CONCENTRATION (PPM)		SCALE READINGS			SCALE READING AVERAGE
K	LI	TRIAL 1	TRIAL 2	TRIAL 3	
2.5	20.0	100.0	100.0	100.0	100.0
1.0	20.0	46.0	43.5	43.0	44.1
0.5	20.0	24.0	24.2	24.7	24.3
0.25	20.0	14.3	13.8	14.1	14.1

THE SCALE READINGS AND CORRESPONDING CONCENTRATIONS OF THE UNKNOWNS ARE SHOWN IN TABLE 16.

TABLE 16/ CONCENTRATION OF POTASSIUM IN UNKNOWNS

SAMPLE	SCALE READING			CONCENTRATION (PPM)			CONC. AVERAGE (PPM)
	TRIAL 1	TRIAL 2	TRIAL 3	TRIAL 1	TRIAL 2	TRIAL 3	
1	16.0	15.7	14.8	0.29	0.28	0.25	0.27
2	12.0	11.0	12.5	0.19	0.17	0.20	0.18
3	12.5	12.0	11.0	0.20	0.19	0.17	0.18

DISCUSSION

THE PRECISION AND ACCURACY ARE NOT AS GOOD AS IN THE SODIUM ANALYSES. FOR SAMPLES 1, 2, AND 3, THE PRECISION AND ACCURACY ARE 7.5%, 11.1%, AND 11.1%, RESPECTIVELY.

ALUMINUM - "ALUMINON" METHOD

This method is recommended for waters containing from 0.001 to 0.25 mg of aluminum in 50 ml of sample. Since the aluminum content in natural waters is usually small and lies within this workable range, this method is suitable for most natural waters. As in the silica method, considerable time is spent in preparing standards, calibration curves, and reagents. Once prepared, however, the analyses can be run quickly and with reasonable confidence.

A spectrophotometer, for use at 525 mμ and providing a light path of 10 cm or longer, is required. Because of the limited light path of our colorimeter, it was necessary to use Sanitary Engineering Department's spectrophotometer.

The following description of the method is taken from 'Standard Methods'. The reader is referred to this work for further details.

Principle

The ammonium salt of aurin tricarboxylic acid, also known as "Aluminon", produces a red to pink lake in dilute aluminum solutions buffered to pH of 6.3. The intensity of the color produced depends on the following: reaction time, temperature, pH, quality of aluminon used, and the quantity and quality of the salts and acids present.

Interference from iron will produce about one-half the color of an equivalent amount of aluminum.

Apparatus

Spectrophotometer, for use at $525 m\mu$, providing a light path of 10 cm or longer and equipped with a green filter having maximum transmittance at $525 m\mu$.

Reagents

All reagents should be prepared from aluminum-free and iron-free distilled water. Also, reagents should be stored in polyethylene bottles.

(1) Acetate buffer solution: Add 3 ml glacial acetic acid to 247 ml 4 N ammonium acetate (76.2 g ammonium acetate dissolved in distilled water and made up to 247 ml).

(2) Aluminon solution: Dissolve 0.1 g of ammonium salt of aurin tricarboxylic acid in 100 ml distilled water.

(3) Standard aluminum solution: Dissolve 8.80 g aluminum potassium sulfate in 1 litre of distilled water. Dilute this solution 1 to 100 for the working standard solution. Then, 1 ml = 0.005 mg aluminum.

Procedure

To insure comparable color development the samples and standards should have the same initial temperature (room temperature ± 2° C is satisfactory). With photometric

COMPARISON, THE READINGS SHOULD BE MADE EXACTLY 15 MINUTES AFTER THE ADDITION OF ALUMINON.

To 50.0 ML OF SAMPLE ADD 2.0 ML OF ACETATE BUFFER SOLUTION AND MIX. ADD 2.0 ML ALUMINON REAGENT AND MIX. READ THE PERCENTAGE TRANSMISSION EXACTLY 15 MINUTES AFTER THE ALUMINON WAS ADDED.

PREPARE A CALIBRATION CURVE (FIG. 5) FROM A SERIES OF 5 OR 6 STANDARDS (TABLE 17) TO COVER THE OPTIMUM RANGE, BY CARRYING OUT THE STEPS ABOVE ON SUITABLE ALIQUOTS OF STANDARD ALUMINUM SOLUTION DILUTED TO 50.0 ML. DISTILLED WATER SHOULD BE USED TO SET THE INSTRUMENT TO 100% TRANSMITTANCE AND ALL THE STANDARDS, INCLUDING A REAGENT BLANK, SHOULD BE READ AGAINST THE DISTILLED WATER. IT IS CONVENIENT TO PLOT MILLIGRAMS OF ALUMINUM IN THE FINAL 54.0 ML OF SOLUTION AGAINST THE PHOTOMETER READINGS.

TABLE 17/ DATA USED IN CALIBRATION PLOT FOR ALUMINUM

ML OF * STANDARD STOCK SOLN.	CONCENTRATION MG/54.0 ML	% TRANSMITTANCE		
		TRIAL 1	TRIAL 2	AVERAGE
0.25	0.00125	83.4	83.3	83.35
0.50	0.0025	82.3	82.4	82.35
0.75	0.00375	82.8	82.8	82.80
1.00	0.005	77.5	78.6	78.05

* STOCK SOLUTION CONTAINS 0.005 MG ALUMINUM PER ML.

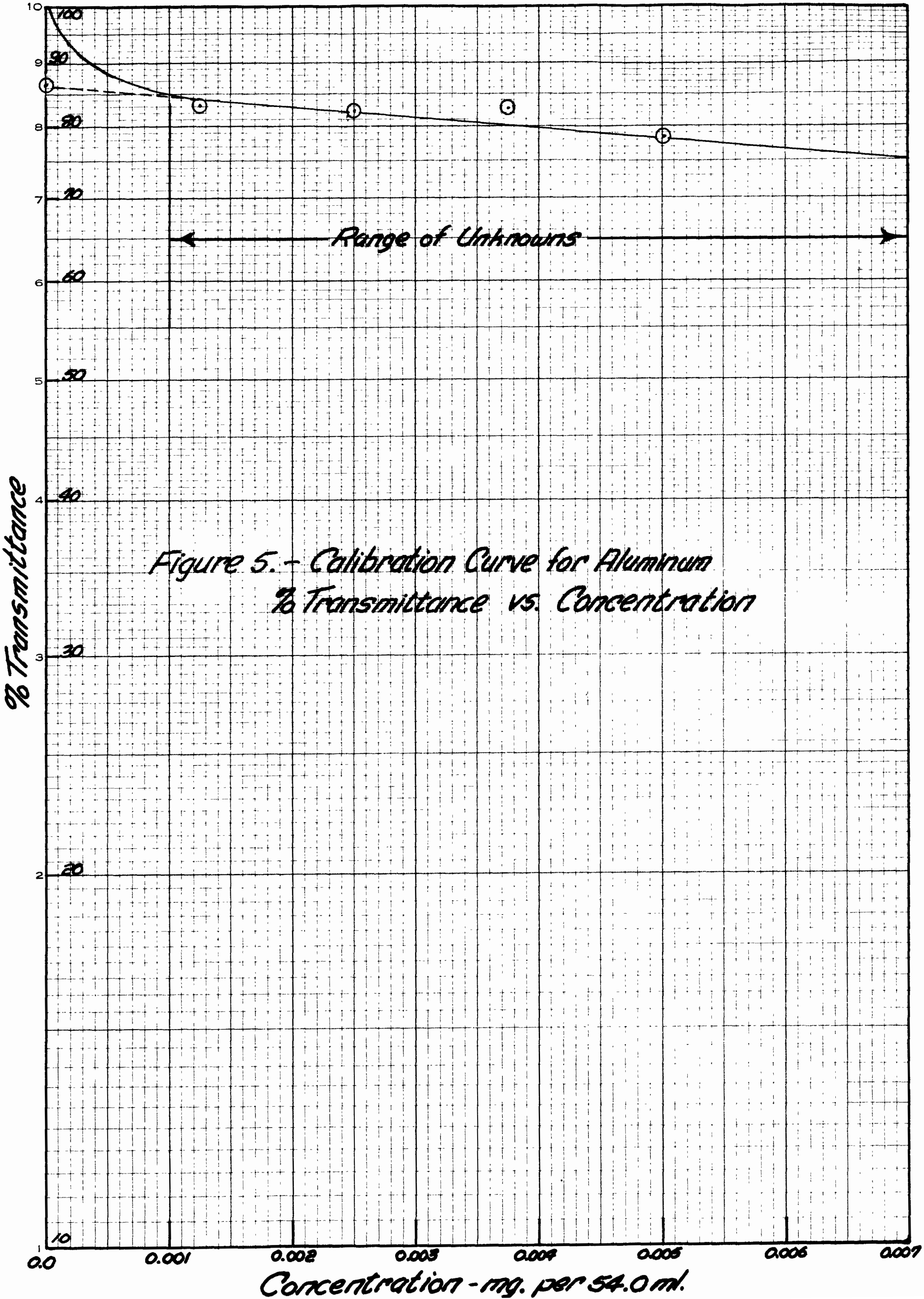

Figure 5.- Calibration Curve for Aluminum
% Transmittance vs. Concentration

THE CALIBRATION CURVE WAS PREPARED FROM THE DATA IN TABLE 17. PER CENT TRANSMITTANCE READINGS FOR THE 3 UNKNOWN WATER SAMPLES, (1, 2, AND 3), CAMBRIDGE TAP WATER (4), AND A REAGENT BLANK (5), TOGETHER WITH THE CORRESPONDING CONCENTRATIONS ARE SHOWN IN TABLE 18.

TABLE 18/ DATA FOR % TRANSMITTANCE AND CONCENTRATION OF ALUMINUM IN UNKNOWNS.

SAMPLE	% TRANSMITTANCE		CONCENTRATION MG/54.0 ML			CORRECTED * CONCENTRATION (PPM)
	TRIAL 1	TRIAL 2	TRIAL 1	TRIAL 2	AVERAGE	
1	78.5	78.6	0.00480	0.00477	0.00478	0.075
2	84.9	84.0	0.00103	0.00128	0.00115	0.008
3	79.2	79.0	0.00430	0.00442	0.00436	0.068
4	82.3	82.3	0.00230	0.00230	0.00230	0.030
5	86.5	86.5	0.00070	0.00070	0.00070	0.000

* THE CORRECTED CONCENTRATION WAS OBTAINED BY SUBTRACTING THE VALUE FOR THE REAGENT BLANK (0.0129 PPM) FROM THE UNCORRECTED CONCENTRATION.

Discussion

The results are probably accurate to within 10% to 50% of the aluminum actually present in the water samples. This low accuracy is proposed because the aluminum concentration was too low to give percentage transmittance readings in the favorable range of 20-80%. If the light path could have been lengthened from 4 cm to 10 cm or longer, then more accurate results would be attainable. Higher accuracy could also be attained by pre-concentrating the sample.

SILICA - COLORIMETRIC SILICOMOLYBDATE METHOD

This method is recommended for relatively pure waters containing from 0.4 to 25 mg/1. silica. Some time is required to prepare the standards and reagents. Once they are prepared, however, the analyses can be run quickly and with considerable confidence.

The method requires the use of colorimetric equipment of a type we do not have in the Geology Department. A spectrophotometer is needed that can be set at the desired wave length (410 $m\mu$) and providing a light path of more than 1 cm. A specific filter of 410 $m\mu$ would be needed for our Bausch and Lomb colorimeter which gives a light path of 1 cm only. Because of this limited light path, the sample would have to be pre-concentrated to give transmittancy of between 20% and 80%, the most favorable range. In lieu of purchasing a new filter and pre-concentrating the sample, the writer used the Sanitary Engineering Department's spectrophotometer. Many thanks are due Dr. C.N. Sawyer for his cooperation and helpful suggestions.

The following description of the method is taken from 'Standard Methods'. The reader is referred to this work for further details, particularly of the principles involved.

PRINCIPLE

AT A pH OF 1.2, AMMONIUM MOLYBDATE REACTS WITH SILICA AND ANY PHOSPHATE PRESENT TO FORM HETEROPOLY ACIDS (SILICOMOLYBDIC ACID AND PHOSPHOMOLYBDIC ACID). THE INTENSITY OF THE YELLOW COLOR IS PROPORTIONAL TO THE CONCENTRATION OF SILICA THAT REACTS WITH THE MOLYBDATE. THE EFFECT OF THE PHOSPHOMOLYBDIC ACID ON THE YELLOW COLOR IS REMOVED BY THE ADDITION OF OXALIC ACID.

APPARATUS

SPECTROPHOTOMETER, FOR USE AT 410 mμ, PROVIDING A LIGHT PATH OF GREATER THAN 1 CM OR, A FILTER PHOTOMETER, PROVIDING A LIGHT PATH OF GREATER THAN 1 CM AND EQUIPPED WITH A VIOLET FILTER HAVING MAXIMUM TRANSMITTANCE AT 410 mμ.

REAGENTS

APPARATUS AND REAGENTS MAY CONTRIBUTE SILICA AND GLASSWARE SHOULD BE AVOIDED WHEREVER POSSIBLE. A BLANK SHOULD BE RUN TO CORRECT FOR ANY SILICA INTRODUCED EITHER THROUGH THE USE OF GLASSWARE OR FROM CONTAMINATED REAGENTS.

(1) AMMONIUM MOLYBDATE SOLUTION: DISSOLVE 10 G OF AMMONIUM MOLYBDATE IN DISTILLED WATER WITH THE AID OF STIRRING AND GENTLE WARMING, AND DILUTE TO 100 ML. FILTER IF NECESSARY.

If the pH is adjusted to 7 or 8 and the solution is stored in polyethylene, it will be stable indefinitely. If the pH is not adjusted a precipitate gradually forms.

(2) Hydrochloric acid, 1 + 1: Mix equal volumes conc HCl and distilled water.

(3) Oxalic acid solution: Dissolve 10 g oxalic acid in distilled water and dilute to 100 ml.

(4) Standard silica stock solution: Fuse 0.2000 g pure quartz powder with 5.0 g sodium carbonate. Dilute to 1 litre. This solution contains 0.2 mg/ml. Weaker solutions may be obtained by diluting suitable aliquots.

Procedure

To 50.0 ml of sample add in rapid succession 1.0 ml 1+1 HCl and 2.0 ml ammonium molybdate solution; mix by inverting; and allow the solution to stand for 5 to 10 minutes. Add 1.5 ml oxalic acid solution and mix thoroughly. Read the color after 2 min. but before 15 min. have elapsed, measuring time from the addition of oxalic acid.

Prepare a calibration curve (Fig. 6) from a series of 5 or 6 standards (Table 19) to cover the optimum range, by carrying out the steps above on suitable aliquots of standard silica solution diluted to 50.0 ml. Distilled water should be used to set the instrument to 100% transmittance and all the standards, including a reagent blank, should be read against the distilled water. It is convenient to plot milligrams of silica in the final 54.5 ml of solution against the photometer readings.

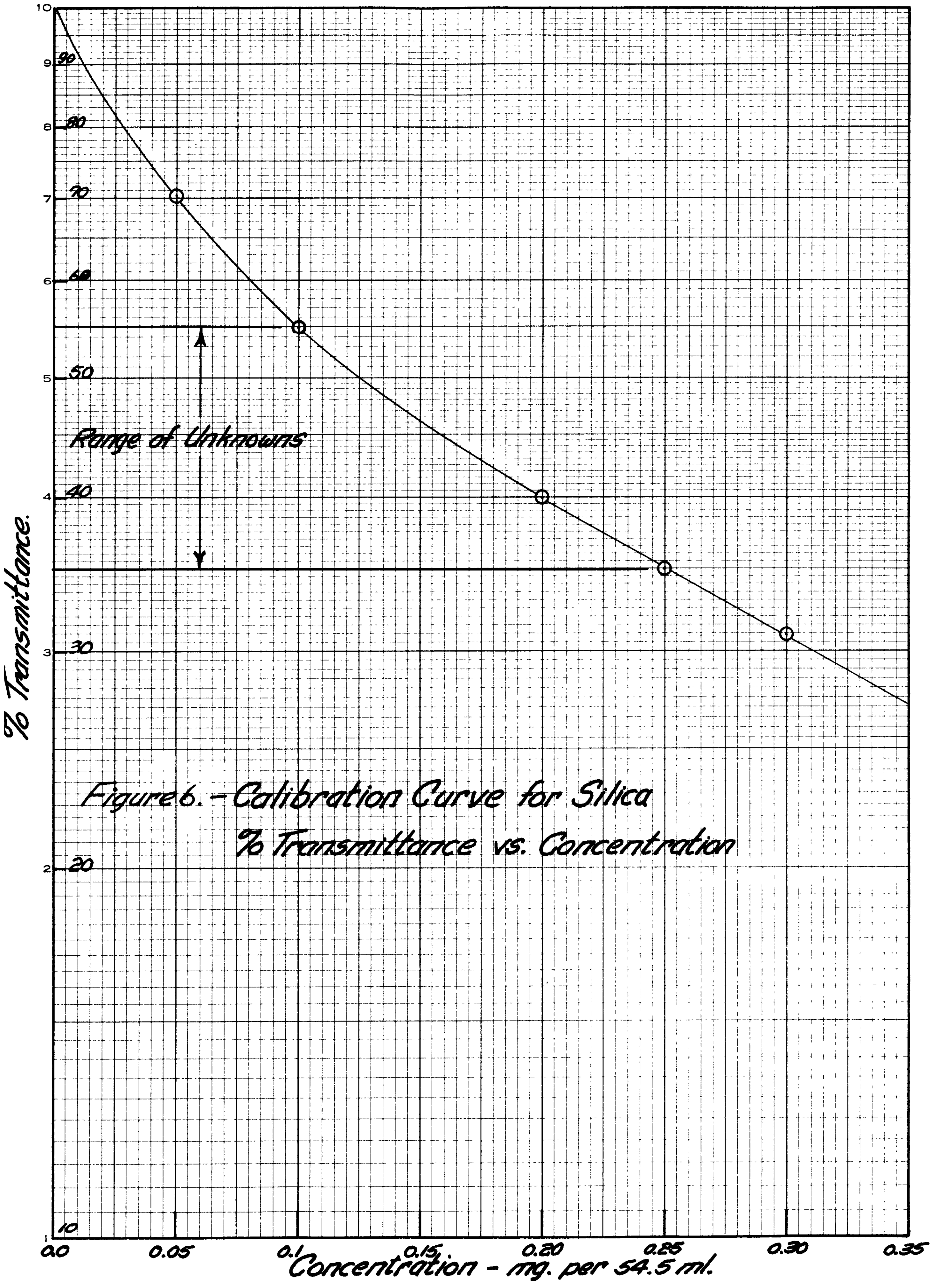

Figure 6. - Calibration Curve for Silica
% Transmittance vs. Concentration

Table 19/ Data Used in Calibration Plot for Silica

Ml of Standard Stock soln. *	Concentration mg/54.5ml	% Transmittance Trial 1	% Transmittance Trial 2	% Transmittance Average
5	0.05	70.2	70.0	70.1
10	0.10	55.0	55.0	35.0
20	0.20	40.0	40.0	40.0
25	0.25	35.0	35.0	35.0
30	0.30	30.9	30.8	30.9

* Stock solution contains 0.01 mg silica per ml

The calibration curve was prepared from the data in Table 19. Percent transmittance readings for the 3 unknown water samples, Cambridge tap water, and a reagent blank, together with the corresponding concentrations are shown in Table 20.

Table 20/ Data for % Transmittance and Concentration of Silica in Unknowns.

	% Transmittance		Concentration mg/54.5ml			Corr. Conc. (ppm) *
Sample	Trial 1	Trial 2	Trial 1	Trial 2	Average	
1	52.0	51.7	0.114	0.116	0.115	1.86
2	42.3	46.3	0.179	0.148	0.163	2.74
3	37.3	37.0	0.227	0.229	0.228	3.93
4	42.8	43.0	0.175	0.173	0.174	2.94
5	88.5	88.3	0.0135	0.0137	0.0137	0.00

* The corrected concentration was found by subtracting the value for the reagent blank (0.251 ppm) from the uncorrected concentration.

DISCUSSION

THE PRECISION AND ACCURACY DEPEND ON THE FOLLOWING; LIGHT PATH, CONCENTRATION OF SILICA, PRESENCE OF INTERFERING SUBSTANCES. ACCORDING TO 'STANDARD METHODS', IF THE ABOVE CONDITIONS ARE ALL FAVORABLE, PHOTOMETRIC MEASUREMENTS MAY BE RELIABLE ± 1% OR BETTER.

IN THE ABOVE ANALYSES THE LIGHT PATH USED WAS 4 CM WHICH GAVE % TRANSMITTANCY READINGS IN THE FAVORABLE RANGE OF 35% TO 55%. ALSO, THE CONCENTRATION OF SILICA WAS IN THE FAVORABLE RANGE AND INTERFERING SUBSTANCES, SUCH AS TANNIN, LARGE AMOUNTS OF IRON, COLOR, TURBIDITY, SULFIDE, AND PHOSPHATE, ARE EITHER ABSENT OR REMOVED BY THE ADDITION OF OXALIC ACID. THUS, THE ABOVE CONDITIONS, WHICH WOULD HAVE AN ADVERSE EFFECT ON THE RESULTS, CAN BE ELIMINATED AND AN ACCURACY OF ± 1% IS PROPOSED FOR THE ANALYSES.

CALCIUM AND MAGNESIUM - HACH METHOD

The Hach Method for total hardness is an easy and quick method of determining the calcium and magnesium content of natural waters. The hardness in waters is attributed to the presence of calcium and magnesium. Thus, by analysing the water for total hardness and calcium, the magnesium content is found by subtraction.

The following description of the method is taken from the catalogue issued by the Hach Chemical Company, Ames, Iowa. For a more detailed discussion, particularly of the principle involved, the reader is referred to p.112 of 'Standard Methods'.

Principle

The titrating agent for the hardness and calcium determinations is disodium dihydrogen ethylenediaminetetraacetate. This compound, with stabilizer has the commercial name TitraVer and reacts with calcium and magnesium to form complex ions. In this way the calcium and magnesium are rendered inactive, yet no precipitate is formed.

The end point of the titration is detected by the use of an indicator that changes sharply from a wine-red to a true blue when the last of the calcium and magnesium is tied up by the standard TitraVer solution.

THE EXACT pH CONTROL OF THE SOLUTION IS ESSENTIAL FOR ACCURATE RESULTS. ANOTHER REAGENT, MONOVER (LIQUID), OR UNIVER (SOLID), PROVIDES THIS ACCURATE pH CONTROL AND ELIMINATES THE INTERFERENCE OF SUCH IONS AS COPPER, MANGANESE, NICKEL, COBALT, IRON, AND OTHER HEAVY METALS.

FOR THE SEPARATE DETERMINATION OF CALCIUM, AN INDICATOR NAMED CALVER THAT CONTAINS AMMONIUM PURPURATE, IS USED WITH THE TITRAVER REAGENT. THIS INDICATOR CHANGES FROM ORANGE TO PURPLE AT THE POINT WHEN ONLY CALCIUM HAS BEEN TITRATED. A STRONG SOLUTION OF SODIUM HYDROXIDE IS USED TO MAKE THE WATER SAMPLE ALKALINE.

TOTAL HARDNESS

REAGENTS

(1) MONOVER OR UNIVER: ABOUT 1 ML OF THE LIQUID (MONOVER) OR 0.5 G OF POWDER (UNIVER) PER 50 ML OF WATER SAMPLE.

(2) STANDARD TITRAVER SOLUTION: THIS REAGENT, USED IN TITRATING FOR HARDNESS AND CALCIUM, IS AVAILABLE IN THE SOLUTION FORM, STANDARDIZED AND READY FOR USE OR IT CAN BE PREPARED FROM TITRAVER POWDER AS FOLLOWS:

WEIGH OUT 4.0 GRAMS OF TITRAVER POWDER AND DISSOLVE IT IN ABOUT 750 ML OF DISTILLED WATER. TO ABOUT 25 ML OF THE STANDARD CALCIUM CHLORIDE SOLUTION, WHICH IS PREPARED AS DESCRIBED BELOW, ADD APPROXIMATELY 1.0 ML OF MONOVER (OR 0.5 G OF UNIVER). TITRATE WITH THE TITRAVER SOLUTION ACCORDING TO THE PROCEDURE BELOW FOR THE DETERMINATION OF HARDNESS. THE SOLUTION, SO PREPARED, SHOULD BE EQUIVALENT TO MORE THAN 1.00 MG OF CALCIUM CARBONATE PER ML. FROM THE TITRATION AND THE VOLUME OF THE SOLUTION, COMPUTE THE

VOLUME TO WHICH THE TITRAVER SOLUTION MUST BE DILUTED TO MAKE IT EQUIVALENT TO 1.0 MG OF CALCIUM CARBONATE PER ML. APPROXIMATELY 1 LITRE OF STANDARD SOLUTION WILL THUS BE PREPARED.

(3) STANDARD CALCIUM CHLORIDE SOLUTION: DISSOLVE 1.000 G OF DRY PRIMARY STANDARD CALCIUM CARBONATE IN A LITTLE DILUTE HYDROCHLORIC ACID. DILUTE TO EXACTLY 1 LITRE. ONE ML OF THIS SOLUTION IS EQUIVALENT TO 1.000 MG OF CALCIUM CARBONATE.

PROCEDURE

MEASURE OUT 50.0 ML OF WATER SAMPLE AND POUR IT INTO A 250 ML FLASK. ADD APPROXIMATELY 1.0 ML OF MONOVER (OR 0.5 G OF UNIVER) AND TITRATE WITH STANDARD TITRAVER UNTIL THE SOLUTION CHANGES FROM RED TO PURE BLUE. THE END POINT IS ABRUPT AND ONE DROP IS ENOUGH TO CAUSE THE CHANGE.

THE TOTAL HARDNESS IS CALCULATED BY MULTIPLYING THE MILLILITRES OF THE TITRAVER SOLUTION REQUIRED IN THE TITRATION BY 20 TO OBTAIN THE TOTAL HARDNESS AS PARTS PER MILLION.

DATA

THE FOLLOWING TABLE 21 IS A SUMMARY OF THE DATA COLLECTED FOR THE TOTAL HARDNESS DETERMINATION IN 4 WATER SAMPLES. SAMPLE NUMBERS 1, 2, AND 3 ARE FROM THE LOCATIONS DESCRIBED IN THE BODY OF THE REPORT. SAMPLE NUMBER 4 IS CAMBRIDGE TAP WATER.

TABLE 21/ DATA FOR TOTAL HARDNESS

SAMPLE	VOLUME TITRAVER ADDED (ML)			AVERAGE	TOTAL HARDNESS (PPM)
	TRIAL 1	TRIAL 2	TRIAL 3		
1	0.32	0.31	0.27	0.30	6.0
2	0.47	0.47	0.46	0.47	9.4
3	0.28	0.37	0.32	0.32	6.4
4	2.60	2.53	2.55	2.56	51.2

DISCUSSION

THE PRECISION AND ACCURACY FOR THIS METHOD ARE EXCELLENT. IN SAMPLES CONTAINING FROM 0-5 MG/L HARDNESS, A PRECISION OF ± 0.1 MG/L IS ATTAINABLE. FOR NATURAL WATERS, THE PRECISION AND ACCURACY WILL BE ROUGHLY THE SAME. THE PRECISION AND ACCURACY FOR SAMPLES 1,2, AND 3 ARE 1.6%, 1.1%, 1.6%, RESPECTIVELY.

THE ANALYST REQUIRES VERY LITTLE EXPERIENCE WITH THIS METHOD IN ORDER TO OBTAIN RELIABLE RESULTS. DR. SAWYER, SANITARY ENGINEERING DEPARTMENT, HAS PROVEN THIS IN HIS LABORATORY. HE HAS TRIED THE METHOD ON SOPHMORES WHO ARE NOT, AS YET, CONSIDERED EXPERIENCED ANALYSTS. INVARIABLY, THE RESULTS THEY OBTAIN ARE BOTH ACCURATE AND RELIABLE.

CALCIUM AND MAGNESIUM

REAGENTS

(1) STANDARD TITRAVER SOLUTION: THE SAME SOLUTION IS USED IN THE CALCIUM TITRATION AS IN THE TEST FOR TOTAL HARDNESS.

(2) SODIUM HYDROXIDE SOLUTION: 4N SODIUM HYDROXIDE IN DISTILLED WATER.

(3) CALVER INDICATOR POWDER: ABOUT 0.1 G OF POWDER PER 100 ML OF WATER SAMPLE.

PROCEDURE

MEASURE OUT 100 ML OF WATER SAMPLE AND POUR IT INTO A 250 ML FLASK. ADD APPROXIMATELY 1.0 ML OF SODIUM HYDROXIDE SOLUTION AND 0.1 G OF CALVER INDICATOR POWDER.

TITRATE WITH STANDARD TITRAVER SOLUTION UNTIL THE COLOR CHANGES FROM ORANGE TO PURPLE. THIS COLOR CHANGE IS MORE SUBTLE THAN THAT OF THE TOTAL HARDNESS AND SOME PRACTICE IS REQUIRED.

THE CALCIUM HARDNESS OF THE WATER, EXPRESSED AS PPM CALCIUM CARBONATE, IS FOUND BY MULTIPLYING THE MILLILITRES OF STANDARD TITRAVER SOLUTION USED BY 10. THE CALCIUM HARDNESS IS THEN SUBTRACTED FROM THE TOTAL HARDNESS TO OBTAIN THE MAGNESIUM HARDNESS.

DATA

Data for the calcium and magnesium determinations are summarized in the following Table 22.

Table 22/ Data for Calcium and Magnesium

Sample	Volume TitraVer added (ml)			Average	Calcium (ppm)	Total Hardness (ppm)	Magnesium (ppm)
	Trial 1	Trial 2	Trial 3				
1	0.23	0.23	0.22	0.23	2.3	6.0	3.7
2	0.62	0.61	0.65	0.63	6.3	9.4	3.1
3	0.39	0.39	0.40	0.39	3.9	6.4	2.5
4	3.70	3.78	3.74	3.74	37.4	51.2	13.8

DISCUSSION

The precision and accuracy are only about one half as good as for the total hardness titration. Thus, in samples containing from 0-5 mg/l of calcium and/or magnesium, a precision and accuracy of 0.2 mg/l is attainable. In terms of percent, this would mean a precision and accuracy of around 5% for calcium and 6% for magnesium.

Because of the subtle color change at the end point some practice is required before reproducible results can be obtained. In view of this, it is advisable to set up a color standard, by adding an excess of TitraVer, to establish the proper color at the end point.