

CANADA
DEPARTMENT OF MINES AND TECHNICAL SURVEYS

MINES BRANCH
INDUSTRIAL MINERALS DIVISION

INDUSTRIAL WATER RESOURCES OF CANADA

Water Survey Report No. 1

Scope, Procedure, and Interpretation
of Survey Studies

By
J. F. J. Thomas



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P R E F A C E

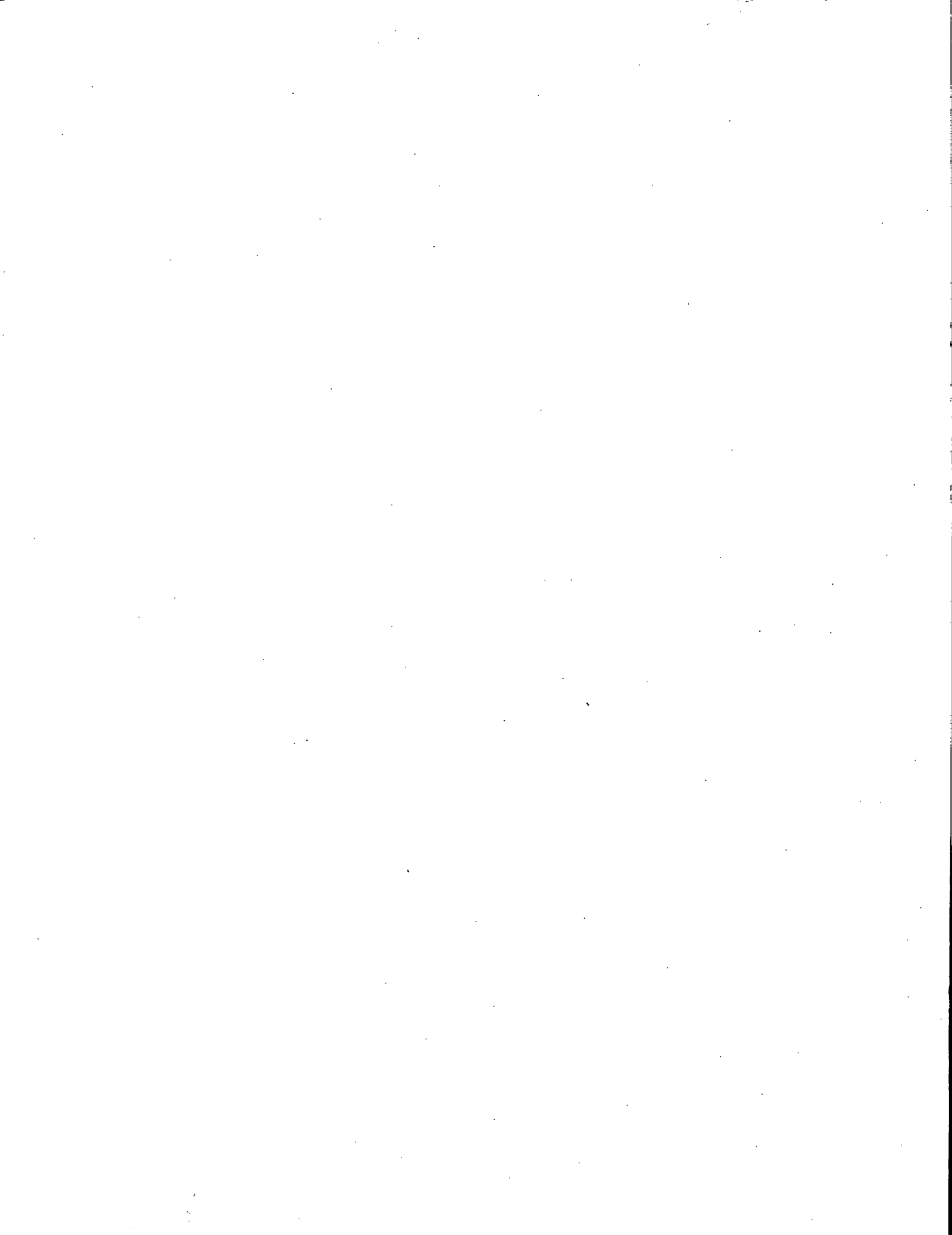
An investigation was commenced by the Department in 1934 on the chemical quality of major surface waters and municipal water supplies that are of importance to industry. During the period 1934 to 1943, H. A. Leverin, then with the Department, took spot samples of the larger lakes, rivers, and municipal water supplies but made no attempt at the time to study seasonal variations in any of these supplies. The survey was curtailed considerably during the early years of the war and was discontinued in 1943. The results of his investigation were published in Mines Branch Report No. 807, and later were revised and published in Report No. 819, both of which are now out of print.

To meet the post-war demands and anticipated demands of industry for information on the quality of waters a more detailed investigation was started in 1946. The results of this study on water quality will be published periodically in a series of water survey reports, each report covering a definite area such as a major drainage basin. No attempt will be made in these reports to study in detail relationships between the individual mineral constituents in water, and between them and other factors, such as river flow and geological features. Such studies, when completed, will be reported in separate papers in the series, as it is considered advisable to publish the chemical data as soon as possible.

The present report gives in some detail the aim and scope of the survey, and, to avoid repetition in subsequent reports of the series, details regarding survey procedures and methods of analysis are also given. Some discussion and tabulated information are included to assist in the interpretation of chemical results to be published from time to time in subsequent reports. The discussion is believed sufficient to aid the reader in assessing the relative value of the chemical data reported in the individual papers. The important subject of the effect of various constituents on the suitability of a water for any particular use will be discussed in later reports of the series.

Although the procedures now being used in collecting samples, in analysing, and for reporting results are presented in this report, it should be emphasized that advantage is being taken continually of experience and improvements in methods and technique.

The author gratefully acknowledges the co-operation he received from W. R. Inman, Chemist, Mines Branch, who was initially in charge of the water analysis laboratory.



DEFINITIONS AND ABBREVIATIONS

Parts per Million (p.p.m.)

One p.p.m. equals one part by weight of the constituent per one million parts by weight of the water. Commonly, one milligram of constituent per litre of water is considered 1 p.p.m. even though one litre of water at room temperature does not weigh exactly 1,000 grams.

Grains per Gallon (g.p.g.)

One g.p.g. equals one grain (weight) of the constituent per gallon of water. This varies depending upon whether the Imperial gallon or U.S. gallon is used. For conversion of g.p.g. to p.p.m. see Table III.

Equivalents per Million (e.p.m.)

This is defined as one equivalent weight of an element, an ion, or a salt in one million weights of solution. The equivalent is the weight, on a relative scale, of that quantity of an element or compound that will exactly react with another element or compound to complete a certain standard chemical reaction. One equivalent of any element will exactly combine with, or be equivalent to, one equivalent of any other element. Thus in any solution such as a natural water containing dissolved salts, the sum of the negative ions (anions) must equal the sum of the positive ions (cations) in terms of equivalents.

Twenty-three parts or 1 equivalent of sodium combine with 35.5 parts or 1 equivalent of chlorine to form sodium chloride; then 23 mgms. of sodium in 1,000,000 mgms. of water is 1 e.p.m.

Milligram Equivalents per Litre (m.eq./l.)

Milli equivalents per litre are equivalent to e.p.m. when it is assumed that 1 ml. of the water weighs 1 gram. 1 litre (1,000 ml.) will then weigh 1,000,000 milligrams. Thus, 23 mgms. sodium per litre of water is equal to 1 equivalent (as milligrams) per litre = 1 milligram equivalent per litre.

Second-foot (s.f.) or Cubic Foot per Second (c.f.s.)

This unit is used to express the discharge of a stream, that is, the number of cubic feet of water passing a given point per second.

Gallons per Minute (g.p.m.)

This unit is used to measure the flow of water, usually the discharge from a pump or from a plant or treatment unit.

Gallons per Day (g.p.d.)

Another measuring unit of discharge.

Million Gallons per Day (m.g.d.)

A discharge unit, commonly used in municipal pumpage statistics.

Tons per Acre-foot (t.a.f.)

One t.a.f. equals one ton of dissolved salts carried in one foot of water spread over one acre, that is, this volume of water on evaporation would leave one ton of material.

Millilitre (ml.)

This unit is used to define the volume of a liquid in the metric scale. As is customary, it is employed instead of cubic centimetre and for all practical purposes 1 ml. is considered identical to 1 c.c.

Degrees Centigrade (°C.)

Unit of temperature on the Centigrade scale.

$$^{\circ}\text{C.} = \frac{^{\circ}\text{F.} - 32}{1.8}$$

Degrees Fahrenheit (°F.)

Unit of temperature on the Fahrenheit scale. For conversion from Centigrade to Fahrenheit or vice versa see Table II.

Cation

The basic ions in water which carry a positive charge or valence, such as calcium, magnesium, sodium, potassium, and iron, are called cations, since they migrate to the cathode under the influence of an electric current.

Anion

The acidic constituents or those negatively charged ions in water that migrate to the anode are called anions. The principal anions in water are carbonate, bicarbonate, sulphate, chloride, nitrate, and fluoride.

Residue on Evaporation (R.O.E.)

The evaporation of a definite quantity of a clear water leaves a residue of salts previously dissolved in the water. This value may or may not correspond with the sum of constituents as found by analysis, depending upon loss or retention of various waters of hydration and crystallization, inclusion of fine colloidal matter, etc.

Total Dissolved Solids or Dissolved Solids (T.D.S.)

This is customarily used to designate the same value as residue on evaporation. Some workers refer to sum of constituents as dissolved solids. In this survey the term "total dissolved solids" refers to residue on evaporation dried at 105°C. unless otherwise indicated. The term "residue on evaporation" is preferably used.

Sum of Constituents (S.C.)

This is used in this report to designate the total of all major ions as p.p.m. found in the water by analysis, including silica (SiO₂). The value of the bicarbonate ion found is converted to carbonate to permit comparison with R.O.E. Sum of constituents is at times referred to as dissolved solids (calculated).

Total Residue (T.R.)

This is generally used to indicate the total residue obtained on evaporation of a turbid water. Total residue includes the suspended matter present and is therefore R.O.E. plus suspended matter.

Residue on Ignition (R.O.I.)

Heating the R.O.E. to a definite temperature drives off various waters of hydration and causes loss of organic matter. The difference between R.O.E. and R.O.I., or *Loss on Ignition (L.O.I.)*, is often referred to as organic matter, although this is not necessarily true.

Electrical Conductivity (E.C.) or Specific Conductance

A water containing dissolved salts will conduct an electric current, the amount of current depending upon the amount and nature of dissolved salts (ions) present. The conductance is measured in units called mhos (1 mho is the reciprocal of 1 ohm of resistance) and is usually expressed in micromhos at a temperature of 25°C.

> an abbreviation used to express "greater than".

< an abbreviation used to express "less than".

TABLE I
Useful Equivalents in Water Analysis and Treatment

*Volume equivalents—*to four significant figures

Gallons (Imp.)	Gallons (U.S.)	Cubic inches	Litres
0.8327	1.0	231.0	3.785
1.0	1.201	277.4	4.546
0.003606	0.004329	1.0	0.01639
0.22	0.2642	61.02	1.0
220.0	264.2	61,020.0	1,000.0

*Weight equivalents—*to four significant figures

Grains	Avoirdupois, lbs.	Grams	Short tons	Metric tons
1.0	0.0001429	0.06480
7,000.0	1.0	453.6	0.0005	0.0004536
15.43	0.002205	1.0
.....	2,000.0	907,200.0	1.0	0.9072
.....	2,205.0	1,000,000.0	1.102	1.0

*Area equivalents—*to four significant figures

Square feet	1 square cm.	1 square metre	1 square kilometre	Acres	Square mile
0.001076	1.0	0.0001
1.0	929.0	0.0929
10.76	10,000.0	1.0	0.000001
.....	1.0	247.1	0.3861
.....	0.004047	1.0	0.001563

*Linear equivalents—*to four significant figures

Feet	Rods	Miles	Centimetres	Kilometres
1.0	0.06061	0.0001894	30.48	0.0003048
16.5	1.0	0.003125	502.9	0.005029
0.03281	0.001988	0.000006214	1.0	0.00001
5,280.0	320.0	1.0	160,900.0	1.609
3,281.0	198.8	0.6214	100,000.0	1.0

1 quart	= 2 pints
1 gallon	= 4 quarts
1 barrel	= 31.5 gallons (U.S.)
1 millilitre (ml.)	= 1,000 cubic millimetres
1 litre	= 1,000 millilitres
1 cubic metre	= 1,000 litres
1 cubic foot	= 7.481 gallons (U.S.)
	6.229 gallons (Imp.)
1 cubic foot (water)	= 62.33 pounds
1 cubic foot	= 1,728.0 cubic inches
1 quart (liquid)	= 57.7 cubic inches
1 gallon	= 231.0 cubic inches
1 barrel (liquid)	= 7,276.5 cubic inches

Avoirdupois weight

1 dram	= 27 $\frac{1}{8}$ grains
1 ounce	= 16 drams = 437 $\frac{1}{2}$ grains
1 pound	= 16 ounces = 7,000 grains
1 short ton	= 2,000 pounds
1 long ton	= 2,240 pounds

Metric weight

1 microgram	= 0.001 milligram
1 milligram	= 0.001 gram
1 centigram	= 0.01 gram
1 decigram	= 0.1 gram
1 kilogram	= 1,000 grams
1 metric ton	= 1,000 kilograms

1 ounce (avoirdupois)	= 28.35 grams
1 acre-inch	= 27,154 U.S. gals. = 22,611 Imp. gals.
1 acre-foot	= 325,851 U.S. gals. = 271,336 Imp. gals.
1 acre-foot	= 43,560 cu. ft.
1 second-foot	= 7.48 gals. (U.S.)/sec. = 448.8 g.p.m.
1 second-foot	= 6.23 gals. (Imp.)/sec. = 373.8 g.p.m.
1 second-foot	= 1.933 acre-feet/day.
1 p.p.m.	= 0.00136 tons/acre-ft.
1 p.p.m.	= second-feet x 0.0027 tons per day.
1 boiler HP/hour	= 4 gals. water evaporated per hour.
1 gal. (U.S.)	= 8.33 lbs.
1 gal. (Imp.)	= 10 lbs.
1 lb./1,000 gals.	= 100 p.p.m.

TABLE II
Temperature Conversion Charts

°C. → °F.

$^{\circ}\text{C.} = \frac{^{\circ}\text{F.} - 32}{1.8}$

°C.	°F.	°C.	°F.	°C.	°F.
0	32.0				
1	33.8	16	60.8	31	87.8
2	35.6	17	62.6	32	89.6
3	37.4	18	64.4	33	91.4
4	39.2	19	66.2	34	93.2
5	41.0	20	68.0	35	95.0
6	42.8	21	69.8	36	96.8
7	44.6	22	71.6	37	98.6
8	46.4	23	73.4	38	100.4
9	48.2	24	75.2	39	102.2
10	50.0	25	77.0	40	104.0
11	51.8	26	78.8	41	105.8
12	53.6	27	80.6	42	107.6
13	55.4	28	82.4	43	109.4
14	57.2	29	84.2	44	112.2
15	59.0	30	86.0	45	113.0

Degree equivalents

°C.	°F.
0.1	0.18
0.2	0.36
0.3	0.54
0.4	0.72
0.5	0.90
0.6	1.08
0.7	1.26
0.8	1.44
0.9	1.62
1.0	1.80
°F.	°C.
0.1	0.06
0.2	0.11
0.3	0.17
0.4	0.22
0.5	0.28
0.6	0.34
0.7	0.39
0.8	0.45
0.9	0.50
1.0	0.56

°F. → °C.

$^{\circ}\text{F.} = 1.8^{\circ}\text{C.} + 32$

°F.	°C.	°F.	°C.	°F.	°C.
30	-1.11				
31	-0.56	56	13.33	81	27.22
32	0.0	57	13.89	82	27.78
33	0.56	58	14.44	83	28.33
34	1.11	59	15.00	84	28.89
35	1.67	60	15.56	85	29.44
36	2.22	61	16.11	86	30.00
37	2.78	62	16.67	87	30.56
38	3.33	63	17.22	88	31.11
39	3.89	64	17.78	89	31.67
40	4.44	65	18.33	90	32.22
41	5.00	66	18.89	91	32.78
42	5.56	67	19.44	92	33.33
43	6.11	68	20.00	93	33.89
44	6.67	69	20.56	94	34.44
45	7.22	70	21.11	95	35.00
46	7.78	71	21.67	96	35.56
47	8.33	72	22.22	97	36.11
48	8.89	73	22.78	98	36.67
49	9.44	74	23.33	99	37.22
50	10.00	75	23.89	100	37.78
51	10.56	76	24.44	101	38.33
52	11.11	77	25.00	102	38.89
53	11.67	78	25.56	103	39.44
54	12.22	79	26.11	104	40.00
55	12.78	80	26.67	105	40.56

TABLE III
Conversion of Units

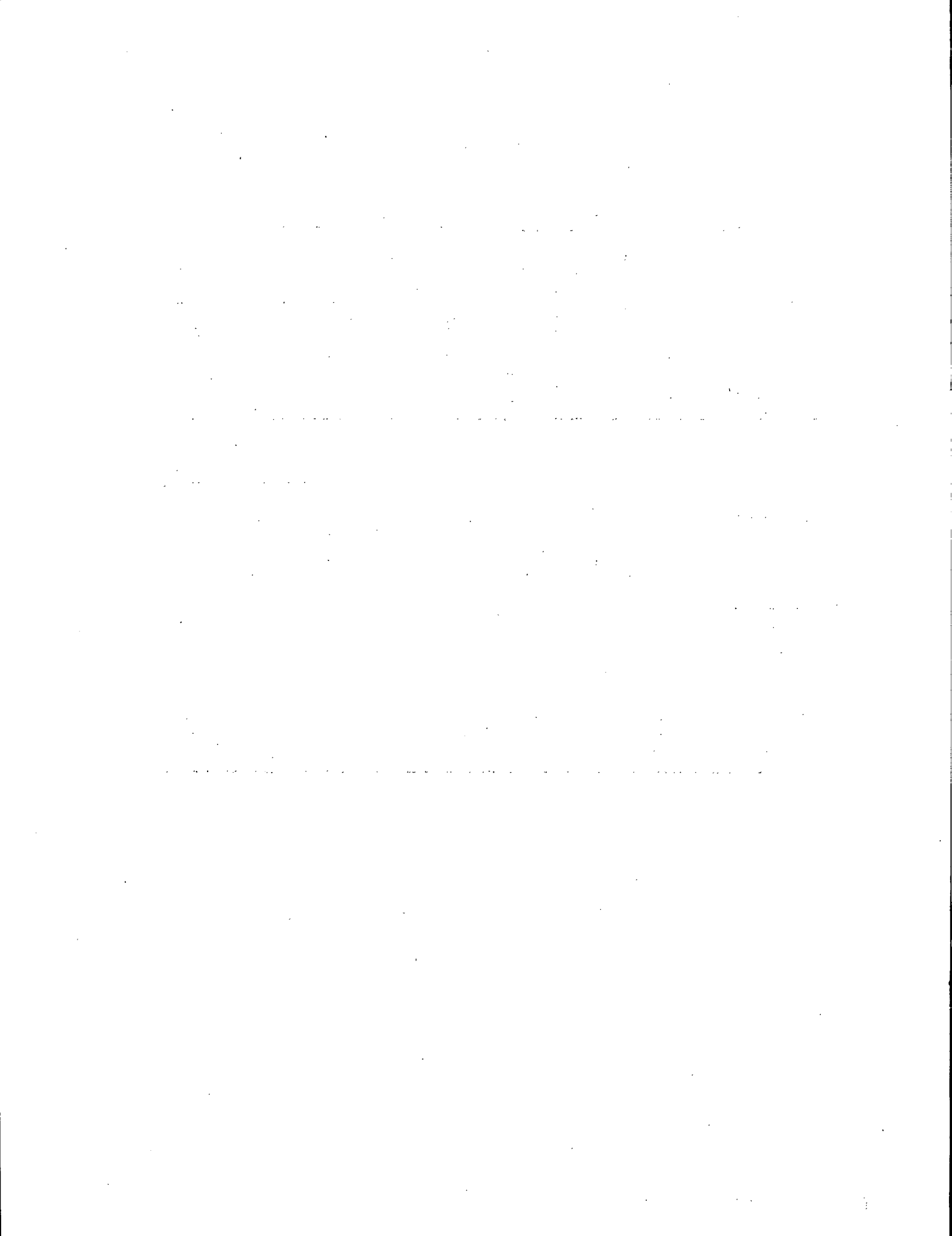
(a) Water Analysis Equivalents

Unit	P.p.m.	Milligrams per litre (mgm./l.)	Parts per 100,000 (Pts/100,000)	Grains per gallon (U.S.) (g.p.g.)	Grains per gallon (Imp.) (g.p.g.)
1 part per million (p.p.m.).....	1	1	0.1	0.0584	0.07
1 milligram per litre (mgm./l.)....	1	1	0.1	0.0584	0.07
1 part per hundred thousand.....	10	10	1.0	0.584	0.7
1 grain per gal. (U.S.).....	17.1	17.1	1.71	1.0	1.2
1 grain per gal. (Imp.).....	14.3	14.3	1.43	0.833	1.0

(b) Hardness of Water Units

(Hardness is normally expressed as p.p.m. CaCO₃, that is, all hardness salts are converted to the calcium carbonate equivalent.)

Unit	P.p.m. CaCO ₃	Parts per hundred thousand, CaCO ₃	G.p.g. (U.S.) CaCO ₃	G.p.g. (Imp.) CaCO ₃	Clark degree	French degree	German degree	E.p.m. CaCO ₃
1 part CaCO ₃ per million.....	1.0	0.1	0.0584	0.07	0.07	0.1	0.0560	0.02
1 part CaCO ₃ per 100,000.....	10.0	1.0	0.584	0.7	0.7	1.0	0.560	0.2
1 grain CaCO ₃ per gal. (U.S.)....	17.1	1.71	1.0	1.2	1.2	1.71	0.958	0.342
1 grain CaCO ₃ per gal. (Imp.)....	14.3	1.43	0.833	1.0	1.0	1.43	0.800	0.286
1 English (Clark) degree.....	14.3	1.43	0.833	1.0	1.0	1.43	0.800	0.286
1 French degree.....	10.0	1.0	0.584	0.7	0.7	1.0	0.560	0.2
1 German degree.....	17.9	1.79	1.04	1.24	1.24	1.79	1.0	0.358
1 equivalent per million.....	50.0	5.0	2.92	3.51	3.51	5.0	2.79	1.0



INDUSTRIAL WATER RESOURCES OF CANADA

Scope, Procedure, and Interpretation of Survey Studies

INTRODUCTION

The chief purpose of the present survey is to determine the chemical character of major Canadian water supplies available for industrial and domestic use. Since many industrial processes must use a water of a definite chemical character some limits of tolerance for quality, based on experience, have been set up by many industries. These limits, some of which are given in Table IV, serve merely to indicate certain characteristics of a water that enter into acceptability for different processes, but the limits are affected by variations in the processes and by the quality desired in the final product. When a water does not meet these general requirements it must be treated unless some other suitable supply can be found. Today almost any water can be treated by usual or special methods to produce a water of any desired quality, but economics determine the extent to which treatment is practicable.

Chemical analysis of a water is necessary to determine whether treatment is needed to meet limiting requirements, the type of treatment required, and the cost. Therefore, a determination of the utility of a water for any industrial process depends largely upon the interpretation of the results of analyses of representative samples of the water.

The variety of uses of water made by industries and the tremendous quantities of a suitable water required for their operation are not generally realized. Table V outlines the quantities of water required in the production of major commodities.

Water is used in industry chiefly as a solvent in many processes, as a raw material in the manufacture of other products, to transport materials, to produce power, for steam generation, for condensing and cooling, for washing and cleansing, for waste treatment and disposal, and for fire protection.

A number of other reasons why reliable data on water quality are of importance to this country are given below.

(1) Because of Canada's rapid industrial growth and its expected growth the demand for satisfactory supplies of water of suitable quality will continue to increase. As the density of population increases, it becomes more difficult to obtain water suitable for municipal and larger industrial uses, and as water is one of industry's chief raw materials all data regarding it will be of great importance in the location of future industrial plants.

(2) Industrial expansion will lead to contamination of available surface waters unless a carefully controlled waste disposal program is initiated. Pollution of surface waters causes many troubles, including eventual destruction of much wild life. Experience in highly industrialized areas in other countries has shown that many problems arise regarding water pollution and the disposal of trade wastes, including problems on the analysis of waters to determine the extent and nature of the pollution and on the important question of the treatment of such wastes to make them acceptable for discharge to rivers. Some knowledge of the water now available will assist in determining the extent and nature of any pollution in years to come, especially if periodic checking of quality is carried out, though it is essential that any such data be supplied by one disinterested agency so that the data would be acceptable in cases of dispute.

(3) As the population and the industrial use of water increase, ground water sources often become depleted or inadequate and surface supplies have to be utilized. Even now in certain parts of Canada this condition is arising, a major contributing factor being the increased use of ground water for cooling purposes and for air-conditioning. It is essential, then, that data be

TABLE IV*

Some Tolerance Limits of Water Quality in Industry

Industry or use	Colour	Hardness as CaCO ₃	Iron as Fe	Allowable manga- nese as Mn	Total solids	Alkalinity as CaCO ₃	Other requirements**
Baking.....	10		0.2†	0.2			P
Brewing, light beer.....			0.1†	0.1	500	75	P. NaCl less than 275 p.p.m. (pH 6.5-7.0)
Brewing, dark beer.....			0.1†	0.1	1,000	150	P. NaCl less than 275 p.p.m. (pH 7.0 or more)
Canning, legumes.....		25-75	0.2†	0.2			P
Canning, general.....			0.2†	0.2			P
Carbonated beverages.....	10	250	0.2 (0.3)†	0.2	850	50-100	P. Organic colour plus oxygen consumed, less than 10 p.p.m.
Cooling.....		50	0.5†	0.5			No corrosiveness
Food, general.....			0.2†	0.2			P
Ice.....	5		0.2†	0.2			P. SiO ₂ less than 10 p.p.m.
Laundering.....		50	0.2†	0.2			
Paper and pulp:							
Groundwood.....	20	180	1.0†	0.5			No grit, corro- siveness.
Kraft pulp.....	15	100	0.2†	0.1	300		
Soda and sulphite pulp....	10	100	0.1†	0.05	200		
High-grade papers.....	5	50	0.1†	0.05	200		
Rayon (viscose):							
Pulp production.....	5	8	0.05†	0.03	100	Total 50 Hydroxide 8	Al ₂ O ₃ less than 8 p.p.m. SiO ₂ less than 25 p.p.m. pH 7.8 to 8.3.
Manufacture.....		55	0.0	0.0			
Tanning.....	10-100	50-135	0.2†	0.2		Total 135 Hydroxide 8	
Textiles, general.....	20		0.25	0.25			
Dyeing.....	5-20		0.25†	0.25	200		Constant com- position.

* Data taken from a Progress Report of the Committee on Quality Tolerances of Water for Industrial Uses, by E. W. Moore; New England Water Works Association, vol. 54, p. 263, 1940.

** P indicates that potable water, conforming to U.S. Public Health Standards, is necessary.

† Limit given applies to both iron alone, and the sum of iron and manganese.

TABLE V*
Industrial Demand for Water

Product or industry	Production unit	Water required in U.S. gallons to produce one unit
Airplane engines	1 engine (testing)	50,000 to 125,000
Alcohol	1 gallon	100
Aluminium	Pound	160
Brewing (beer)	1 barrel	470
Butadiene	Pound	160
Canning and preserving**	Case (No. 2 cans)	7.5 to 250
Cement	Ton	750
Coke	Ton	3,600
Distilling: grain	1,000 bushels grain mashed	600,000
molasses	1,000 gallons, 100-proof	8,400
cooling water	1,000 gallons, 100-proof	120,000
Electric power	Kilowatt	80
Gasoline	Barrel	357
Ice manufacture	Ton	244
Iron ore (brown ore)	Ton	1,000
Meat (slaughterhouse and packing)	100 hogs	1,100
Milk, cream, butter	1,000 pounds	110 to 250
Oil refining	Barrel	770
Paper	Ton	39,000
Paper board	Ton	15,000
Rail freight	Ton/mile	0.1
Rayon	1,000 pounds produced	160
Soap	1,000 pounds	250
Soft drinks	Case	2.5
Steam power	Ton of coal	60,000 to 120,000
Steel (finished)	Ton	65,000
Sugar (cane, refining only)	Ton	1,000
Tanning	100 pounds rawhide	800
Textiles	1,000 pounds processed	1,000 to 30,000
Whiskey	Gallon	80
Wood pulp: groundwood	Ton	5,000
soda	Ton	85,000
sulphate	Ton	64,000
sulphite	Ton	60,000
Woollens and worsted fabrics	1,000 pounds finished	70,000
Wool scouring	1,000 pounds	1,260

* Reproduced from Journal of the American Water Works Association, vol. 38, No. 1 (January 1946), and vol. 42, No. 8 (August 1950) by permission of the A.W.W.A.

** Excluding fish.

available on the seasonal variations in the quality of surface water supplies in these areas. It is important also to know whether the surface water was originally of a quality that could be restored if properly controlled waste disposal is initiated and maintained.

(4) Solution of problems arising in industry regarding the use of any water, particularly corrosion problems, requires knowledge of the chemical quality of the water. Recent evidence indicates that the destructive corrosion of galvanized iron by hot and cold water is very closely related to the chemical composition of the water.

(5) The amount of minerals and other materials carried by a water is of importance to the hydro-electric industry, as excessive evaporation and sedimentation in reservoirs cause silting that results in loss of reservoir capacity. Some study of the sediment carried by a river may be considered a part of any investigation of the quality of its waters.

(6) When waters are to be used for irrigation it is desirable to know the amount and character of dissolved matter, as certain chemical elements such as boron and sodium may adversely affect the growth of many crops.

(7) Geochemical prospecting by means of careful study of the quality of waters also is possible. In such a survey river and lake waters are analysed for small quantities of metals, such as copper, zinc, and lead, in an effort to trace and locate mineralized areas. The possibilities of this field have yet to be adequately explored.

(8) As a major raw material, water may be classed as an important industrial mineral. Therefore, as with other natural resources, the Federal Government in co-operation with the provinces attempts to assess the quantity and quality of waters available for various uses in Canada. Studies on the quantity of waters available are carried out mainly by the Engineering and Water Resources Branch, Department of Resources and Development, which publishes periodic discharge records on major Canadian rivers.

It is believed that the development of industrial processes demanding a higher grade of water, and the deterioration of water supplies owing to the normal growth of population and industry, and to denudation of the soil causing flooding and consequent variability of supply, will eventually bring to the public, including many industrial users themselves, a much greater appreciation of the value of water.

GENERAL

Water is among the most important of a country's natural resources, as no industry can function without it. It owes its great usefulness in industry to its varied physical properties and its value as a solvent. Conditions of temperature and vapour pressure determine whether it occurs as a liquid, a solid, or a vapour.

Water is in constant circulation from the ocean to the land and back again. Ocean and inland waters are evaporated by the heat of the sun and by wind, and part of this water vapour is distributed as rain, snow, or hail over the land where it circulates by means of lakes, ponds, snowfields, and glaciers, or flows in streams from higher to lower levels. This natural circulation of water from low to high levels and its subsequent return to low places on the solid surface of the land is of prime importance to the inhabitants of the earth.

Many factors affect the chemical character of waters and vary the suitability of the waters for different uses. The principal factors affecting the chemical quality, in particular of surface waters, are: natural conditions such as precipitation, topographic and geological features, and vegetation; and human activities regarding the use of the water and the disposal of waste materials.

Natural Conditions

No other liquid will dissolve so many substances as will water, which during its circulation from ocean to land and back to ocean does not remain pure. Rain-water while falling picks up

gases such as carbon dioxide, as well as bacteria, dust particles, etc., floating in the air. If the atmosphere is contaminated with industrial fumes, gases such as sulphur dioxide and carbon monoxide are also adsorbed or dissolved.

In its passage across or under the land, water dissolves salts from the soil. The amount and nature of the material dissolved is related directly to the solubility of the materials and the length of time they are in contact with water. The quantities of salts dissolved are at times very large, especially when the water has passed deep into the earth's crust before reappearing on the surface, but if the water passes rapidly over the land, especially over soils or rocks that are only sparingly soluble, the quantity of material dissolved may be relatively small.

Thus, the chemical quality of natural waters depends largely upon the rate of precipitation, as rain, snow, or hail, and upon the geological and topographical features of the land over which such precipitation and run-off occurs. Geological features determine to some extent the amount of solution that occurs. Waters that have percolated through limestones or dolomites, for instance, will be hard; those that have passed through regions of alkalis will be alkaline; and the run-off from swamps will be coloured and contain much organic matter. Water that is in contact with organic matter of either vegetable or animal origin may become charged with such matter or with gases caused by decomposition of the material. Most surface waters contain organic matter present as micro-organisms, decayed algæ, or plant growth. Organisms and bacteria may have a pronounced effect on the amount and character of chemicals dissolved in the water and on their analytical determination.

Topographical features determine how fast precipitation drains off the land into a main stream, or in other words, the length of time the water will be in contact with soluble materials. The discharge of a river is directly related to precipitation and topography. The relationship between chemical quality and precipitation or discharge varies. It has been noted in work to date that some rivers change rapidly in chemical quality with increased discharge, whereas others are little affected by wide variations in flow. Many rivers show decreased dissolved mineral content with increased flow, but the opposite is true with other rivers, depending upon the character of land drained, the extent of forestation along the stream, and other factors.

The nature of the geological formations and topography determines also how much and how fast water percolates into the ground storage table, and thereby, the amount of chemicals dissolved. The extent to which the base flow of a river is dependent upon the ground-water inflow has much to do with variation in quality of river water. Because of the length of contact with material and the mixing that occurs, ground waters are usually relatively constant in quality and so in times of low precipitation, when the river is largely dependent upon ground-water inflow, the river water will remain relatively constant and of a character similar to this inflow.

Water flowing over or under the ground may also carry varying amounts of insoluble or suspended matter such as silt, decayed organisms, and vegetation. In many river waters the amount of this suspended matter is very large and of considerable importance. In other waters the suspended matter may be colloidal and difficult to remove.

With so many factors varying it is almost impossible to predict water quality in any area until long-term studies have established the relationship between precipitation (discharge) and chemical quality.

Human Activities

Industrial and other gases in the atmosphere will contaminate the water falling as rain, snow, or hail.

Probably the major human activity affecting water quality is the industrial and domestic use of surface and ground waters, with subsequent return to the land of water carrying all manner of sewage and industrial waste. The diversion of water for other uses and the effect of deforestation, construction, farming, etc., which change the rate of run-off and cause rivers to flood or to

dry up, can also seriously affect water quality. Dams, for example, tend to smooth out variations in river water quality, permit loss of suspended matter, restrict flow and normal run-off, and may even allow precipitation or concentration of soluble material in the storage basins.

The amount and nature of micro-organisms, plant growth, bacteria, and algæ present in a water are often increased or changed by human activities within a drainage basin and these organisms and growths may have a pronounced effect on water quality.

SCOPE OF INVESTIGATION AND PROCEDURE

Past studies of the chemical quality of waters in Canada have been limited in scope and did not consider the important factor of seasonal variation in surface water quality. The present investigation was begun in 1946 to rectify these shortcomings and to obtain more recent information on chemical quality.

The collection of water samples truly representative of the whole supply is a major problem in a survey of this nature. Experience has shown that ground waters and large bodies of surface waters such as the Great Lakes vary little in chemical quality seasonally or over a period of years, so that samples collected at various times and at different locations will be fairly representative of the whole supply. Notable changes in quality have been observed, however, in certain large bodies of water over long periods of time. The water quality of rivers and small lakes, which are partly fed by run-off, often varies widely from season to season and in many cases from year to year depending upon climatic conditions and other factors. With such waters some program of periodic sampling of representative portions is required and, as the changing geological formations along a stream, the type and drainage area of tributaries, and the amount of entering wastes may all change a river along its length, careful location of sampling points is a matter of considerable importance.

It is recognized that the collection of daily samples of a variable supply such as a river over a period of two or three years with a complete analysis of composite samples of several days' collections is the preferred program in a survey of this nature. However, such an extended investigation is not feasible at present because of the large territory to be covered, the limited facilities available, and the need for some data within a reasonable time. Although it is desirable to have regional laboratories when studying an area of the size of Canada, this is not practicable and therefore all samples are shipped to the Department's laboratories at Ottawa for analysis.

Some preliminary studies were carried out in 1946 on several rivers near Ottawa to assist in determining future methods of sampling and analysis. From this work* a general scheme of analysis and a program of sampling were formulated, the extent of the area to be covered at one time and the number of sampling locations being determined largely by the facilities, including personnel available for analyses and field work.

In the procedure being followed twenty to thirty sampling locations are established within the drainage basin under study, the locations being chosen so that some information is obtained on all the larger tributaries. Monthly samples are collected at these stations, usually for a period of one year, and whenever possible extra samples are obtained at periods of high and low river flow. When time permits, and it is deemed advisable, owing to the importance of the supply or to its possible contamination and variability, daily sampling is done at certain stations for the 1-year period. These daily samples are composited thrice monthly and are completely analysed. If possible, sampling stations are established where river levels and river discharge records can be obtained. Gauge readers of the Engineering and Water Resources Branch, Department of Resources and Development, have been used as collectors at many locations. In many cases the co-operation of municipal waterworks plants has made it possible to obtain satisfactory samples with little trouble.

* Water Survey Report No. 2, Part I (1952); Mines Branch Report No. 834, Dept. of Mines and Technical Surveys, Ottawa.

In an area studied in the above manner, spot sampling is carried out for a period during each summer; check samples are taken at the monthly stations, and many other samples are taken throughout the drainage basin. A mobile laboratory is used to collect these spot samples and a number of tests are done immediately in the field. The remainder of the water collected is shipped to the laboratory for complete analysis. In any area under study an attempt is made to visit all municipal waterworks plants and to obtain data regarding the operation of the civic system, including the source, treatment, consumption, industrial use, and any major problems regarding the use or treatment of the water.

It is hoped to cover almost the entire country in this manner on the basis of one major drainage area at a time. If possible, spot samples will be taken at certain locations in these areas in later years and, if considered necessary, a yearly check on each area will eventually be maintained at two or three stations.

Information and data thus obtained will be published periodically as Water Survey Reports. One section of each report will cover the quality of surface waters, and another all the available information, including analyses of civic supplies within the area. When such information on the chemical quality of most major supplies has been obtained, consideration can be given to the suitability of each supply for various uses, and problems regarding treatment of those waters to adapt them to such uses can be investigated.

SAMPLING PROCEDURE

To obtain correct quality determinations it is important that sampling points be so located that samples taken will be truly representative of the flow of a main river or tributary. A tributary entering the main river may not mix for some miles downstream or it may be in such volume and of such character as to significantly influence the main river quality for a considerable distance. One of the sampling difficulties encountered in Canada is the frozen condition of lakes and rivers for several months of the year, which requires that a hole be kept open in the ice. The question of transportation of samples also limits the choice of sampling location.

Whenever possible a visit is made to an area under study to establish suitable sampling locations and arrange for the collection of samples. If possible, a sampling station is chosen where collection can be made from the centre of a bridge or from a wharf or a boat. With the co-operation of municipalities and industries that use the water satisfactory samples are often obtained directly from their pumps or intake wells.

During the summer when spot sampling is carried out samples are usually obtained from surface supplies with a special sampler that collects water at any desired depth. This instrument, made of brass, holds about three-quarters of a gallon and has an opening in the top and another in the bottom normally closed by rubber stoppers. These stoppers are on a brass rod with bushings at each end, and a spring permits both to be open while the sampler is lowered. At the required depth the rope is jerked and the rod pulls up the two stoppers, closing the openings, and the weight of the water keeps them closed while the sampler is hauled from the river. By means of a stop-cock at the base of the sampler and a short rubber tube, the water is immediately drawn off for the field tests without excessive aeration of the sample. In sampling civic wells, the raw water is usually collected directly into the sample bottle with a hose connection from a tap on the pump. Raw surface waters are often sampled with the brass sampler direct from the sump well at the water-works plant. The final, treated water (municipal water) is generally drawn directly into the sample bottle from a tap at the water-works plant.

The sample container should be of a type that will not affect the chemical quality of the water appreciably during shipment or subsequent storage, and should be tightly stoppered as the entrance of air may cause changes, such as precipitation of dissolved iron or manganese, and loss of water by evaporation or spillage. Pressure-sealed bottles are preferred as containers but

these are not readily available in a size that will hold the 1½ to 2 litres of water required for a complete analysis. The ordinary soft-glass Winchester container that holds about ½ gallon, closed with either a plastic screw top or a glass stopper, is fairly satisfactory. It is probable that these bottles will permit some entrance of air with some samples during shipment but it is not believed possible to prevent this in a survey of this nature without excessive inconvenience and cost. Even if expensive so-called air-tight containers were used it is doubtful if the analyst would be justified in assuming that no air contact or oxidation has occurred, since there is always uncertainty as to immediate and proper sealing by the different collectors, as well as the possibility of "breathing" of the container owing to the abrupt changes in temperature and pressure occurring during shipment.

The following sampling instructions outline the methods being used by the Mines Branch for monthly and daily sampling. These instructions are supplied to all collectors.

INSTRUCTIONS RE COLLECTION OF WATER SAMPLES

Frequent Sampling

(This will include all sampling other than daily sampling; that is, weekly, monthly, or thrice-yearly sampling.)

Time of Sampling

A definite date is chosen for sampling at each location, which should be adhered to as closely as possible so that sampling will be at regular intervals of time. Should the date fall on a Sunday or holiday or when it would mean a special trip to ship the sample immediately, it is permissible to advance, or delay the sampling a day or two. Sampling on each date should be carried out about the same time of day.

Sampling Procedure

The half-gallon, glass bottles, as received, have been cleaned and are ready for use. They are closed either by a plastic screw top or a glass stopper. The neck of the bottle and stopper should not be handled excessively or allowed to become contaminated with dirt, etc., when sampling. Sampling is to be done by one of the following methods:

A. By Use of Supplied Metal Samplers and Bottles. This method is to be used whenever possible. Either a small metal sampler holding a 12-ounce pressure-stoppered bottle (citrate of magnesia type) may be used and the water transferred to the half-gallon bottle for shipment, or the large metal sampler holding the half-gallon bottle may be used directly. In either case a method that will give an integrated sample of the water should be used. To obtain such a sample the approximate depth of the river at the sampling point should first be determined, for example, from a bridge. Then, with the open bottle in the sampler swinging in an arc twice the depth of the water, the bottle is quickly dropped into the river. By allowing the bottle to sink and at the same time drift down with the river current it will fill with water and be near the bottom when directly below the collector. If not filled, the procedure is repeated until sufficient has been collected. In this way portions of the river water at all depths are obtained. The small bottle is filled in one swing, but several swings are required to fill the half-gallon bottle; in fast water usually three swings are required, and it is necessary to add extra weights to the sampler in order to cause the air-filled bottle to sink.

Whenever it is impossible to sample from a surface supply in the above manner the bottle in the sampler may be lowered directly to the depth desired (usually 4 to 5 feet) and allowed to fill. All bottles should be rinsed with some of the water before final sampling and collection. When the large bottle is filled to the mark shown thereon (1,500 c.c. or 2,000 c.c. volume) it should be immediately tested for water temperature, *tightly stoppered*, and labelled.

B. By Drawing Water Directly from a Tap or Pump. The water should be run to waste long enough to clear the tap, pumps, and all pipes of any water that has lain therein. Running for 5 minutes is usually ample.

The bottle should be rinsed once or twice with the water and then filled directly to the mark *in such a manner as not to cause too much turbulence and aeration of the water.*

The water is then tested for temperature and the bottle is *immediately tightly stoppered* and labelled.

C. From Shore or by Wading and Sampling Directly into the Large Sampling Bottle. At locations where sampling is possible only from a low wharf, from a boat, or by wading off shore, it is satisfactory if the large bottle, after one rinsing, is immediately held at arm's length below the surface until filled. It can then be drained to the mark and stoppered. It is preferable to remove the stopper from the bottle under the surface of the water but it may also be filled by quickly plunging the opened bottle below the surface so as to prevent entrance of surface scum, dirt, or dust.

Sampling from shore or near shore is not altogether satisfactory because of shore contamination, still water, etc. When possible, wade out or use a long pole or a boat so that the sample is obtained from the flowing part of the stream.

Identification of Sample

Each bottle will either have attached a stamped tag or will have stamped directly on it the following:

1. Where sample taken.....
 2. Date sampled.....
 3. Temperature of water.....
 4. Level of water.....
 5. Weather.....
- Signature.....

This information should be recorded as soon as possible after sampling. "Where sample taken" requires the name of the river, lake, or supply, and the location on the river or lake. "Date sampled" requires the day, month, year, and time of day. If the collector has been supplied with a thermometer he will report the temperature of the sample when it is drawn from the river, lake, or tap.

If a gauge is available at the point of sampling or nearby, the gauge level of the water is to be reported. If a gauge is not available, a comment as to whether the water is very high, high, normal, low, or very low will suffice under "Level of Water". Under "Weather" any information that would indicate how the weather preceding the sampling might influence the water should be given; for example, heavy rain, snow, and adverse winds on a lake.

Shipment of Bottles

The large bottles for frequent sampling will be shipped in wooden cases by *express prepaid* to the collector some time prior to his designated date of sampling.

The sample should be returned to the laboratory as soon as possible after it has been taken, since storage in the bottle may cause changes in the water. Therefore, after sampling, the bottle should be *tightly stoppered*, the box closed with the key ring and shipped by the first outgoing *express collect to the return address stencilled on the container*.

High and Low Water Samples

It is desirable to obtain high and low water samples, particularly when sampling is no more frequent than monthly. When such samples are requested, extra bottles will be shipped some time prior to these expected periods, and the collector is to use his judgment if no gauge is available as to when low water and high water occur and take samples in the usual manner.

Daily Sampling

Time of Sampling

A small sample is to be taken every day and, if possible, at the same location and at the same time each day.

If a collector is ill or is to be away for some time, he should arrange to have someone else carry out the sampling during his absence.

Sampling Procedure

All daily samples are taken with the 12-ounce pressure-capped bottle, of which each collector will receive a supply, together with a small metal sampler. A clean bottle is placed in the sample holder and filled in the manner described under method A above.

When the small sample bottle is filled it is to be emptied to the designated mark, the temperature taken, then stoppered, the identification tag completed, and the bottle placed in the case.

Identification

Unless otherwise directed, similar identification is required for each daily sample as outlined under this heading above.

Shipment of Bottles

The 12-ounce daily sampling bottles come in cases of ten or twelve. These will be shipped *express prepaid* to the collector prior to his sampling date and either an extra case or a few extra bottles will be shipped initially to allow for breakage or loss.

When the samples for the first 10 days of the month are taken they are shipped to the designated laboratory by *express collect* immediately after the tenth sample is obtained. This procedure is repeated for the next 10-day interval and the last shipment of each month will hold eight, nine, ten, or eleven samples, depending upon the month and year.

At the laboratory these different samples are tested for certain values and each set of bottles is mixed and the composite sample is completely analysed. Empty, clean, small sampling bottles will be returned by *express prepaid* to the collector.

Precautions re Sampling

1. Care in sampling to obtain a representative sample from the same location.
2. Preventing contamination or excessive aeration of the water sample.
3. Complete identification of each sample.
4. Strict adherence to the above approved procedure; in particular, tight stoppering of the bottle.
5. Immediate shipment of the monthly samples or daily sets to avoid long storage.

ANALYTICAL PROCEDURE

EFFECT OF STORAGE TIME ON WATER SAMPLE

An important factor to be considered in determining the chemical quality of a water is the length of storage on the bottled sample, especially if the bottle is not air-tight. Many data have been and are being collected on this subject. Various samples have been stored and tested after different periods of storage and analyses made at the time of sampling have been repeated on the same water after storage periods as long as one year. These studies have indicated major changes in some waters and on certain determinations on storage, which have led to the inclusion of information regarding the length of storage in all reports of analyses. A number of analyses reported in the literature are possibly of doubtful value because the effect of this storage factor has been ignored.

Some waters will store for many months with little apparent change in chemical quality, whereas others show changes within a few weeks, such changes probably being somewhat dependent upon the air-tightness of the container. There is some indication that certain waters may stand for periods up to 200 days with little change and then rapidly lose calcium. The changes most commonly noted are loss or gain of carbon dioxide with corresponding change in pH and alkalinity. Normally, waters will lose carbon dioxide and develop a phenolphthalein alkalinity. Some of these waters have shown at times a 50 per cent loss of calcium with corresponding decrease in total hardness. Soluble iron and manganese salts may also be precipitated as oxides by contact with air (oxidation) during storage. The colour in most highly coloured surface waters seems to decrease very rapidly on storage. Many surface waters, unless stored in the dark or treated with chlorine, develop algæ and bacterial growth, which may cause many of the above changes and may also colour the water and make it turbid and very difficult to handle in analysis. Unless care is taken to store samples some distance from the laboratory, hydrochloric acid, ammonia, and other fumes may cause marked changes in the water.

Cases are cited in the literature of a pick-up of silica when a water, especially a basic water, is stored for any period in soft-glass bottles. Experience in the Mines Branch laboratory to date has indicated wide variation in silica on storage, and there appears to be some possibility of a change-over of the silica into different forms, some of which may not react to standard tests. Turbidity, which is an expression of an optical approximation of the particle size, changes markedly on storage. The nitrate-nitrite-ammonia equilibrium also changes on storage, depending upon many factors, including bacterial action.

Samples are analysed as quickly as possible, and it is believed that with most waters storage of a month or less causes little change if the bottle is tightly stoppered and kept in the dark at room temperature.

PRETREATMENT OF SAMPLE

Another factor of major importance that is usually neglected in most analytical reports on waters is the method of treatment of the sample prior to analysis; that is, whether the analysis is carried out on the filtered, shaken, or supernatant water. An analysis on a shaken sample

may give somewhat misleading information if the water has an appreciable turbidity, since it may then include a part of the calcium, silica, etc., in the insoluble matter.

Filtering of highly turbid waters is very time-consuming and may also cause error owing to the removal of colour, adsorption of soluble salts on the suspended matter, etc. Taking into account the many factors involved, the pretreatment and analysis discussed below was finally developed and is now in use.

SCHEME OF ANALYSIS

When deciding upon any scheme of analysis such factors as purpose of the data, accuracy desired, speed of analysis, and adaptability to sampling program and routine laboratory work, must be taken into account.

Study of the suspended matter carried by a surface water at different periods is an involved problem and should be carried out as a separate survey. However, since turbidity or suspended matter is very important in the treatment and use of a water, some information on them is believed desirable when reporting chemical quality. Examination of a water for trace metals such as lead, copper, zinc, etc., for less common constituents such as phosphate, ammonia, and iodine, and for industrial contaminants such as cyanide, chromium, and phenol, is also considered a special study, as very large quantities of water are required and extremely sensitive and time-consuming methods of analysis are often necessary. Boron and fluoride, although normally present in very small amounts, are included in the analytical scheme because they are of special significance to a large percentage of water users. Iron and manganese are often present only in very small amounts but are very important. However, for reasons given in the discussion of the interpretation of these determinations, an accurate evaluation of iron or manganese should be made a special study.

The reported analysis should give a clear picture of the major chemical constituents of the water supply that are important to most users. Especially in cases where the samples cannot be analysed immediately, consideration must be given to the possibility of aeration, with resulting oxidation of iron and manganese and loss of carbon dioxide and consequent decrease in calcium and total hardness.

The scheme of analysis in use permits, within a few days after receipt of a sample, determination of the important constituents that have been found to change appreciably on storage even though complete analyses may be necessarily delayed. By checking for calcium and alkalinity as soon as possible and then again later when the final analysis is started, any major change in the carbonate-carbon dioxide equilibrium that would cause loss of calcium carbonate is noted and the necessary corrections can be made. Early determination of the chloride content permits acidification of the sample to dissolve any precipitated calcium carbonate or iron oxide if this is necessary when the final analysis is to be carried out. The scheme also permits an estimate of suspended matter and turbidity and eliminates in certain tests the need for filtering turbid waters.

However, it should be noted that with turbid waters any iron and manganese present may still be oxidized and precipitated as oxides, and since no initial value for soluble iron is determined, no correction is possible for this loss. Since such turbid waters must be filtered or allowed to settle for almost all uses this water as tested is actually more like the water that any process would receive in regard to iron content. This matter and others are discussed in more detail below, under the individual determinations. With relatively clear waters, such as well waters or civic supplies, the method gives a satisfactory measure of the total or dissolved iron content.

For a short period after survey work was commenced in 1946, tests were carried out on the shaken sample and several determinations such as conductivity and soluble silica were not carried out. (Water Survey Report No. 2.) Then, until June 15, 1950, essentially the same scheme as reported below, using the supernatant or filtered water, was employed, but no immediate testing

was carried out. On most samples storage prior to testing was short; however, some samples did have lengthy storage and changes in pH, alkalinity, hardness, etc., when recognized, required special attention and correction. Since June 15, 1950, in an effort to eliminate errors due to long storage and to permit closer correlation of field and laboratory analytical results, "immediate" testing of all samples for certain values has been carried out within a few days of receipt in the laboratory, although the main analysis is often not done for some weeks or months later. However, *storage time* on these is still being reported as *the time in days between date of sampling and date of starting the final analysis, unless otherwise indicated.*

Immediate Testing. All samples other than those already tested in the field or which can be completely analysed within a few days of receipt are treated as follows within a few days of arrival in the laboratory, care being taken not to disturb the settled water:

- (1) Pertinent data regarding the sample is recorded and a field number is assigned.
- (2) The approximate amount (in ml.) of the sample is recorded and a note made of any unusual visual characteristics of the sample.
- (3) On opening the bottle any marked odour is noted and a quantity of supernatant water is removed and tests for temperature, pH, conductivity, colour, alkalinity, total hardness, calcium (direct titration method), and, at times, chloride are carried out. Usually 200 to 250 ml. supernatant water is required for the tests and a correction is made for this removal on the values for turbidity, total iron, suspended matter, and "suspended matter, ignited".
- (4) The bottle is then shaken and some water is removed for determination of turbidity, following which it is returned to the bottle.
- (5) The bottle is then carefully stoppered, and set aside in the dark until final testing.
- (6) The results of the above tests are recorded under the pertinent field number and the bottle is marked to indicate the future analysis procedure, dependent upon the turbidity found and the type of analysis desired; that is, F_T , S_{Fe} , F , etc., where F_T refers to full analysis, turbidity >3 p.p.m., etc.

Secondary or Final Analysis. Generally a full analysis (F) is carried out, but where the quantity of water is limited or where data are already available to show that the supply is remaining relatively constant as to quality, a shorter analysis (S) is done, as this decreases laboratory time and is considered to give sufficient information for survey purposes. Both schemes of analysis permit assessing the accuracy of the test work.

When a final analysis is to be started, a set of eight samples requiring the same general analysis—that is, F , S , or F_T —is usually chosen and the following procedure is carried out:

- (1) All samples are assigned a laboratory number and pertinent data regarding date of analysis, analyst, etc., are recorded.
- (2) If the water had previously been acidified, the pH is rechecked. If only alkalinity was determined during immediate testing, alkalinity, pH, or other necessary determinations are now carried out to check if calcium has precipitated, and if so, appropriate measures are taken either to determine such precipitate by test or to calculate the amount from initial data.
- (3) Analysis is then carried out according to the following general scheme:
 - A. Full Analysis— F_T —turbidity >3 p.p.m.
 F —turbidity 3 or <3 p.p.m.
 F_{x, x_1} —complete analysis with extra determinations required where x may be total silica, boron, iron, etc.
 - B. Short Analysis— S , or S_{x, x_1}
 - C. Special Analysis— $Sp.$ —determinations required are listed.

FULL OR COMPLETE ANALYSIS

Type F_T

(If original turbidity >3 p.p.m.)

Shake sample, remove 500 ml. and filter through an asbestos mat in a Gooch crucible to determine Suspended Matter and Suspended Matter Ignited.

At same time remove 100 ml. of the shaken sample and determine total iron in a silica dish.

On the filtrate from the above 500 ml. or clear supernatant make the following determinations:

Residue on evaporation
Residue on ignition
Calcium*
Magnesium*
Sulphate
Nitrate
Soluble iron
Soluble silica
Sodium
Potassium
Fluoride
Chloride, if not done previously

Type F

(If original turbidity 3 or <3 p.p.m.)

On shaken or supernatant water (usually the latter) make the following determinations:

Residue on evaporation
Residue on ignition
Calcium*
Magnesium*
Sulphate
Nitrate
Soluble iron
Soluble silica
Sodium
Potassium
Fluoride
Chloride, if not done previously

It is to be noted that in this group if the slight turbidity was partly or wholly due to precipitated salts (for example, iron) or to organic growth, special treatment will be required. If due to iron salts it is usual to request F_{Fe}—that is, a total iron determination which will be carried out on the shaken sample, due consideration being given to any removal of supernatant water prior to shaking.

SHORT ANALYSIS—S

Normal turbidity

On supernatant water (filtering if necessary) do tests for:

Calcium*
Magnesium*
Sulphate
Nitrate
Sodium
Potassium
Soluble silica
Chloride, if not done previously

Turbidity due to iron salts

Shake and remove 100 ml. in a silica dish for determination of iron salts, then on supernatant or, if necessary, on filtered sample, do tests for:

Calcium*
Magnesium*
Sulphate
Nitrate
Sodium
Potassium
Soluble silica
Chloride, if not done previously

It should be noted that although the standard procedure of the American Public Health Association** places the limit for removal of suspended matter prior to analysis at a turbidity of 1 p.p.m., it is considered for our survey purposes that up to 3 p.p.m. turbidity causes little error in the analysis of most of Canada's natural waters. Accordingly, on this basis the procedure of analysis is broken into two classifications with special attention to those waters in which turbidity is largely due to iron salts. In very few cases are waters received in the laboratory on which settling during shipment and settling in the laboratory, for a day or so, has not brought the supernatant portion below 3 p.p.m. turbidity. If the suspended matter is so colloidal in nature as not to settle quickly the partly settled water is centrifuged or filtered through a Gooch prior to immediate testing.

The above scheme is believed satisfactory for the purpose of this survey and has been found to cover analysis of the natural waters studied so far in Canada.

* Periodically carried out only to check immediate test results on calcium, magnesium, and total hardness.

** Standard Methods for the Examination of Water and Sewage, 9th Edition (1946)—American Public Health Association, 1700 Broadway, New York 17, N. Y.

METHODS OF ANALYSIS

The methods of analysis being used in this investigation are outlined below. The determinations are listed alphabetically rather than in the order in which they are made in the laboratory or as given in the above scheme of analysis. The detailed methods are not given unless these are not standard or the standard method has been greatly modified. The procedure being used is indicated and the reader is referred to the technical literature for details. Most of the methods employed are those given in Standard Methods for Examination of Water and Sewage, 9th Edition, American Public Health Association, New York, (1946), hereafter referred to as "Standard Methods" or in ASTM Standards on Industrial Water, December 1949, American Society for Testing Materials, Philadelphia, Pa. A few methods and procedures of technique are taken from other sources such as Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists, 6th Edition, Wash., D.C., 1945.

Improvements that may make it necessary to amend survey analytical procedures from time to time are continually being developed. Particular consideration is always being given to improving the accuracy and speed of analyses.

Acidity

Total acidity is determined by the method outlined in "Standard Methods", page 31, that is, titration of 50 or 100 ml. of the water with 0.02 N sodium hydroxide solution (carbonate-free) to the end point with phenolphthalein indicator.

Mineral acidity is similarly determined by titration to the end point with methyl orange indicator.

Alkalinity

The method, outlined in "Standard Methods", pages 31-32 is used. This is titration with 0.02 N H_2SO_4 to the end points with phenolphthalein and methyl orange.

Fifty or a hundred ml. of the supernatant or clear water is pipetted without excessive aeration into a white porcelain casserole or an Erlenmeyer flask over a white surface. About 4 or 5 drops of phenolphthalein indicator solution are added. If the indicator is pink, there is a phenolphthalein alkalinity and the solution is titrated with 0.02 N H_2SO_4 with gentle stirring until the pink coloration just disappears. The amount of phenolphthalein alkalinity is reported as p.p.m. $CaCO_3$, and is equal to ml. of 0.02 N H_2SO_4 titrated $\times 1,000 \div$ ml. of sample taken. If the phenolphthalein indicator does not turn pink on addition, there is no phenolphthalein alkalinity.

Methyl orange alkalinity or total alkalinity is determined by adding to the sample after determination of the phenolphthalein alkalinity two drops of methyl orange indicator and titration of this yellow solution with the standard acid until the colour changes to orange. The total alkalinity as p.p.m. $CaCO_3$ is then the total ml. of $H_2SO_4 \times 1,000 \div$ ml. of sample. The methyl orange end point is delicate and too much indicator must not be used. Familiarity with the end point is necessary to obtain accurate results. Various indicators and mixtures of indicators have been used to facilitate the determination of this value.

Aluminium

Aluminium is determined only in certain waters, for example, civic supplies, and whenever its presence is suspected.

When determination is necessary the colorimetric procedure given in "Standard Methods", page 50, is used; that is, comparison of the colour of the unknown when treated with the ammonium salt of aurin tricarboxylic acid (aluminon) at pH 6.3 with standard aluminium solutions similarly treated.

Boron

The method used is that developed by E. C. Wilcox and other workers whereby the addition of mannitol to a neutral, unbuffered solution of mixed salts containing boron causes the solution to become acid. The quantity of standard base required to titrate this solution back to the initial pH is a measure of the boron present.

This method is given in detail in "Standard Methods", pages 87-90. Electrometric titration is carried out, but during the initial removal of free carbon dioxide by acidification and boiling methyl red indicator is used instead of bromothymol blue indicator.

Bromide

Bromide is rarely determined in survey work. It is determined, however, on sea water samples, on a few brackish waters received, and on ground waters from certain areas.

The method used is essentially the tentative method for iodide and bromide as given in the Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists, 6th Edition, (1945), Wash., D.C., page 646. The bromide is set free by treatment with chlorine water and compared in Nessler tubes with standard bromide solutions similarly treated.

Calcium

Initially, calcium was determined by Method B (volumetric) outlined in "Standard Methods", page 60; that is, precipitation of calcium as the oxalate, followed by solution in sulphuric acid, and titration with standard (0.1 N) potassium permanganate solution. Normally, the filtrate obtained from the determination of soluble iron was divided into two equal parts, one of which was used for the determination of calcium and magnesium and the other of sulphate.

The direct titration of calcium, using an organic sequestering agent (disodium dihydrogen ethylenediamine tetra-acetate dihydrate) and an ammonium purpurate indicator, is the method now generally used in routine survey analysis. Volumetric method B, above, is employed only to check the results of the direct titration in doubtful analyses and in waters of special types, such as very high-calcium waters.

Calcium can also be determined indirectly. The total hardness of the water is first determined, as outlined below under "Hardness", page 30, by titration with the sequestering agent and suitable indicator. All calcium is then removed from another sample by adding a fixed amount of ammonium oxalate, permitting to stand for 5 to 10 minutes, and then filtering off the precipitated calcium oxalate. Total hardness, which is now all magnesium hardness, is redetermined on this filtrate and the difference between the original total hardness and the hardness due to magnesium salts is the calcium hardness. The amount of calcium present is then calculated.

Carbon Dioxide

The free or uncombined carbon dioxide (CO_2) may be determined by calculation from total carbon dioxide and pH, from total alkalinity and pH, or by direct titration. These methods are discussed in "Standard Methods", pages 32-36, and in ASTM Standard Method D513-48T. The subject is also discussed below under alkalinity, page 54. Carbon dioxide is normally determined only at the time of sampling. Even then, owing to unavoidable aeration when sampling, the determination is often of little value.

Carbon dioxide is determined in the field by titration in the usual manner. A 100-ml. sample of the water is collected in a glass cylinder or short form Nessler tube by allowing the water to flow without turbulence from the field sampler into the cylinder; 10 drops of phenolphthalein indicator solution are added; and the sample is titrated with N/50 NaOH or N/44 Na_2CO_3 with gentle stirring until a faint permanent pink colour that persists for several minutes is developed. The free carbonic acid (CO_2) is reported as p.p.m. CO_2 .

Chloride

Chloride was originally determined in the Mines Branch laboratory by the Mohr method ("Standard Methods", page 73, and ASTM Standard Method D512-49); 50 ml. of the relatively

clear or supernatant sample is titrated with a standard silver nitrate solution using potassium dichromate solution as indicator. When the chlorides are 100 p.p.m. or greater, a smaller aliquot is pipetted off and diluted to 50 ml. Detection of end point of the reaction can be facilitated by the use of yellow glasses, or by working under yellow light. In the field tests, yellow glasses are used. Precautions, as outlined in "Standard Methods" and other texts, must be taken to ensure removal of colour, sulphites, and H_2S before testing for chloride.

A method* using dilute $Hg(NO_3)_2$ added to acidified water in presence of diphenylcarbazone indicator is now being used. This procedure is claimed to be more sensitive and less critical as to end point.

Colour

Colour determined on the water as sampled is often "apparent" colour, which, since it may include any colour or colour effect caused by the presence of colloidal or suspended matter, is not always a reliable value. Apparent colour is generally what is determined in the field, although many waters have such a low turbidity that "true" colour is also determined. The colour determined in the laboratory on the settled or supernatant water is "true" colour. If the suspended matter or turbidity is so colloidal in nature as not to settle within a few days, the water is either centrifuged or treated with 60 per cent solution of calcium chloride (1 ml. to 100 ml. water). This latter treatment is reported to cause settling of the colloidal matter with little loss of colour. Filtering will remove colour from waters.

Colour is determined in several types of apparatus, all using a comparison of the colour of the water against platinum-cobalt standards. The unit of colour is the colour produced by 1 mg. of platinum per litre (1 p.p.m.) as potassium chloroplatinate (K_2PtCl_6) dissolved in acidified water; the amount of cobalt salt added can be varied, depending upon the hue desired. Comparison is made against these standard colour solutions in Nessler tubes or against glass disks that have been related to these standards. The different methods are described in "Standard Methods", pages 14-15.

In the Mines Branch laboratory comparison is made using Nessler tubes and standard solutions, or the Taylor comparator and a standard colour slide. In the field the Taylor comparator is used, and occasionally the glass disks and equipment designed by the United States Geological Survey for field work. When the colour is very low comparison with Nessler tubes and prepared standard solutions is sometimes also employed in field work.

Conductivity (Specific Conductance)

The specific conductance of a solution is determined by the method and with the apparatus recommended by the Quality of Waters Branch, United States Geological Survey, namely a 60-cycle current, 115 volt, Leeds & Northrup laboratory set consisting of: (1) an enclosed switch-type Wheatstone bridge; (2) a pointer-type A.C. galvanometer; (3) an insulating transformer; and (4) a pipette-type conductivity cell. A cell constant of approximately 0.3 has been found satisfactory. A dip cell may also be used.

The pipette is first rinsed with the water under test at constant temperature, then filled, and the resistance is determined. From the resistance, the specific conductance (K), corrected to 25°C, is reported as micromhos, that is, $K \times 10^6$.

Dissolved Oxygen

This determination is made in the field and only periodically on surface supplies. The limitations of the determination are discussed below under "Interpretation of Analytical Results", page 61.

Millar's method, as modified by A. V. DeLaporte, Ontario Department of Health, is generally used, although occasionally the modified Winkler method, as outlined in "Standard Methods", page 130, or ASTM standard method D888-49T, non-referee method A, has been used. The Millar method is not applicable to waters abnormally deficient in oxygen, and it is reported that

* Determination of Chloride in Water, by Frank E. Clarke; Anal. Chem., vol. 22 (1950), pp. 553-5, 1458.

where less than 0.5 ml./l. (0.72 p.p.m.) of oxygen is present, an error is introduced from the amount of ferrous ammonium sulphate required to dissipate the colour of the methylene blue. Fifty ml. of the sample are carefully drawn from the sampler into a 100 ml. short-form Nessler tube, being introduced below a cover of paraffin oil. In the field the water is introduced by allowing it to flow slowly from the sampler into the bottom of the Nessler tube through a rubber tube with a glass extension. To the water is added with a pipette, below the oil cover, 5 ml. of an alkaline tartarate solution (60 grams caustic soda and 175 grams sodium-potassium tartarate dissolved in 500 ml. of water), and a drop of the methylene blue indicator* is then added. Finally, with a 10-ml. graduated pipette the ferrous ammonium sulphate solution is run in just below the surface of the liquid with gentle stirring with the pipette until the blue colour is just discharged. If sufficient care is taken to prevent undue agitation or aeration, the test can be done with little error without using the paraffin oil cover. The oil cover causes contamination of all glassware and presents a cleaning problem when working in the field.

The pipette reading gives the number of ml. of oxygen present per litre of water. One ml. of oxygen/litre = 1.43 p.p.m. of oxygen. Theoretically, 1 ml. of the ferrous ammonium sulphate solution does not equal 1 ml. of oxygen when using a 50-ml. sample, but the above strength gives results of close approximation. The ferrous ammonium sulphate is standardized by testing the solution against water of known oxygen content prepared by shaking distilled water until saturated with air, taking the water temperature, and determining the amount of oxygen present at that temperature from reference tables, such as Roscoe and Lunt's data (Sutton's Volumetric Analysis, 12th Edition, page 618). Figure 1 also shows the solubility of oxygen in distilled water at normal atmospheric pressure at various temperatures. The solubility varies in relation to the extent and type of dissolved matter present, that is, the amount of oxygen in water at saturation decreases with increasing salt content in the water.

Dissolved Solids (Total Dissolved Solids—T.D.S.)

This term was previously applied by most water analysts to the residue obtained on evaporation of a water to dryness, but more correctly it designates the total quantity of electrolyte present in the water as found by addition of the amounts of each element or ion found by analysis or determined from the conductivity.

Since bicarbonates of the alkaline earths do not exist in solid form, and alkaline earth chlorides decompose to varying degrees, as do some organic compounds when dried at the required temperature, the residue on evaporation and drying does not always truly represent the amount of dissolved salts present in a water. (See Interpretation of Analytical Results, page 48.)

In all Departmental reports the term "residue on evaporation" is normally used and has the meaning formerly given to the term "dissolved solids". The term "sum of constituents" is used to designate the dissolved salts as determined by computation from the analysis.

Fluoride

Essentially the Sanchis method as modified by Scott, namely the non-distillation method A, "Standard Methods", page 76, is used. In this method, the colour of a zirconium-alizarin lake is changed by the formation of an un-ionized zirconium fluoride salt, and comparison is then made with standard fluoride solutions similarly treated.

Five-ml. portions of acid zirconium alizarin are accurately measured from a 5-ml. volumetric pipette to 100 ml. of a water sample and to standard solutions of fluoride made up to 100 ml. The solutions are mixed and after 1-hour standing the colour of the unknown water is compared with the standard solutions. Fluoride may be determined on the sample as received, but if the turbidity of the water is 25 p.p.m. or greater, determination should be made on the supernatant or filtered water. The supernatant water, regardless of the original turbidity, is usually taken for the determination of fluoride in this survey.

* Methylene blue indicator—0.1 gram of blue methylene blue in 100 ml. of distilled water.

Most other substances interfere only when present in amounts greater than normally found in natural waters, but care must be taken to remove these interfering substances when they exceed the limits outlined in the above reference.

Hardness

Total hardness is determined by calculation from the amount of calcium and magnesium ions found by analysis. The method of calculation is given on page 51.

The recent methods for the determination of total hardness and of calcium by direct titration have been studied by the Mines Branch and are being used increasingly in the routine survey work. This method of determining total hardness is based on the titration of a water sample with an organic sequestering agent that forms un-ionized complexes with calcium and magnesium. The titration is done in the presence of an indicator dye whose colour depends upon whether calcium and magnesium ions are present or absent. The pH is adjusted with a buffer solution. The sequestering agent, ethylenediamine-tetra-acetic acid or disodium dihydrogen ethylenediamine tetra-acetate dihydrate, is sold by many firms under various trade names such as Verse-ne, Sequestrene, Iminol D, etc. Different firms have developed indicator dyes for use with this method.

For additional information regarding this method, reference should be made to the Hall Laboratories, Inc., Pittsburgh, Pa.; W. H. & L. D. Betz, Gillingham and Worth Sts., Philadelphia 24, Pa.; and other suppliers of the reagents; and to recent technical papers, including those of the Journal of the American Water Works Association, vol. 42, pp. 33-56 (January 1950).

In the field, hardness is determined by direct titration with this organic sequestering agent and an indicator.

Hydrogen Sulphide

Hydrogen sulphide tests are not standard procedure except occasionally on ground waters in the field; 500 ml. of water are carefully collected into a glass-stoppered bottle or flask holding 10 ml. of standard (N/100) iodine solution and 1 gram of potassium iodide crystals. The bottle is stoppered, shaken, and allowed to stand a few minutes. The excess iodine is then titrated with standard (N/100) thiosulphate solution. The thiosulphate solution used to standardize the iodine solution is such that 1 ml. N/100 iodine solution is equivalent to 0.1704 mg. H_2S .

Because of the instability of the solutions and the loss on standing of H_2S as a gas or as precipitated sulphur it is necessary to make this determination in the field. Aeration must be carefully guarded against when collecting and testing the water sample.

Free or uncombined H_2S may be calculated as outlined in "Standard Methods", page 153, if the pH of the sample and the total dissolved sulphide concentration are known. Hydrogen sulphide, free and uncombined, is reported as p.p.m. H_2S .

Iron

Iron is determined in routine analyses by colorimetric method C, "Standard Methods", page 52, using orthophenanthroline at pH 2.0 to pH 9.0 to give a pink to red colour, which is compared in the spectrophotometer or against similarly prepared standards in Nessler tubes. A.S.T.M. standard method D1068-49T also describes the phenanthroline method for iron.

Total iron is normally determined only on waters with a turbidity of 3 p.p.m. or greater when a complete analysis is carried out. It is not determined when the turbidity is lower than 3 p.p.m. unless all the turbidity is apparently due to precipitated iron.

When 500 ml. of the shaken sample are taken for the determination of suspended matter in turbid waters, 100 ml. of the same shaken water are drawn off into a silica dish for the determination of total iron. This water is evaporated to dryness, ignited, and digested with 2 ml. HCl,

the residue is then baked at 110° to 150°C. on a hot plate. A few drops of HCl are then added, and the material is washed into a beaker. Methyl red indicator is added, the solution is heated to nearly boiling, just neutralized to methyl red with NH₄OH, and digested for one-half hour to one hour. The precipitate is filtered out hot and washed with hot water and a few drops of HCl(1:1) into a 50-ml. volumetric flask, and then 1 ml. 10 per cent hydroxylamine hydrochloride solution, 3 ml. 0.2 per cent orthophenanthroline solution, and 3 ml. 50 per cent sodium acetate solution are added. The colour developed is measured against a reagent blank in a spectrophotometer and reported as p.p.m. Fe.

Dissolved (soluble) iron is determined on the filtrate from the test for total silica or on a portion of the clear water. Ammonium chloride (NH₄Cl) is added, the solution is heated to boiling, neutralized with NH₄OH to methyl red indicator, and the iron is precipitated in a manner similar to the procedure outlined above for total iron. In a similar manner, the colour is developed with orthophenanthroline and the amount of iron is determined in the spectrophotometer as p.p.m. Fe.

A small correction is made in the value for total iron to correct for the removal of supernatant water when immediate tests were carried out. The interpretation of values reported in this survey for total and dissolved iron, especially on turbid waters, is discussed in some detail on page 53.

Loss on Ignition

The residue on evaporation, after final weighing, is ignited (thermostatically controlled) at dull red heat (500°-550°C.) for one hour in a muffle furnace, cooled, and weighed to constant weight as residue on ignition. Residue on evaporation minus residue on ignition gives the loss on ignition in p.p.m.

Magnesium

Initially, the filtrate from the volumetric determination of calcium was tested for magnesium by the gravimetric method using diammonium hydrogen phosphate solution in the manner outlined in method A, "Standard Methods", page 60, or A.S.T.M. standard method D511-42.

More recently, the magnesium in most waters has been determined with satisfactory accuracy by calculation from the determination of total hardness and calcium by direct titration with suitable indicators and an organic sequestering agent: this value is checked when necessary, either by the above-mentioned gravimetric method, or, more often, by a modification of colorimetric method B, "Standard Methods", page 60, using brilliant yellow instead of titan yellow.¹

Manganese

Manganese is not determined as routine in this survey and is rarely present in water in a sufficient amount to affect the chemical balance of an analysis.

When manganese is determined, the procedure given in "Standard Methods", page 57, is used. By this procedure manganous compounds present in the water are oxidized by ammonium persulphate to permanganate and the permanganate colour is compared against standard solutions or equivalent standard glass disks. A.S.T.M. method D858-49 employs oxidation of manganous compounds by potassium periodate to permanganate.

Metals

Tests for heavy metals such as lead, copper, and zinc are not normally made, but, mainly for the purpose of geochemical prospecting, consideration is being given to determining these by sensitive field methods.

When laboratory tests are made for these metals accepted procedures given in "Standard Methods" are used.

¹ Photometric Determination of Magnesium with Brilliant Yellow. Analytical Chemistry, Vol. 20, pp. 1156- (1948).

Nitrate

Nitrate nitrogen is determined by the usual phenoldisulphonic acid method as given in "Standard Methods", page 69. In the Mines Branch laboratory the yellow colour developed by the phenoldisulphonic acid, nitrate, and strong KOH, is compared with standards in Nessler tubes, or occasionally with standard glass disks. When tested for in the field, nitrates are determined by a similar method, comparison being made against standard nitrate colour disks in the Hellige comparator. Ground waters, high in nitrate, are tested by reduction of the nitrate to ammonia, followed by distillation and nesslerization. Waters having a colour of 10 p.p.m. or greater should be decolorized by adding 3 ml. aluminium hydroxide suspension, stirring well, allowing to stand for a few minutes, filtering, and washing.

Chlorides affect this determination in proportion to both the chloride and nitrate concentration. Where chlorides are 30 p.p.m. or greater, a standard solution of silver sulphate is added to the cold solution until all but about 1 p.p.m. of chloride is precipitated.

If nitrite (NO_2) is present in an amount greater than 1 p.p.m. it should be oxidized by heating the sample for a few minutes with several drops of H_2O_2 (free from nitrate), or dilute KMnO_4 may be added until a faint pink coloration persists. The nitrate equivalent of the nitrite thus oxidized is subtracted from the final nitrate reading.

Nitrate tests because of the possible changeover due to oxidation of nitrites or reduction due to bacterial action, etc., are best carried out immediately after sampling. Nitrate nitrogen is reported in survey work as p.p.m. NO_3 .

Nitrite

Nitrite nitrogen is determined by the method outlined in "Standard Methods", page 71, using the colour reaction with alpha naphthylamine acetate and sulphanilic acid. The colour developed is compared against prepared nitrite standards similarly treated in Nessler tubes. When tested for in the field, nitrite is determined in a similar manner and comparison is made against standard nitrite colour disks in a Hellige comparator.

Care must be taken to decolorize highly coloured waters with aluminium hydroxide, and if large quantities of chlorine have been added to waters, the naphthylamine acetate should be added before the sulphanilic acid.

Nitrites are an indication of pollution, but the test should be carried out soon after sampling since there may be a change in the nitrogen equilibrium ($\text{NH}_3\text{-NO}_2\text{-NO}_3$) due to bacterial action, etc. Nitrites are reported as p.p.m. NO_2 .

pH Value

pH may be determined potentiometrically or by comparison with standard indicators and buffer solutions using various comparators or colorimeters. The accepted methods, both colorimetric and potentiometric, are outlined in "Standard Methods", pages 28-30. pH is normally determined potentiometrically in this laboratory and in the field.

Since the pH value changes rapidly in many waters owing to loss or gain of CO_2 and change in temperature, pH should be determined at the time of sampling, and the water temperature noted.

Phosphate

Phosphate is not determined in routine survey work. If determined, the colorimetric procedure outlined in "Standard Methods", page 79, namely treatment of a phosphate-containing water with ammonium molybdate to form the coloured phosphomolybdate, reduction of this with amino-naphthol-sulphonic acid and comparison against standards similarly treated, is employed.

Potassium

In early survey work, potassium was not normally determined, total alkalis being determined by usual gravimetric methods ("Standard Methods", page 62) and reported as p.p.m. Na.

Alkalis are now determined with the flame photometer (Perkin-Elmer Model 52A) with much saving in time as well as the determination of separate values for sodium and potassium.

Residue on Evaporation

The residue on evaporation of a quantity of the clear water is determined in this survey by the procedure given in "Standard Methods", page 20, and in A.S.T.M. tentative method D1069-49T, (Method B), except that these methods recommend 103°C. as the drying temperature, whereas the Mines Branch laboratory uses about 105°C. The effect of varying the temperature of drying is discussed on page 48.

Residue on evaporation will include both dissolved solids and suspended matter unless the water has no turbidity. In this survey, if the turbidity is 3 p.p.m. or less, the supernatant water, or water as received, is measured out. If turbidity is higher than 3 p.p.m. the filtrate, or a part thereof from the determination of the suspended matter, is taken. Where the specific conductivity is below 1,500 micromhos at 25°C., 500 ml. of the sample are evaporated. Above this figure, 200 ml. are evaporated. Residue on evaporation is reported in parts per million.

Silica

At the start of the survey only gravimetric or total silica was determined. Then, for some time, tests were made for both gravimetric and colorimetric silica, but in more recent work only colorimetric silica is normally determined.

Total (gravimetric) silica is determined by the decomposition of soluble silicates with HCl to form silicic acid, precipitation of the partly dehydrated silica by complete evaporation, and final dehydration by ignition, followed by volatilization of the silica as silicon tetrafluoride (SiF_4).

If less than 2 mgms. nitrate is present the residue on ignition (at 550°C. of residue on evaporation) is taken up with water and after addition of 1 ml. HCl (1:1) is evaporated to dryness. The residue is then moistened with a few drops of HCl and taken up with hot water. In the case of high non-carbonate waters—high in CaSO_4 , which dissolves with difficulty—this operation has to be repeated, often with the addition of several millilitres of HCl. The residue is then filtered and washed with hot water and the precipitate is dried, ignited in a platinum crucible, and weighed. Silica is then volatilized on a hot plate with hydrofluoric acid and a drop of H_2SO_4 , after which the residue is ignited, cooled, and weighed. The difference between the two weighings is silicon tetrafluoride, which is reported as parts per million SiO_2 . Any residue remaining in the platinum dish is dissolved in hydrochloric acid and added to the original filtrate.

When the nitrate in the sample is in excess of 2 mgms. (4 p.p.m. when 500 ml. is used), the residue on ignition should be transferred to a silica or porcelain dish, because the free chlorine formed on adding dilute HCl will attack the platinum dish.

Colorimetric silica, or, as it is often called, "soluble silica", is determined by A.S.T.M. tentative method D-859-47T, non-referee method C, using the spectrophotometer for colour measurement. This method develops the yellow silicomolybdate complex by treatment with ammonium molybdate followed by reduction to the heteropoly blue with sodium sulphite. When the silica content is very low, a similar method using amino-naphtholsulphonic acid as the reductant is employed.

Silica is sometimes determined in the field by a similar method, except that comparison is made against standard glass disks in the Hellige comparator. Another method using essentially the same procedure (reduction to the heteropoly blue) is also used at times in the field, comparison being made with a battery-operated photometer.

Sodium

Sodium is now determined similarly to potassium in the flame photometer and is reported as p.p.m. Na.

Sulphate

On the other half of the filtrate from the determination of iron, soluble sulphate is determined by the standard gravimetric method as outlined in method A, "Standard Methods", page 83, or in A.S.T.M. standard method D516-49. This is the precipitation of the sulphate ion with BaCl_2 as BaSO_4 and determination by weighing. Sulphites, if present, must be determined and subtracted from the value for sulphate.

Sulphide

Sulphides are rarely found in appreciable amounts in natural waters unless these are heavily contaminated with sewage. Un-ionized hydrogen sulphide may be present in ground waters, however, and is occasionally determined.

If sulphides are present or suspected they are tested for by methods described in "Standard Methods".

Sulphite

Sulphites are rarely found in natural waters and are not normally determined.

If present or suspected, they are determined according to the volumetric procedure given in "Standard Methods", page 86, namely, a measured quantity of the water is added to an excess of standard 0.025 N iodine solution. The iodine solution remaining after reduction by the sulphite present is determined with sodium thiosulphate solution using starch as an internal indicator.

Sum of Constituents

The sum of constituents is the quantity in parts per million of the main constituents found in water by analysis. The values used in obtaining the sum are generally SiO_2 , Fe, Mn, Ca, Mg, Na, K (or Na and K combined), CO_3 equivalent of HCO_3 , SO_4 , Cl, F, and NO_3 . When other elements are present in significant amounts these also are included in the sum. The carbonate equivalent of bicarbonate is used, since bicarbonate is converted to the corresponding carbonate on evaporation to dryness and the sum of constituents will then compare more accurately with the residue on evaporation. To determine the carbonate equivalent either divide by 2.03 the bicarbonate value obtained from the total alkalinity by multiplying by 1.22, or multiply the total alkalinity, if all is bicarbonate, by 0.601.

Suspended Matter

If the turbidity of the water is greater than 3 p.p.m., the bottle containing the sample (1,500 to 2,000 ml.) is shaken well and a measured volume, usually 500 ml., is filtered on an asbestos mat in a Gooch crucible, dried at $103^\circ\text{--}105^\circ\text{C}$. for one hour, and weighed. The amount of suspended matter is reported in parts per million. When large amounts of suspended matter are present a smaller test volume of the sample may be advisable. Correction is made in the value for suspended matter for the error due to removal of supernatant water for immediate testing as outlined on page 24.

Difficulty in obtaining a clear filtrate may occur when finely divided or colloidal sediment is present. With these waters the sample is allowed to settle or is centrifuged to obtain a quantity for the determination of residue on evaporation.

Suspended Matter, Ignited

After determination of suspended matter dried at 105°C ., the material in the Gooch crucible is ignited in a muffle furnace at red heat ($500^\circ\text{--}550^\circ\text{C}$.) for one hour, cooled and weighed, and reported as "suspended matter, ignited". Correction is again made for initial removal of supernatant water.

The loss in weight represents to some extent the amount of organic matter in the suspended material and some analysts report it as such. It is not normally reported in this survey.

Temperature

The room temperature of the water is recorded when the sample is opened for testing, primarily for use in calculating values such as saturation index.

A standard laboratory thermometer is used. Special thermometers are supplied to collectors for determining the temperature of the water when sampled.

Turbidity

Turbidity is expressed as an optical estimate of the suspended matter, and is measured by comparing the extent of interference with the passage of light through the sample with similar interference by standard suspensions of known turbidity.

The present standard for turbidity measurements is the depth of suspension required for the image of the flame of a standard candle to disappear when observed through the suspension. The standards, which are prepared from fuller's earth in distilled water, are standardized against the Jackson (candle) turbidimeter as outlined in "Standard Methods", page 12. The several turbidimeters on the market are standardized against the candle turbidimeter and permit determination of low turbidities. In the Mines Branch laboratories the Hellige turbidimeter, which applies the principle of the Tyndall cone in an effort to eliminate the effect of colour in turbidity measurements, is used.

Turbidities greater than 7 p.p.m. are determined in the field on streams and lakes with the field apparatus of the United States Geological Survey, which consists of a calibrated rod or tape with a platinum reflecting point at the end. For turbidities lower than 7 p.p.m. comparison is made against standard suspensions in bottles or in Nessler tubes.

REPORTING ANALYTICAL RESULTS

The analytical results are reported in the laboratory on special forms as parts per million (p.p.m.), and are also converted to equivalents per million (e.p.m.) and the accuracy of the analysis is checked. *These results, together with all pertinent information, such as location of sampling, source, and depth of sampling, are then transferred to special punch cards for indexing and filing.

Chemical analyses on waters are reported in the Water Survey Reports only as parts per million, but by using Tables III, VI, and VII the data can be converted either to grains per gallon, to equivalents per million, or to hypothetical combinations.

The results are generally reported to three figures, but these may not in all cases be significant, and much depends upon the method of analysis, type of water, etc. The reported results are either those found by the laboratory or have been decreased by one figure. Although zero or nil concentration is reported for some constituents (for example, chloride), this simply means that none was found within the sensitivity of the method used and, if present, is of no known importance to the usefulness of the water.

HYPOTHETICAL COMBINATIONS

In some cases it is advantageous to combine the ions into suspected compounds for interpretation of the character of the water. This method of reporting was previously very popular, but as the exact combinations are unknown and there are several methods of combination used, this procedure has gradually been discontinued. The methods of combination used are generally based on assumptions, the main one being that combination is in accordance with decreasing solubility of compounds.

* Kindly refer to definitions for p.p.m. and e.p.m. on p. 7. As there indicated, mgm./l. and meq./l. are more correct, since these are weight to volume ratios, but in normal test work error introduced by use of weight to weight ratios (p.p.m.) and (e.p.m.) is only about 3 in one thousand.

When analyses of all major acids and bases have been made it is customary to proportionate the small error of analysis so that the cations and anions will balance; otherwise, when determining the hypothetical combinations the error must be considered due to the non-determination of some radicle or ion such as phosphate or iron. The error is sometimes balanced by assuming additional alkali or alkalinity. Occasionally, when the error is positive, silicate ion is assumed present and is used to balance hypothetical combinations.

TABLE VI
Chemical Ions and Equivalents

Ion	Atomic or Molecular Weight	Equivalent Weight	Reacting weight* (1 ÷ equivalent weight)
Aluminium (Al ⁺⁺⁺).....	26.98	8.99	0.11123
Ammonium (NH ₄ ⁺).....	18.04	18.04	0.05543
Antimony (Sb ⁺⁺⁺).....	121.76	60.83	0.01644
Arsenic (As ⁺⁺⁺).....	74.91	24.97	0.04005
Barium (Ba ⁺⁺).....	137.36	68.68	0.01456
Bicarbonate (HCO ₃ ⁻).....	61.02	61.02	0.01639
Boron (B ⁺⁺⁺).....	10.82	3.61	0.27731
Bromide (Br ⁻).....	79.916	79.916	0.01251
Calcium (Ca ⁺⁺).....	40.08	20.04	0.04990
Carbonate (CO ₃ ⁻).....	60.01	30.005	0.03333
Chloride (Cl ⁻).....	35.457	35.457	0.02820
Chromium (Cr ⁺⁺⁺).....	52.01	8.668	0.11536
Copper (Cu ⁺⁺).....	63.54	31.77	0.03148
Fluoride (F ⁻).....	19.00	19.00	0.05263
Hydrogen (H ⁺).....	1.008	1.008	0.99206
Hydroxide (OH ⁻).....	17.008	17.008	0.05880
Iodide (I ⁻).....	126.91	126.91	0.00788
Iron (Fe ⁺⁺).....	55.85	27.93	0.03581
Iron (Fe ⁺⁺⁺).....	55.85	18.62	0.05372
Lead (Pb ⁺⁺).....	207.21	103.60	0.00965
Magnesium (Mg ⁺⁺).....	24.32	12.16	0.08224
Manganese (Mn ⁺⁺).....	54.93	27.47	0.03641
Nitrate (NO ₃ ⁻).....	62.01	62.01	0.01613
Nitrite (NO ₂ ⁻).....	46.01	46.01	0.02173
Phosphate (PO ₄ ⁼).....	94.98	31.66	0.03159
Potassium (K ⁺).....	39.100	39.100	0.02558
Silicate (SiO ₃ ⁻).....	76.06	38.03	0.02630
Silver (Ag ⁺).....	107.88	53.94	0.18539
Sodium (Na ⁺).....	22.997	22.997	0.04348
Strontium (Sr ⁺⁺).....	87.63	43.82	0.02282
Sulphate (SO ₄ ⁻).....	96.06	48.03	0.02082
Tin (Sn ⁺⁺).....	118.70	59.35	0.01685
Zinc (Zn ⁺⁺).....	65.38	32.69	0.03059

* Reacting weights are defined and explained in some detail below under balancing of analytical results. P.p.m. of ion multiplied by reacting weight give e.p.m. of ion (see Table VII).

TABLE VII
Conversion Factors; e.p.m. to p.p.m. and vice versa

Ion	p.p.m. to e.p.m.	e.p.m. to p.p.m.	Ion	p.p.m. to e.p.m.	e.p.m. to p.p.m.
Ca ⁺⁺	0.04990	20.04	CO ₃ ⁻	0.03333	30.01
Mg ⁺⁺	0.08224	12.16	OH ⁻	0.05880	17.01
Ba ⁺⁺	0.01456	68.68	H ₂ PO ₄ ⁻	0.01031	97.00
Sr ⁺⁺	0.02282	43.82	HPO ₄ ⁻	0.02084	47.99
Zn ⁺⁺	0.03059	32.69	PO ₄ ⁼	0.03159	31.66
Cu ⁺⁺	0.03148	31.77	SO ₄ ⁻	0.02082	48.03
Pb ⁺⁺	0.00965	103.60	HSO ₄ ⁻	0.01030	97.07
Na ⁺	0.04348	23.00	SO ₃ ⁻	0.02498	40.03
K ⁺	0.02558	39.10	HSO ₃ ⁻	0.01234	81.07
NH ₄ ⁺	0.05543	18.04	S ⁻	0.06238	16.03
H ⁺	0.99206	1.008	HS ⁻	0.03024	33.07
Fe ⁺⁺	0.03581	27.93	Cl ⁻	0.02820	35.46
Fe ⁺⁺⁺	0.05372	18.62	Br ⁻	0.01251	79.92
Al ⁺⁺⁺	0.11123	8.99	I ⁻	0.00788	126.91
Mn ⁺⁺	0.03641	27.47	F ⁻	0.05263	19.00
Mn ⁺⁺⁺	0.05461	18.31	NO ₃ ⁻	0.01613	62.01
HCO ₃ ⁻	0.01639	61.02	NO ₂ ⁻	0.02173	46.01
			SiO ₃ ⁻	0.02630	38.03

"Standard Methods" recommends combinations of cations with anions in the following order, using equivalents per million: the cations Ca⁺⁺, Mg⁺⁺, NH₄⁺, Na⁺, and K⁺ are combined in order with the anions CO₃⁼, OH⁻, SO₄⁼, Cl⁻, and NO₃⁻. Iron is generally reported as iron oxide and silica as colloidal silica. Minor constituents such as fluorides are not normally considered.

The calculation of hypothetical combinations is best illustrated with a typical analysis of a surface water.

WATER ANALYSIS REPORT

(Parts per million)

Thompson River near Kamloops, B.C.

(Composite of daily samples taken August 11-20, 1950, inclusive.)

Date analysed.....	November 16, 1950
Storage time.....	92 days
Sampling temperature.....	17.8°C. (average of 10 samples)
Test temperature.....	21.5°C.
pH.....	7.4
Colour.....	5
Alkalinity (phenolph.).....	0
Alkalinity, total (methyl orange).....	32.6
Suspended matter, dried (105°C.).....	7.0
Suspended matter, ignited (500°-550°C.).....	5.6
Residue on evaporation, dried (105°C.).....	56.2
Residue on evaporation, ignited (500°-550°C.).....	47.4
Loss on ignition.....	8.8
Specific conductance (conductivity).....	78.6 micromhos at 25°C.
Calcium (Ca).....	11.4
Magnesium (Mg).....	1.6
Total iron (Fe).....	0.46

WATER ANALYSIS REPORT—Continued

(Parts per million)—Continued

Thompson River near Kamloops, B.C.—Continued

Soluble iron (Fe).....	0.03
Sodium (Na).....	1.8
Potassium (K).....	0.6
Carbonate (CO ₃).....	0
Bicarbonate (HCO ₃).....	39.8
Sulphate (SO ₄).....	6.9
Chloride (Cl).....	0
Fluoride (F).....	0.10
Nitrate (NO ₃).....	0.5
Silica (colorimetric) (SiO ₂).....	8.3

Using Table VII the main constituents are converted to e.p.m. and the error between anions and cations proportionately distributed as outlined below under "Palmer Classification", page 64.

Cations	p.p.m.	e.p.m.	Corrected e.p.m.	Anions	p.p.m.	e.p.m.	Corrected e.p.m.
Ca	11.4	0.5689	0.5725	HCO ₃ as CO ₃	19.57	0.6523	0.6482
Mg	1.6	0.1316	0.1324	SO ₄	6.9	0.1437	0.1428
Na	1.8	0.0783	0.0788	Cl	0	0	0
K	0.6	0.0153	0.0154	NO ₃	0.5	0.0081	0.0081
Fe	0.03			F	0.1
	15.43	0.7941	0.7991		27.07	0.8041	0.7991

The calcium combines first with the carbonate ion to form 0.5725 e.p.m. CaCO₃ leaving 0.6482 - 0.5725 = 0.0757 e.p.m. CO₃⁼; 0.0757 e.p.m. magnesium ions are considered to combine with this CO₃⁼ to give 0.0757 e.p.m. MgCO₃ leaving 0.0567 e.p.m. Mg⁺⁺. The 0.0567 e.p.m. Mg⁺⁺ are now combined with 0.0567 e.p.m. SO₄⁼, since there is no hydroxide, leaving 0.1428 - 0.0567 = 0.0861 e.p.m. of SO₄⁼. All the Na (0.0788 e.p.m.) now is combined with 0.0788 e.p.m. SO₄⁼ giving 0.0788 e.p.m. Na₂SO₄, leaving 0.0073 e.p.m. SO₄⁼; 0.0073 e.p.m. K form 0.0073 e.p.m. K₂SO₄ leaving an excess of 0.0081 e.p.m. K which are then combined with 0.0081 e.p.m. NO₃⁼ to give 0.0081 e.p.m. KNO₃. The 0.03 p.p.m. iron may be considered present as 0.09 p.p.m. Fe₂O₃.

The analysis expressed as hypothetical combinations then becomes:

	e.p.m.	Equivalent weight	p.p.m.
CaCO ₃	0.5725	× 50.04 =	28.65
MgCO ₃	0.0757	× 42.16 =	3.19
MgSO ₄	0.0567	× 60.19 =	3.41
Na ₂ SO ₄	0.0788	× 71.03 =	5.60
K ₂ SO ₄	0.0073	× 87.13 =	0.64
KNO ₃	0.0081	× 101.11 =	0.82
	0.7991		42.31
		SiO ₂ (colloidal)....	8.3
		Fe ₂ O ₃	0.09
		Total.....	50.7

The Association of Official Agricultural Chemists in their recent text (7th Edition, 1950), recommend combining NO₂⁼, NO₃⁼, BO₃⁼, and AsO₄⁼ ions with Na⁺, I⁻ and Br⁻ ions with K⁺,

and PO_4^- ions with Ca^{++} . They then assign residual basic ions in the following order: NH_4^+ , Li^+ , K^+ , Na^+ , Mg^{++} , Ca^{++} , Sr^{++} , Mn^{++} , Fe^{++} , and Al^{+++} with the anions Cl^- , SO_4^- , CO_3^- , and HCO_3^- . If there is insufficient carbonate to combine with all Ca^{++} , the residual Ca^{++} is joined to SiO_2 to form CaSiO_3 , and Mn^{++} , Fe^{++} , and Al^{+++} are then calculated as oxides.

Another method said to be widely employed, and occasionally used in this laboratory, is that employed by the Illinois Water Survey*. In this method, which is essentially the same as that recommended by the Association of Official Agricultural Chemists, K^+ , Na^+ , NH_4^+ , Mg^{++} , Ca^{++} , Fe^{++} , and Al^{+++} are combined in order with NO_3^- , Cl^- , SO_4^- , and then all residual bases are combined with CO_3^- . Employing this scheme, the hypothetical combinations of the analysis of the Thompson River, taking into consideration the iron and fluoride ions, become:

	e.p.m.	p.p.m.
CaCO_3	0.5740	28.72
MgCO_3	0.0715	3.01
MgSO_4	0.0613	3.69
Na_2SO_4	0.0789	5.60
K_2SO_4	0.0021	0.18
KF	0.0053	0.31
KNO_3	0.0080	0.81
FeCO_3	0.0011	0.06
	<hr/>	<hr/>
	0.8022	42.38
Silica.....	8.3
	<hr/>	<hr/>
Total.....		50.68

Fluoride has been combined in the above with potassium as if it were chloride ion.

It will be noted that the two schemes give very similar results. The greatest difference is in the manner of combining or reporting the iron, silica, and quantities of minor constituents.

PERCENTAGE OF CONSTITUENTS

Reporting the percentage of any constituent with regard to the total quantity of inorganic matter dissolved in a water has some advantage when comparing the quality of waters from different basins. This percentage may be calculated from the p.p.m. of each constituent and the total sum of constituents (p.p.m.), or from a formula per cent based on equivalents per million. The method used will depend upon the completeness of the analysis, the type of water, and the use to be made of the value determined. The former is generally used for waters low in ionized substances where analysis is quite complete, while the latter is more often used in technical studies, particularly of a geochemical nature.

The Thompson River analysis would then be reported as follows:

	Total Inorganic Matter		Formula** per cent
	p.p.m.	per cent	
Calcium.....	11.4	22.4	35.4
Magnesium.....	1.6	3.1	8.2
Sodium.....	1.8	3.5	4.9
Potassium.....	0.6	1.2	1.0
Iron.....	0.03	0.1	0.1
Carbonate.....	19.57	38.5	40.6
Sulphate.....	6.9	13.6	9.0
Fluoride.....	0.1	0.2	0.3
Nitrate.....	0.5	1.0	0.5
Silica.....	8.3	16.4	—
	<hr/>	<hr/>	<hr/>
Sum of constituents.....	50.80	100.0	100.0

This water contains mostly calcium carbonate but has a relatively high percentage of silica.

* Bartow, Wadden, Parr, and Palmer: The Mineral Content of Illinois Waters; University of Illinois Bulletin, vol. 6, No. 3.

** See also page 66.

ACCURACY AND ACCEPTABILITY OF ANALYTICAL RESULTS

The accuracy of a complete analysis is indicated by the error in balance between the constituents found in the water in appreciable quantities, including the acid radicals—sulphate, chloride, and nitrate, and the bases—calcium, magnesium, sodium, and potassium. Alkalinity in most waters is a measure of the excess of the bases over the strong acids and is generally due to bicarbonate, carbonate, or hydroxide ions.

The analytical results are chemically balanced in equivalents per million, in most cases to an accuracy of 1 to 2 per cent or better. The results are also checked by comparing residue on evaporation against sum of constituents, specific conductance against sum of constituents, or specific conductance against residue on evaporation. These methods of checking the accuracy of results are described below, the analysis of the Thompson River being used as an example.

It is emphasized that although all reported analyses show acceptable accuracy there may be traces of metallic and other ions present, such as copper, lead, zinc, aluminium, phosphate, and ammonia, that are not normally determined in the scheme of analysis used. These and others that are determined, such as iron, fluoride, and nitrate, may be in such small amounts as not to materially influence either the over-all accuracy, or the usefulness of the water except for very special purposes. Checking of analyses in the described manner will indicate if the water has in solution an appreciable amount of an ion that is not normally determined.

The criteria used to reject or accept analytical results on waters vary according to the purpose of the analysis, the accuracy of the methods used, extent of analysis, and the laboratory concerned. A criterion described some years ago by R. B. Dole* is considered by some workers to be somewhat exacting, especially for routine survey work. Otto M. Smith** used a less exacting standard in his survey of Oklahoma waters. Both these criteria are given in Table VIII.

TABLE VIII

Criteria for Rejecting or Accepting Analyses

Dissolved Solids		Maximum Excess				Maximum Error of Combining Values	
Not Less Than	Less Than	Determined T.D.S. (R.O.E.) over Sum of Constituents (S.C.)		Sum of Constituents over Determined T.D.S. (R.O.E.)			
p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	Per cent	Per cent
—	50	15*	23**	5*	8**	15*	22**
50	100	20	30	6	9	7	10
100	200	30	45	8	12	5	7
200	300	40	60	12	18	4	6
500	1,000	50	75	16	24	3	5
1,000	2,000	—	—	—	—	2	3

Generally, analytical results in the Mines Branch survey check without including silica (SiO_2) as silicate ion (SiO_3^-) well within the requirements of the criteria suggested by Dole. Most waters have balanced errors below 1 per cent. A few waters, generally those with a very low content of solids, have errors up to 4 or 5 per cent, but these errors also are usually within Dole's requirements.

* Quality of the Surface Waters in the United States. Part 1—Analyses of Waters East of the One Hundredth Meridian, by R. B. Dole, U.S. Geol. Surv., Water Survey Paper No. 236.

** The Chemical Analyses of the Waters of Oklahoma, by Otto M. Smith; Oklahoma Agricultural and Mechanical College, Division of Engineering. Publication No. 52 (1942).

DETERMINATION OF ACCURACY

Balancing Acidic and Basic Constituents

The results of an analysis reported in p.p.m. by the laboratory are grouped into acidic and basic constituents (anions and cations), converted to equivalents per million (Table VII) and the accuracy of the analyses is determined as illustrated below, the analysis of the Thompson River being used as an example.

	Cations	p.p.m.		Reacting value	=	e.p.m.
Calcium.....	Ca ⁺⁺	11.4	×	0.04990	=	0.56886
Magnesium.....	Mg ⁺⁺	1.6	×	0.08224	=	0.13158
Sodium.....	Na ⁺	1.8	×	0.04348	=	0.07326
Potassium.....	K ⁺	0.6	×	0.02558	=	0.01535
Sol. iron.....	Fe ⁺⁺	0.03	×	0.03581	=	0.00107
Total Cations.....		15.43				0.7951
	Anions	p.p.m.		Reacting value	=	e.p.m.
Carbonate.....	CO ₃ ⁻	0	×	=
Bicarbonate.....	HCO ₃ ⁻	39.8	×	0.01639	=	0.65232
Sulphate.....	SO ₄ ⁻	6.9	×	0.02082	=	0.14366
Chloride.....	Cl ⁻	0	×	=
Fluoride.....	F ⁻	0.1	×	0.05263	=	0.00526
Nitrate.....	NO ₃ ⁻	0.5	×	0.01613	=	0.00807
Total Anions.....		47.3				0.8093
Silica.....	SiO ₂	8.3				

Silica is not included with the anions since it is assumed to be present as colloidal silica (SiO₂) even though the test method is considered to measure dissolved or crystalloidal silica. Per cent error is

$$\frac{\text{Sum of cations (e.p.m.)} - \text{sum of anions (e.p.m.)}}{\text{Total ions (e.p.m.)}} \times 100 = \frac{-0.0142}{1.6044} \times 100 = -0.9 \text{ per cent.}$$

The results are therefore 0.9 per cent high on the anion side.

With some waters, especially alkaline waters or waters low in solids and relatively high in silica, it may be necessary to include the silica as silicate (SiO₃⁼) anion. In the above example, if silica is assumed to be present as silicate, the error is proportionately greater, at about -15.0 per cent. It is not customary to include silica as a silicate with this type of water.

Most chemists compare only the cations Ca, Mg, Na, and K against the anions CO₃, HCO₃, SO₄, Cl, and NO₃ and assume silica present as colloidal silica. Iron, too, is often assumed to be present in a colloidal form. Iron and fluoride are generally in such small amounts that they are not considered in the chemical balance.

Comparison of Residue on Evaporation or Residue on Ignition with Sum of Constituents

The residue on evaporation or residue on ignition, depending upon the drying and ignition temperatures, are to some degree a measure of the matter dissolved in water. Therefore, addition of all ions found in the water from a relatively complete analysis should agree closely with one of these values.

Because bicarbonates on evaporation and drying are precipitated as carbonates the bicarbonate must be converted to carbonate when calculating sum of constituents. Silica must also be included since it will be weighed as residue on evaporation and drying.

$$\begin{aligned} \text{In the above typical analysis: R.O.E.} &= 56.2 \text{ p.p.m.} \\ \text{R.O.I.} &= \frac{47.4}{8.8} \text{ p.p.m.} \\ \text{L.O.I.} &= 8.8 \text{ p.p.m.} \end{aligned}$$

Sum of Constituents:

Cations.....	=	15.4 p.p.m.
Anions		
SO ₄	=	6.9 p.p.m.
Cl	=	0 p.p.m.
F	=	0.1 p.p.m.
NO ₃	=	0.5 p.p.m.
HCO ₃ →CO ₃	= $\frac{39.8}{2.03}$	= 19.6 p.p.m.
Silica (SiO ₂)	=	<u>8.3</u> p.p.m.
		= <u>35.4</u> p.p.m.
Sum of Constituents (S.C.)	=	50.8 p.p.m.

Therefore, difference between R.O.E. and S.C. = $56.2 - 50.8 = 5.4$ p.p.m., that is, R.O.E. is in excess of S.C. by 5.4 p.p.m.

Many highly coloured waters and waters having a high loss on ignition show a closer check between S.C. and R.O.I. In many of the waters studied to date comparison between S.C. and a value midway between R.O.E. and R.O.I. gives a very close check, indicating that the presently recommended drying temperature of 105°C. is possibly somewhat too low and the ignition temperature of 500°C. somewhat too high.

In the above example, comparison against R.O.I. gives a difference of $47.4 - 50.8 = -3.4$ p.p.m. and comparison with a value midway between R.O.E. and R.O.I. = $\frac{(56.2 + 47.4)}{2} - 50.8 = 51.8 - 50.8 = 1.0$ p.p.m.

Comparison of Conductivity (E.C.) and R.O.E. or R.O.I.

An additional check on the analytical data may be obtained by comparing the specific conductance with the dissolved solids as determined by R.O.E. or R.O.I. It has been found by various workers that in many waters the ratio $\frac{\text{R.O.E.}}{\text{E.C.}}$ will be relatively constant, varying between 0.5 and 0.7, but generally giving quite close agreement on one particular type of water. The inherent nature of the tests and the type of water—whether it is highly coloured, whether non-carbonate hardness is present, etc.—will decide if the ratio will be about 0.5, 0.6 or 0.7 and whether the comparison is best made with R.O.E. or R.O.I.

In the above example—

$$\frac{\text{R.O.E.}}{\text{E.C.}} = \frac{56.2}{78.6} = 0.715$$

$$\frac{\text{R.O.I.}}{\text{E.C.}} = \frac{47.4}{78.6} = 0.60$$

$$\frac{(\text{R.O.E.} + \text{R.O.I.})}{2} = \frac{51.8}{78.6} = 0.66$$

Comparison of Sum of Constituents and Conductivity

Both these values are essentially a measure of the same quantity, namely, the amount of dissolved salts present, and should agree similarly as R.O.E. and conductivity when the interpretation of each value is considered. Since S.C. should compare with R.O.E. or R.O.I. the same value of the ratio with conductivity—that is, 0.6 to 0.7—should be found.

In the above example, the ratio is $\frac{50.8}{78.6} = 0.65$.

DETERMINATION OF ACCEPTABILITY OF ANALYTICAL RESULTS

The different methods of checking analyses should agree within certain limits. If they do not, re-examination of the water for possible error or for the presence of an appreciable amount of some constituent not normally determined is carried out.

It is difficult to lay down hard and fast rules for acceptability, since the type of water, method of analysis, and temperature of drying and ignition may all influence the balance obtained. Dole's original table, reproduced in Table VI, is based on a T.D.S. or R.O.E. dried at 180°C., and not at 105°C., as in the Mines Branch laboratory. For this reason it has generally been the practice to use either the R.O.I., if L.O.I. is small and apparently due to organic matter, or the value midway between R.O.E. and R.O.I., if the water has a high loss on ignition or is such that loss of water of hydration and appreciable breakdown of chlorides, etc., is suspected.

The principal means of checking an analysis is by the per cent error found. Considering the Thompson River example it will be noted that this water falls in the group with dissolved solids of not less than 50 p.p.m. but less than 100 p.p.m. In fact, if R.O.I. is used the dissolved solids may be considered as less than 50 p.p.m. The error permissible here is 7 or 15 per cent using Dole's values, and 10 or 22 per cent using Smith's figures. This analysis is, therefore, very acceptable. With this water, an excess of R.O.E. or T.D.S. over S.C. of 20 p.p.m. (Dole) and 30 p.p.m. (Smith) is permitted. Therefore, the analysis is again acceptable, since the difference found is only 5.4 p.p.m.

If R.O.I. instead of R.O.E. is used for comparison, S.C. is in excess by 3.4 p.p.m. Dole permits 6 p.p.m. excess and Smith 9 p.p.m. in this case. Thus the analysis again checks satisfactorily.

INTERPRETATION OF ANALYTICAL RESULTS

The value of any analysis is determined by its accuracy, and by the extent to which the information can be interpreted for different purposes.

Any water analysis may be divided conveniently into four groups, namely:

1. Determination of physical and other characteristics.
2. Determination of suspended and other non-ionized matter.
3. Determination of dissolved (ionized) matter.
4. Determination of plant life, bacteria, etc.

The fourth determination is concerned primarily with the potability of a water and is not made in the Mines Branch laboratories since it is essentially a separate study. Most work of this kind is done by the provincial departments of health, particularly on supplies for municipal use. Biological studies including the microscopic examination of waters to determine the extent and nature of plant life such as algæ and plankton also require special treatment, since very frequent and on-the-spot examination is necessary. No such study has been attempted in this survey even though plant life does cause taste, odour, and other problems in certain uses.

Some comments on the methods and results of analyses for the first three groups of tests are given here to assist in interpreting the results being published in Water Survey Reports. Only brief remarks on the effect of the various constituents on the usefulness of a water are included.

GROUP 1: PHYSICAL CHARACTERISTICS

The major physical characteristics determined as routine in the present survey are temperature, colour, and turbidity. Some report of odour is made if this is very apparent. Some surface tension tests have been made; pH and electrical conductivity are included in this group although they are not truly physical characteristics.

Temperature

It is of value to certain industries to know the range of water temperature since, for cooling and condensing purposes, low temperatures are necessary. High temperatures in surface waters during the summer also accelerate the growth of plant life and bacteria. Also, an abnormally high water temperature may indicate excessive use of the water by industries, causing possible contamination and increased need of cooling for re-use.

Many values such as pH and various equilibria change with temperature, and thus the interpretation of some test results depends upon knowing the temperature at which the tests were carried out. In most survey reports this is room temperature, but in the field the temperature varies between sampling temperature and air temperature. This partly accounts for the variations, especially in pH and alkalinity, often found between field and laboratory results.

Odour and Taste

Odour is not normally determined in routine survey work, but samples that have a decided odour are noted. Odour and taste are intimately related, both being important in many water uses such as in the household, in the manufacture of pharmaceuticals, and in the food industry.

Since many odours may appear and disappear rapidly, odour should be determined as soon as the water is sampled. Algæ, decomposing vegetation, pollution, industrial trade wastes, etc., may all cause characteristic odour and tastes in water. Storage for any period may cause either intensification or loss of odour.

pH

pH, a measure of the hydrogen-ion concentration, is the negative exponent of the logarithm of the hydrogen-ion concentration. Therefore, a low pH has a greater hydrogen concentration and is more acid, as shown in Table IX; pH 7 is neutral; pH less than 7 is on the acid side; and pH greater than 7 is on the alkaline side. Most surface waters are in the pH range 6.0 to 8.0, the majority being slightly on the alkaline side. Ground waters, owing to their high carbonic

acid content, are more often slightly acid. Some natural waters may also have free mineral acidity present and a low pH. Although the quantitative measure of the alkalinity or acidity of a water is determined by titration with standard acids or bases, this does not give the concentration of hydrogen ions present. Rather, it reports the quantity available if neutralized to a definite end point (*See Acidity*, p. 54).

pH is quickly and accurately determined but should be done as soon as possible after sampling. The pH of a water depends upon the quantity and state of dissolved salts and the extent of ionization of these or hydrolysis. In many waters salts are held in solution only as bicarbonates by the so-called half-combined carbon dioxide. There is also present a varying amount of so-called free or aggressive carbon dioxide which in water is dissolved as carbonic acid, a weak

TABLE IX
pH and Hydrogen-ion Concentration

pH	H ⁺ *	
n·00	1·0 x 10 ⁻ⁿ	
n·05	8·91 x 10 ⁻⁽ⁿ⁺¹⁾	
n·10	7·94 x 10 ⁻⁽ⁿ⁺¹⁾	
n·15	7·07 x 10 ⁻⁽ⁿ⁺¹⁾	
n·20	6·31 x 10 ⁻⁽ⁿ⁺¹⁾	
n·25	5·62 x 10 ⁻⁽ⁿ⁺¹⁾	
n·30	5·01 x 10 ⁻⁽ⁿ⁺¹⁾	
n·35	4·46 x 10 ⁻⁽ⁿ⁺¹⁾	
n·40	3·98 x 10 ⁻⁽ⁿ⁺¹⁾	
n·45	3·54 x 10 ⁻⁽ⁿ⁺¹⁾	
n·50	3·16 x 10 ⁻⁽ⁿ⁺¹⁾	
n·55	2·82 x 10 ⁻⁽ⁿ⁺¹⁾	
n·60	2·51 x 10 ⁻⁽ⁿ⁺¹⁾	
n·65	2·24 x 10 ⁻⁽ⁿ⁺¹⁾	
n·70	1·99 x 10 ⁻⁽ⁿ⁺¹⁾	
n·75	1·78 x 10 ⁻⁽ⁿ⁺¹⁾	
n·80	1·58 x 10 ⁻⁽ⁿ⁺¹⁾	
n·85	1·41 x 10 ⁻⁽ⁿ⁺¹⁾	
n·90	1·26 x 10 ⁻⁽ⁿ⁺¹⁾	
n·95	1·12 x 10 ⁻⁽ⁿ⁺¹⁾	
(n+1)·00	1·00 x 10 ⁻⁽ⁿ⁺¹⁾	
		Examples:
		(1) pH = 2·65
		n = 2
		pH 2·65 = 2·24 x 10 ⁻⁽ⁿ⁺¹⁾
		= 2·24 x 10 ⁻³ mols hydrogen-ion
		per litre.
		(2) pH = 9·55
		n = 9
		pH 9·55 = 2·82 x 10 ⁻⁽⁹⁺¹⁾
		= 2·82 x 10 ⁻¹⁰ mols hydrogen-ion
		per litre.

* Hydrogen-ion concentration in mols per litre (gram-molecular weights per litre.)

acid. The amount of free carbon dioxide varies with temperature, pressure, and the amount and character of other salts affecting the equilibrium. Therefore, pH will also change rapidly owing to loss or gain of CO₂, with variation in temperature, atmospheric pressure, etc. Aeration will disturb the vapor pressure of CO₂ to a marked extent. The change in pH is most marked in surface waters of low hardness and low total solids, and in ground waters high in CO₂. During determination of pH on these waters the change is continual, pH drifting rapidly until final stabilization of the equilibrium at room temperature is reached. Substances such as ferrous iron will cause drifts in pH owing to oxidation when waters containing them are exposed to air. In some waters there is present a sufficient amount of so-called buffer salts, which ionize or hydrolyze to keep the pH constant. All these factors, particularly storage time and temperature, must be considered when interpreting reported pH values.

pH is of major importance in many uses since it is partly a measure of the various equilibria. It is used as a control tool in many applications, such as in the control of corrosion by adjustment of the Langelier saturation index (which is discussed more fully on page 67), in the coagulation and treatment of water supplies, and in many processes such as bleaching, dyeing, brewing,

photography, electroplating, ore dressing, and photo-engraving. The determination of pH of water is, therefore, very useful and will, if properly interpreted with other determined values, assist greatly in assessing the usefulness of a water.

Colour

A major problem for many uses arises from the colour of the process water. The effect of high colour depends largely upon the type of colour and what causes it. Much of the colour in highly coloured natural waters is considered to be due to humic acid and organic matter leached from decaying vegetation, including various tannins and other vegetable dyes. In some waters iron or manganese compounds are thought to be combined either loosely or intimately with these tannins or organic acids. This colour, which is essentially colloidal, can cause serious trouble in many industrial processes such as the production of fine papers, white textiles, pharmaceutical products, and steam.

In some uses certain colouring matter is said to be advantageous. For example, the adsorptive and coagulative action of some of the coloured colloids is said to aid in the prevention of scaling in boilers. Colouring matter that has dispersive properties may seriously interfere with removal of hardness, especially by hot-process, lime-soda softeners. In many other uses the colour causes only an æsthetic effect by lowering the attractiveness and consequently the high grade of the product. In municipal water supplies and in artificial ice manufacture, for example, these humates make the product less acceptable to consumers. A colour of less than 10 p.p.m. generally causes no trouble in domestic water supplies. Certain swamp waters may have colours of 200 p.p.m. or greater that must be removed before the waters can be used for many purposes.

Iron and manganese compounds, such as the bicarbonates, not only cause coloration but the salts may precipitate out and give rise to even more serious problems. In more polluted waters colour may be caused by trade wastes and sewage, which may also be poisonous and injurious to health.

Tests for colour are based primarily on one shade of colour standard and no acceptable simple tests are available to distinguish the compounds causing colour. The standard colours do not always match the natural colours found, and if any turbidity is present a serious error will arise. Since many of the colouring materials are colloidal they may segregate and settle out, be absorbed by other suspended material, or be bleached by sunlight, so that colour determinations should always be carried out as soon as possible after sampling.

"True" colour, which is a measure of the colour of a water caused by substances in solution is determined only if all suspended matter has been removed, that is, if the turbidity is zero. Where the turbidity is greatly in excess of 3 p.p.m., suspended matter is considered to seriously interfere and a true value for colour is not obtained. It is difficult to get an absolutely true colour when there is high colloidal turbidity. This must be removed by centrifuging or settling, as all filtering materials tend to remove colour to some extent. Even the settling of suspended matter may absorb some colour.

Owing to the nature of the test and its limitations, many colour values must be accepted with reservation. The personal error in judging colours, changes on standing, difficulty with turbidity, etc., all tend to make the value in many instances something of an approximation. Even so, colours above a certain value do have deleterious effects and must be removed. For control of process water, colour determinations carried out with the same standard and by the same worker under similar conditions are of value once the desired limiting colour value has been set.

"Standard Methods", taking certain of these errors into account, considers colour should be expressed only in whole numbers as follows:

Colour between	Record to nearest
1 and 50 p.p.m.	Unit
51 and 100 p.p.m.	5
101 and 250 p.p.m.	10
251 and 500 p.p.m.	20

Turbidity

As previously noted, turbidity as determined depends partly on the particle size of the suspended matter, and is not an accurate measure of the amount. It is readily seen that aggregation or settling of particles, or loss or adsorption of colour on such particles in storage, will influence the turbidity measurement, which, therefore, should be carried out immediately after sampling.

As with colour, the personal error when determining turbidity by accepted methods may be appreciable. Consequently, values reported must be interpreted as being somewhat in the order of the value given, even though the standard adopted from "Standard Methods", page 14, is as follows:

Turbidity between	Record to nearest
0 and 1 p.p.m.	Tenth
1 and 10 p.p.m.	Unit
11 and 100 p.p.m.	5
101 and 400 p.p.m.	10
401 and 700 p.p.m.	50
700 p.p.m. and greater	100

Turbidity affects virtually all uses of a water, the effect depending largely upon whether it is due to clay, silt, or other soils, to bacterial decomposition products, to iron oxides, to finely divided organic matter, to microscopic organisms, or to trade waste products or other pollution. No tests are normally made in routine survey studies to differentiate the type of turbidity or its cause. For almost all uses, turbidity, which in each water has some relation to suspended matter, will cause trouble and must be removed or decreased to a limiting value.

Conductivity (Specific Conductance)

Determination of specific conductance of an aqueous solution containing dissolved matter is one of the more useful tools in control of water as a raw material for many uses and in the interpretation of a water analysis.

All aqueous solutions containing any dissolved mineral matter have the property of conducting an electrical current. Measurement of the current under standardized conditions gives a physical constant for each solution, known as specific conductance or conductivity. This constant, although giving a measure of the amount of dissolved matter, gives no indication of the relative quantities of substances present.

The conductance of a water varies with the amount of dissolved gases and with the amount, nature, and degree of ionization of the ionized components (electrolytes) present. It varies also with the ion (that is, whether OH^- or SO_4^- ion), the temperature, and with possible hydration or combination of ions. Some substances that are only partly ionized affect the conductivity very slightly. Generally, the specific conductance of a solution decreases with dilution and increases with temperature—on the average about 2 per cent per degree Centigrade rise. Thus, two waters having the same amount of dissolved matter by weight may yet have different conductivities. However, there is usually for one water, such as a river, a relatively constant relationship between the amount of dissolved matter or sum of constituents and conductivity, so that any major change in mineralization of the water is quickly noted. This ratio is usually

$$\frac{\text{R.O.E. or R.O.I. (dissolved solids in p.p.m.)}}{\text{Conductivity in micromhos at } 25^\circ\text{C.}} = 0.6 \text{ to } 0.7$$

The determination is therefore very useful for purposes of process control and as a measure of the changing mineralization of waters.

GROUP 2: INSOLUBLE MATTER

Dirt and other insoluble matter in a water must be removed before the water can be used for most purposes, the extent of removal depending upon the specific end use. Thus, the amount of filtering, the rate of filter-bed back-wash, and other operations are dependent upon the nature and amount of insoluble matter present. Some laboratories carry out a "filtrability" or "determination of resistance to filtration" test to indicate the effect of different suspended matters on filters.

The amount of suspended matter in a surface water, such as a river, will generally vary more widely than any other value. Such variation may be hourly, seasonal, with river flow, with wind direction, or with location and depth of sampling. Some laboratories do no tests to indicate the amount of turbidity or suspended matter present. However, some indication of the amount of matter carried in suspension is believed of advantage, even recognizing the inherent error and variability of the determination.

A small amount of some dissolved salts may be removed by filtration, or by settling of the suspended matter, owing to occlusion and adsorption on the suspended particles. In waters turbid with fine colloidal matter it is difficult to remove all suspended matter and there may be some inclusion of small amounts of suspended matter reported as residue on evaporation (dissolved solids). When interpreting analyses on these turbid waters the above points should be kept in mind, especially when comparison is being made with analyses of clearer samples.

Removal of suspended matter by coagulation and filtering removes most of the pathogenic organisms present, the remainder being killed by chlorination, so that the water is safe for domestic use.

The impurities that may be suspended in natural water vary from colloidal to very large particles that are held in suspension by the turbulence or velocity of the water. The latter is often referred to as sediment-load. Silt or suspended matter is not an uncommon constituent in some ground waters. Such insoluble matter may be any type of soil or rock with which the water has been in contact, decaying vegetation particles, larger living or dead organisms, iron oxide, various types of trade waste, municipal sewage, fibres, etc.

No attempt has been made in these studies to distinguish the type of suspended matter except that ignition gives some indication of the amount of organic material present.

A study of the amount and to some extent of the character of sediment or suspended load is normally carried out as a special sediment study requiring special apparatus and technique in sampling and the collection of many samples, usually one to three a day, but hourly at times of rapid flow changes.

GROUP 3: DISSOLVED OR IONIZED MATTER

Residue on Evaporation, Loss on Ignition, Dissolved Solids, Sum of Constituents

Evaporation of a clear water having no turbidity or suspended matter should, theoretically, leave all materials that were dissolved in the water, hence the original use of the terms "total dissolved solids" or "dissolved solids" for this value. However, any fine colloidal matter, including colour, colloidal silica, and other organic matter such as micro-organisms, will also be reported as dissolved matter on evaporation to dryness of many waters. In most cases this error is quite small.

Various temperatures have been used to dry the residue, although most water analysts dry at 103°, 105°, or 110°C. In this survey 103° to 105°C. was used, since this is the standard recommended by "Standard Methods". However, other workers use 180°C., claiming that drying at that temperature to constant weight or even for one hour is preferable, since practically all the water of crystallization and that mechanically held by residues of ordinary amount from the usual types of natural waters are driven off. Virtually all organic matter is said to be more or less carbonized and the residue is reduced in weight when dried at 180°C., but at this higher

temperature greater breakdown of some chloride and carbonate salts is more likely. Thus, evaporation to dryness of a natural water will not necessarily give the true value of dissolved salts present, since the amount of water of crystallization and water of hydration lost, the amount of occluded water retained, and the breakdown of salts such as carbonates, chlorides, etc., depend upon the temperature of drying and the type of water under study.

With certain types of waters it has been reported that the value of residue on evaporation will agree closely with the sum of constituents as found by analysis. This is usually true of clear colourless water of moderate concentration, bicarbonate in nature, if the bicarbonate is converted to the corresponding carbonate when computing the sum of constituents. Residue on evaporation of these waters will therefore have the same usefulness as specific conductance and will agree with that value. Other waters, in particular those containing appreciable quantities of calcium sulphate and calcium chloride, may have a residue greater than the sum of constituents, and waters high in magnesium carbonate or very high in nitrate may have residues on evaporation lower than the sum. As might be expected, in highly coloured water containing appreciable organic matter or organic acids the sum of constituents may agree more closely with the residue on ignition. With some waters closer agreement is noted between the sum of constituents and a value intermediate between residue on evaporation at 105°C. and residue on ignition at 500° to 550°C. The sum of constituents may, therefore, be considered a more accurate value for the dissolved solids than residue on evaporation in all waters where the analysis carried out is relatively complete and accurate, and when silica and iron are properly considered. Residue on evaporation, however, is of value in many analyses—provided the above limitations are recognized—especially for checking the accuracy of the analytical procedure as discussed under "Acceptability of Results".

Residue on ignition is similarly dependent, in varying degrees, upon the temperature of ignition and type of water being tested.

Loss on ignition in the past was often erroneously called organic matter. Although loss on ignition often indicates the loss due to burning of carbonaceous organic matter, there may be appreciable error with some waters owing to varying loss or retention of water of hydration and breakdown of carbonates, chlorides, etc.

There seems to be a need for a complete restudy of this matter, and for the use of the same drying temperature by all chemists. Residue on evaporation is at present used to check the accuracy of an analysis, though conductivity will serve the same purpose, and to determine the amount of dissolved material that would deposit on land or in reservoirs. It would perhaps be more accurate in this latter case to allow the water to dry at a temperature more akin to that found in the atmosphere in the locality under study. Then, by adding the amount of suspended matter to this value or by evaporation of the shaken sample, the amount of total matter deposited would be determined.

In comparing results reported by various laboratories on residue on evaporation, residue on ignition, dissolved solids per acre-foot, or dissolved solids carried per day by a stream, the above remarks should be kept in mind since, unless the temperature and method of drying and of ignition are similar, quite wide variations may be found for these values on the same water.

Alkaline Earths

Calcium and magnesium are the alkaline earths usually found in appreciable amounts in natural waters and they may be accurately determined. Their presence is due to the action of carbon dioxide and water on limestone, dolomite, clays, and other soils and rocks. They are usually present in water as calcium and magnesium bicarbonates, sulphates, or chlorides, these being the main salts causing hardness in water supplies. Calcium carbonate and magnesium carbonate are only sparingly soluble in water unless sufficient carbon dioxide is present to dissolve them as bicarbonates. There are, in a water, equilibria between these salts and carbon dioxide according to the following equations: $\text{Ca}(\text{HCO}_3)_2 \rightleftharpoons \text{CO}_2 + \text{CaCO}_3 + \text{H}_2\text{O}$; $\text{Mg}(\text{HCO}_3)_2 \rightleftharpoons \text{CO}_2 + \text{MgCO}_3 + \text{H}_2\text{O}$. Important factors in these equilibria are pH, alkalinity, and temperature.

Natural waters usually contain little or no strontium and barium, but, if present, they will be included as calcium unless care is taken in analysis. Similarly, a large excess of magnesium over calcium may cause trouble in determining calcium unless the latter is re-precipitated. In most waters so far studied calcium is appreciably greater than magnesium.

Hardness

Hardness of water supplies presents one of the most important problems in the use of water. Soap, instead of forming a lather as a sodium stearate, oleate, etc., reacts with the alkaline-earth salts ($\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$, CaSO_4 , etc.) to form calcium and magnesium stearates and oleates, which being insoluble settle out as the familiar curd. Thus, in hard water much soap is used in softening the water, before advantage can be taken of its cleansing and lathering properties.

In this survey, waters of various hardnesses are classified as follows:

- Hardness of 1 to 60 p.p.m. as CaCO_3 —soft water*
- Hardness of 61 to 120 p.p.m. as CaCO_3 —medium-hard water
- Hardness of 121 to 180 p.p.m. as CaCO_3 —hard water
- Hardness greater than 180 p.p.m. as CaCO_3 —very hard water

Medium-hard waters are satisfactory for most uses except in high pressure boilers and in some industrial processes. When the upper range of hardness, classification on 121 to 180 p.p.m., is reached, softening is usually necessary and economical, and waters with about 200 p.p.m. hardness definitely require softening for most purposes.

Total hardness in a water in regard to its capacity to consume or precipitate soap is also due to the presence of iron, aluminium, strontium, barium, zinc, manganese, brines, and free acids. Normally, these are present in insignificant amounts and the hardness reported is due to the calcium and magnesium ions only, except in acid waters containing appreciable quantities of iron, aluminium, and manganese. In very few analyses in this survey is there enough iron dissolved in the water to influence the total hardness value appreciably in so far as this is industrially important. Besides being classified into hardness due to calcium salts, "calcium hardness", and hardness due to magnesium salts, "magnesium hardness", hardness is also grouped into carbonate or non-carbonate hardness.

Carbonate hardness, formerly called "temporary" hardness, is due to carbonates or bicarbonates of calcium and magnesium and is known from the determination of alkalinity in a water in which the alkalinity is due to hydrolysis of these salts. The non-carbonate hardness, due to alkaline earth sulphates or chlorides, is not removed by boiling and was formerly called "permanent" hardness. Alkalinity is normally expressed as p.p.m. CaCO_3 and is therefore equivalent in bicarbonate waters to the carbonate hardness. Subtraction of this from the total hardness will give the amount, if any, of non-carbonate hardness. When the total hardness as p.p.m. CaCO_3 is equal to or less than the total alkalinity, no non-carbonate hardness is present. The total hardness is then all carbonate hardness and the difference, if any, between the two is sodium bicarbonate.

These "sodium bicarbonate" waters are usually soft. They are often specially noted in Water Survey Reports and a separate alkalinity figure is included in the reported analysis, or this figure may be determined by dividing the figure for bicarbonate by 1.22. In acid waters the hardness is all non-carbonate. In the Water Survey Reports, total hardness and non-carbonate hardness are tabulated, and alkalinity and carbonate hardness are readily determined by subtraction of the non-carbonate hardness value from the total hardness figure as illustrated below.

In past analyses, and in many still being published, hardness of a water is reported as p.p.m. CaCO_3 based on the standard soap solution test. Much work has been done over the years on this test and on a somewhat similar test using a palmitic acid solution, and for some time tests by one or both of these methods were carried out in the mobile field laboratory. Comparison of

* Below 30 p.p.m. as CaCO_3 is sometimes classed as "very soft".

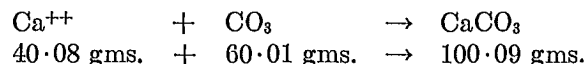
the results so obtained with values of hardness calculated from the determination of the amounts of all ions contributing to hardness strengthens the view that the soap test does not necessarily represent the true amount of hardness-producing salts, as the agreement between the results is often poor. Inherent in this soap test are possible errors, including the personal factor involved and a salt effect in highly mineralized waters. The soap test appears to give only a value for the consumption of soap and it is believed should be called the "soap-consuming power". With certain waters this is equivalent to the amount of hardness salts that would cause incrustation in boilers, piping, etc., but in other waters this does not appear to be so.

The direct titration of hardness using an organic sequestering agent, as discussed above, under hardness, page 30, in the Mines Branch laboratory is now being used and close agreement has been obtained on most waters between the value determined by this method and that calculated from the amount of calcium and magnesium found by direct analysis. Since early in 1950, hardness determined on water immediately after sampling in the field has been carried out by means of this titration method.

There are few processes in which the hardness of a water is not important. In the municipal use of water its effect on soap consumption is readily apparent; in steam making, and in the use of water as coolant, hardness causes increased scaling and plugging of lines, condensers, etc. Hard water affects dyeing and washing of textiles, leather tanning, electroplating, photographing, beverage manufacture, etc. In some processes such as brewing, however, a certain amount of non-carbonate hardness is beneficial.

Calculation of Hardness of Waters

In natural waters the more common compounds that cause hardness are normally expressed as equivalent p.p.m. of CaCO_3 .



That is, every part of Ca^{++} present is equivalent to $\frac{100.09}{40.08} = 2.497$ or 2.5 parts CaCO_3 , and

every part of Mg^{++} present is equivalent to $\frac{100.08}{24.32} = 4.11$ parts CaCO_3 . Iron or any other

heavy metal or alkaline earth will cause hardness, and its equivalent as p.p.m. CaCO_3 may be similarly calculated: usually these are present in such small amounts as not to influence the total hardness appreciably and are not considered. Iron, if present, will usually be in the form of ferrous bicarbonate, and the iron hardness as CaCO_3 is determined as follows:

$$\text{Fe (p.p.m.)} \times \frac{100.09}{55.85} = \text{Fe (p.p.m.)} \times 1.8.$$

Thompson River water (analysis, page 37) has 11.4 p.p.m. Ca^{++} and 1.6 p.p.m. Mg^{++} . The hardness due to calcium is, therefore, $11.4 \times 2.497 = 28.47$ p.p.m. expressed as CaCO_3 . The hardness due to magnesium is $1.6 \times 4.11 = 6.58$ p.p.m. as CaCO_3 . Total hardness in this water is:

Calcium hardness	=	28.47 p.p.m. as CaCO_3
Magnesium hardness	=	6.58 p.p.m. as CaCO_3
Iron hardness	=	0.05 p.p.m. as CaCO_3
Total hardness	=	<u>35.10</u> p.p.m. as CaCO_3

The hardness is also readily calculated from equivalents per million by adding the e.p.m. of all hardness-producing salts and multiplying by 50 to give total hardness as p.p.m. CaCO_3 ; for example, in the above water $(0.5689 + 0.1316 + 0.0011) \times 50 = 0.7016 \times 50 = 35.1$.

The alkalinity to methyl orange reports alkalinity due to bicarbonates, carbonates, and hydroxides. The hardness cations are usually present as compounds with bicarbonates and carbonates, and the alkalinity expressed in terms of p.p.m. CaCO_3 is therefore equivalent to the hardness due to carbonates. Any remaining hardness is due to the presence of CaSO_4 , MgSO_4 , CaCl_2 , etc., that is, it is non-carbonate hardness.

In the example analysis:

Alkalinity = carbonate hardness	=	32.6 p.p.m. as CaCO_3
Non-carbonate hardness.....	=	2.5 p.p.m. as CaCO_3
		—
Total hardness.....	=	35.1 p.p.m. as CaCO_3

The hardness is also readily determined by adding together all magnesium, calcium, and iron salts reported by hypothetical combinations. The analysis, page 39, had $\text{CaCO}_3 = 28.72$ p.p.m.; $\text{MgCO}_3 = 3.01$ p.p.m.; $\text{MgSO}_4 = 3.69$ p.p.m.; and $\text{FeCO}_3 = 0.06$ p.p.m.

The MgCO_3 , MgSO_4 , and FeCO_3 must be converted to CaCO_3 . Then,

	CaCO_3	=	28.72 p.p.m. CaCO_3
MgCO_3 , 3.01×1.19		=	3.58 p.p.m. CaCO_3
MgSO_4 , 3.69×0.831		=	3.07 p.p.m. CaCO_3
FeCO_3 , 0.06×0.864		=	0.05 p.p.m. CaCO_3
			—
Total hardness		=	35.42 p.p.m. CaCO_3

This differs somewhat from previous values, owing to balancing out of analytical error when calculating ions in the hypothetical combinations.

Alkalis

The principal alkalis determined in any water analysis are sodium and potassium. Lithium may also be present in small quantities in some waters. All the common alkali salts are water-soluble and an excess of these increases the total solids content and also the cost of treatment, since the removal of alkali salts is expensive. A high concentration of sodium chloride or other alkali salts may make waters unfit for use because of taste, reaction with other compounds in the industrial process, excessive corrosion, etc. If a water is high in potassium salts it is an important indication of a possible source of potash mineral in the drainage basin. Potassium salts are reported as being more suitable than sodium salts in boiler feedwater treatment and, therefore, high potash waters are preferred.

Most Canadian waters are low in alkalis, except certain ground waters. The ratio of sodium to potassium has been found to be about 2 to 1 or 3 to 1 in most waters studied to date. A high proportion of sodium to other positive ions (cations) is detrimental to crops and limits the use of waters for irrigation.

Initially, the alkalis were determined gravimetrically and all were reported as sodium. In a few cases where no alkalis were determined these have been calculated by assuming all difference between the acids and bases to be due to sodium. Since this is common practice with some analysts and there is, therefore, little check on the accuracy of the analysis, the results reported must be interpreted with this in mind. More recently, sodium and potassium have been determined separately and with greater accuracy in this survey by using the flame photometer.

Metals

Heavy metals are not normally determined in routine survey work even though traces of these may play a more important part in some uses than is generally recognized. For example, traces of copper may accelerate corrosion of iron, aluminium, and galvanized piping, and traces of certain metals are injurious in plating baths. Limits are placed on the amount of Cu, Pb, etc., in water to be used for drinking and cooking. Lead dissolved from lead piping by waters containing free carbon dioxide may have a toxic effect.

Aluminium is often determined in water analyses by precipitating the iron and aluminium group, volatilizing silica, weighing as mixed oxides, and making proper allowance for iron in the precipitated oxides before computing aluminium. In most natural waters the aluminium, and even the iron content, is so small as not to affect materially the over-all chemical balance. Aluminium in small amounts has little known effect in the use of water and its determination was therefore omitted for the sake of speed in the survey.

Iron even in small amounts raises problems in many uses of water and the limit of iron content permitted in many process waters is very low. Iron may be present in water as a soluble salt or possibly in combination with organic acids, as, for example, in colour. Usually if in appreciable amount it is present as the ferrous bicarbonate. Basic waters containing more than 1 p.p.m. ferrous iron in solution normally soon develop a reddish turbidity, often colloidal, by oxidation of the iron to ferric oxide. If this oxidation occurs while the water is being used it will cause staining of fabrics and porcelain, discoloration of dyes, textiles, and paper, and corrosion of materials. Because of this oxidation most surface waters, unless they are quite acid and the iron is present as a soluble chloride or sulphate, seldom contain more than 0.5 p.p.m. iron. However, ground waters may have up to 10 p.p.m. Iron compounds react with soap to precipitate iron stearates and oleates. Thus, if in appreciable quantity, the amount of soluble iron present must be taken into account as a hardness-producing salt when calculating total hardness.

The accurate determination of iron should be done in the field immediately after sampling because of precipitation by oxidation. Normally, in the Mines Branch laboratory, dissolved iron only is determined in relatively clear waters unless it is apparent that some iron oxide has already precipitated, in which case a total iron is also determined. In such clear waters it can be assumed that the precipitated iron was originally in solution. With turbid waters, however, although a determination of dissolved iron indicates only the iron remaining in solution, total iron may be very high because of the inclusion of iron from suspended matter, colour, etc. This error is not usually large in assessing the industrial usefulness of a water, since the dissolved iron reported is the iron that normally remains after coagulation and filtration of turbid surface waters and before use by an industry.

Some ground waters used by industries contain large quantities of dissolved iron, and it is with these that interpretation of the loss of iron by oxidation is important. Total iron reported for these waters can be assumed as having been in solution originally. However, it is difficult in many cases to obtain samples of these ground waters in which some iron has not already been precipitated and lost owing to aeration at the pumps, etc. Another factor that may give a high iron value is determination as total iron of rust particles from piping, well casings, and pumps.

Manganese (Mn) occurs less commonly than iron, but in natural waters the above comments regarding iron and its determination are equally applicable. Manganous compounds will be oxidized and precipitated as various brown to black oxides or hydrated oxides.

In most surface waters examined to date manganese has not been present in appreciable amount and testing for manganese is carried out only when its presence is suspected from the type of precipitate found or from its interference in other test methods.

Manganese may be present in appreciable quantities in acid mine waters and has been found in surface waters naturally filtered through gravel before pumping for use.

Acidity

Although acidity is seldom found in natural waters here surveyed, some waters may be acid owing to uncombined or free carbon dioxide. Others, notably acid mine waters, may be acid owing to hydrolysis of iron and aluminium sulphate and other salts present. Free mineral acid may also be present in these waters.

The literature reports coloured waters that appear to be acid owing to the presence of organic acids. As these acids may be in equilibrium with or combined with bases, such acidity is not normally determined and an error in chemical balance of the analysis will result.

Certain analysts calculate free acidity from pH, but this is not satisfactory for waters high in iron and aluminium salts. No attempt is made to report acidity in this survey.

Alkalinity (Bicarbonates, Carbonates, Hydroxide)

Alkalinity is often referred to as the measurement of the excess of the bases present over the strong acids (chloride, sulphate, and nitrate).

In most Canadian surface waters the principal negative ion (anion) is the bicarbonate. The bicarbonate salts and small quantities of other salts impart by hydrolysis a definite amount of alkalinity to a water. The alkalinity in waters of higher pH (phenolphthalein alkalinity), however, may be due to carbonates which are then slightly soluble or to free hydroxide, which is usually found only in treated waters with quite high pH—for example, in boiler waters. The alkali carbonates and bicarbonates are soluble and are found, sometimes in large amounts, in waters from deep wells near oil fields or from areas of alkali-containing soil.

To date, most Canadian surface waters have shown no phenolphthalein alkalinity, that is, all alkalinity is due to bicarbonates, usually the bicarbonates of the alkaline earths and iron. The alkalinity is then equal to the carbonate hardness, since both are reported as p.p.m. CaCO_3 . In the Water Survey Reports alkalinity is not usually reported, but can be found from the bicarbonate by multiplying by 0.82; it is equal to or greater than the carbonate hardness as reported.

In some waters part of the alkalinity reported as being due to carbonate and bicarbonate may be caused by small amounts of borates, phosphates, or silicates. This error is generally quite small. Organic acids may, however, cause errors of some magnitude in chemically balancing highly coloured, low-mineralized waters since they are combined with bases, yet are not titrated as alkalinity.

Calculation of Bicarbonate, Carbonate, Hydroxide, and Carbon Dioxide

The existing proportions of the three main groups of anions causing alkalinity are determined from the equilibria between CO_2 , alkalinity, and pH, as shown in Table X and in Figures 2, 3, and 4, when CO_2 content and pH are known. Normally, however, CO_2 is calculated from the determined value of alkalinity and pH. The existing proportions of the three forms of alkalinity are found also by titration of the water to definite hydrogen ion concentration end points, using various indicators. Table XI, page 57, shows this relationship, which is based on the assumption that CO_2 and normal carbonate or bicarbonate and hydroxide do not exist together. This assumption has been shown to be not quantitatively correct, but is considered sufficiently accurate for most purposes.

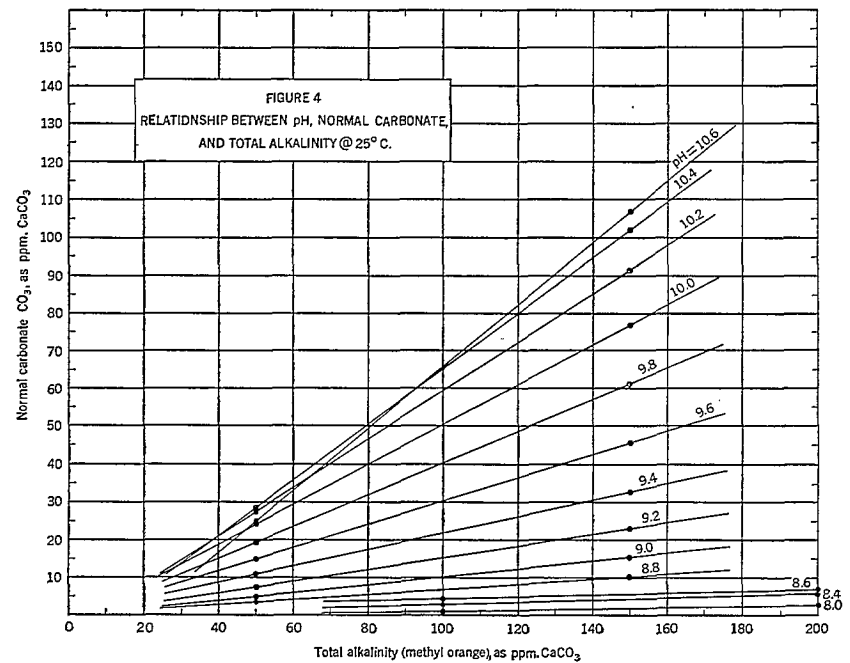
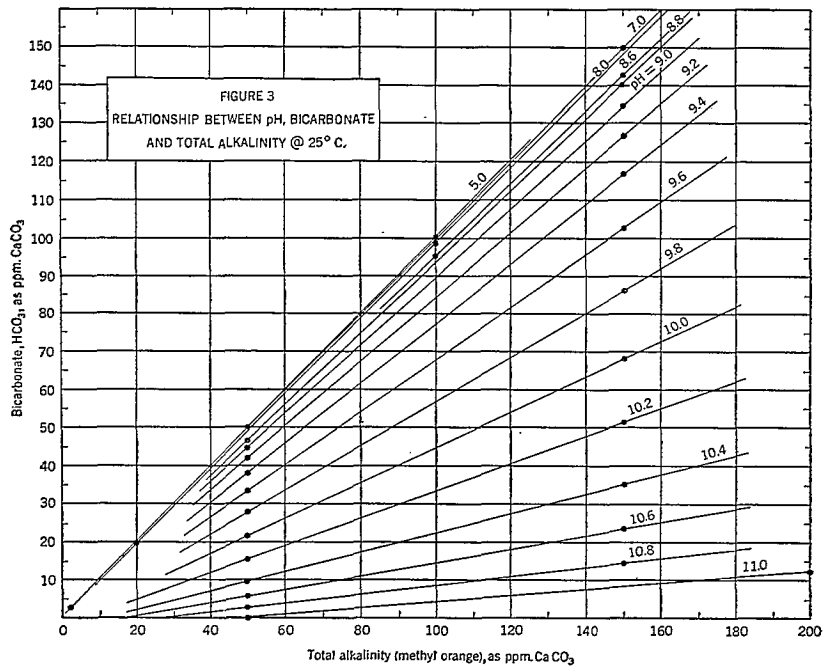
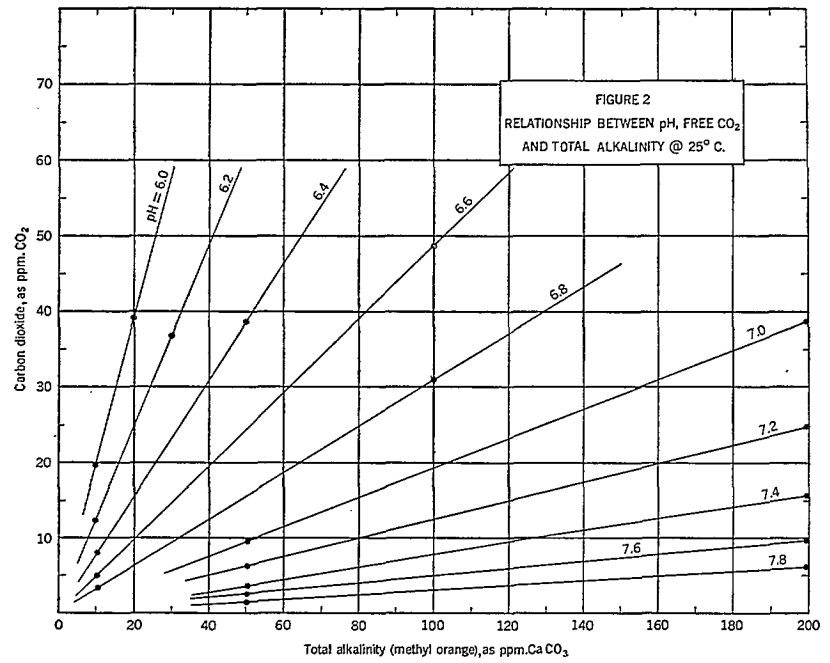
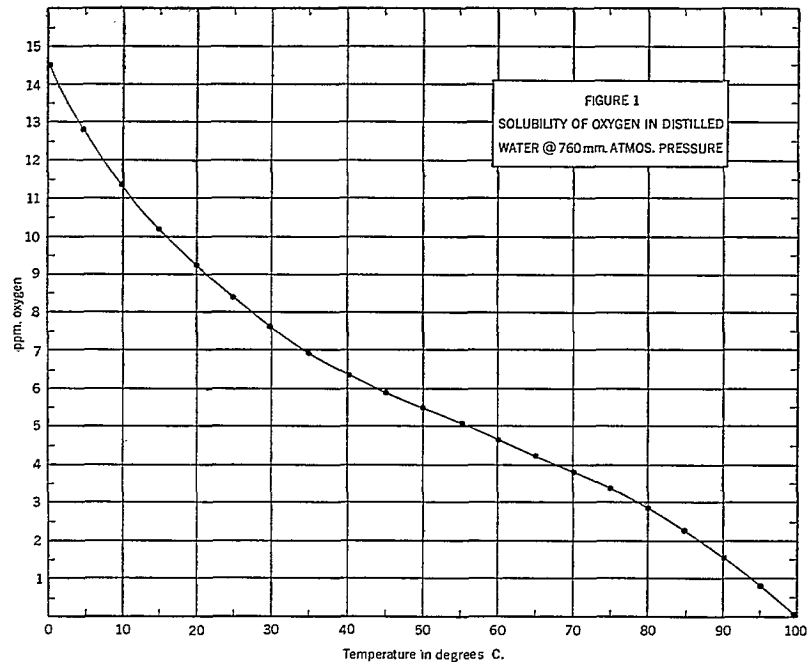


TABLE X*

(Data for Construction of Graphs in Figures 2, 3, and 4)

Relation between pH and Fractional Activities of Alkalinity and Acidity Constituents

pH	Total Alkalinity†	CO ₂	HCO ₃ ⁻	CO ₃ ⁻	OH ⁻
6.0	10	19.5	10.05		
	20	38.9	20.05		
6.2	10	12.3			
	30	36.8			
6.4	10	7.7			
	50	38.7			
6.6	10	4.9			
	100	48.8			
6.8	10	3.1			
	100	30.7			
7.0	50	9.7	50		
	200	38.7	200		
7.2	50	6.1			
	200	24.5			
7.4	50	3.9			
	200	15.6			
7.6	50	2.4			
	200	9.7			
7.8	50	1.5			
	200	6.1			
8.0	20		19.7		
	100	1.9	98.9	1.1	
	200	3.8	198.0	2.2	
8.2	100	1.2			
	200	2.4			
8.4	100		97.3	2.8	
	200		194.5	5.5	
8.6	100		95.5	4.3	
	150		143.0	6.3	
8.8	50		46.5	3.3	
	150		140.0	9.9	
9.0	50		44.5	5.0	0.5
	150		134.5	15.0	0.5
9.2	50		41.9	7.4	0.7
	150		126.8	22.5	0.7
9.4	50		38.1	10.7	1.2
	150		116.1	32.7	1.2
9.6	50		33.2	14.8	2.0
	150		102.3	45.7	2.0
9.8	50		27.4	19.4	3.2
	150		85.9	60.9	3.2
10.0	50		21.2	23.8	5.0
	150		68.2	76.8	5.0
10.2	50		15.1	27.0	7.9
	150		51.1	91.0	7.9
10.4	50		9.8	27.7	12.5
	150		36.1	101.4	12.5
10.6	50		5.5	24.6	19.9
	150		23.8	106.3	19.9
10.8	50		2.3	16.2	31.5
	150		14.6	103.9	31.5
11.0	50		0	0	50.0
	200		12.3	137.7	50.0

† Bicarbonate, carbonate, hydroxide, and total alkalinity are expressed as p.p.m. CaCO₃, carbon dioxide as p.p.m. CO₂.
 * Reproduced from Journal of the American Water Works Association, Vol. 31, No. 58 (1939) by permission of A.W.W.A.

TABLE XI

Relation Between CO_3 , HCO_3 and OH Ions, Determined by Titration

Result of titration	Value of Radical Expressed as p.p.m. CaCO_3		
	Hydroxide	Carbonate	Bicarbonate
$P = 0$	0	0	T
$P < \frac{1}{2} T$	0	2 P	$T - 2 P$
$P = \frac{1}{2} T$	0	2 P	0
$P > \frac{1}{2} T$	$2 P - T$	$2 (T - P)$	0
$P = T$	T	0	0

P = Alkalinity to phenolphthalein

T = Total alkalinity in presence of methyl orange.

The following examples illustrate the use of the table:

1. Given a water with total alkalinity as determined by methyl orange titration = 52.0 p.p.m. as CaCO_3 and with no phenolphthalein alkalinity; that is, $P = 0$ and $T = 52.0$, then,

Hydroxide..... = 0

Carbonate..... = 0

Bicarbonate..... = $52.0 \times \frac{122}{100} = 63.4$ p.p.m. as HCO_3^-

2. Given a water with total alkalinity = 60.0 p.p.m. as $\text{CaCO}_3 = T$ and phenolphthalein alkalinity = 2.0 p.p.m. as CaCO_3 ; that is $P < \frac{1}{2} T$, then,

Hydroxide (OH)..... = 0

Carbonate..... = $2P = 4.0$ p.p.m. as CaCO_3 , or $4.0 \times 0.6 = 2.4$ p.p.m. as $\text{CO}_3^{=}$ Bicarbonate..... = $T - 2P = 60.0 - 4.0 = 56.0$ p.p.m. as CaCO_3 Bicarbonate..... = $56.0 \times \frac{122}{100} = 68.3$ p.p.m. as HCO_3^- .

For most accurate work the various amounts of $\text{CO}_3^{=}$, HCO_3^- , and OH^- in water are calculated from chemical equilibria based on ionization constants. The basic equations are*:

I. (CO_2) = $9.70 \times 10^{10} (\text{H}^+) \times K^x$

II. (HCO_3^-) = $50,000 \times K^x$

III. $(\text{CO}_3^{=})$ = $\frac{5.61 \times 10^{-6}}{(\text{H}^+)} \times K^x$

IV. (OH^-) = $\frac{5 \times 10^{-10}}{(\text{H}^+)}$

where $K^x = \frac{\text{alk.}}{50,000} + (\text{H}^+) - \frac{10^{-14}}{(\text{H}^+)}$ and (HCO_3^-) , $(\text{CO}_3^{=})$, (OH^-) , and $(\text{alk.})^{**}$ are in p.p.m. as

CaCO_3 , (CO_2) in p.p.m. as free CO_2 , and (H) is the hydrogen ion concentration in mols. per litre, the latter being obtained directly from pH, since $\text{pH} = \log \frac{1}{(\text{H}^+)}$. From these equations it will

be seen that free CO_2 , HCO_3^- , OH^- , and $\text{CO}_3^{=}$ can be expressed in terms of alkalinity and hydrogen ion concentration or pH, as follows:

$$K^x = \frac{(\text{HCO}_3^-)}{50,000} = \frac{(\text{CO}_2)}{9.70} \times 10^{10} (\text{H}^+) = \frac{(\text{CO}_3^{=}) (\text{H}^+)}{5.61 \times 10^{-6}} \text{ or } (\text{CO}_2) = \frac{9.70 \times 10^{10} (\text{H}^+) (\text{HCO}_3^-)}{50,000}$$

and so on.

* Reproduced from Journal of the American Water Works Association, vol. 31, pp. 51-66 (1939) by permission of A.W.W.A.

** Total alkalinity to methyl orange.

These equations are based on the value of ionization constants such as K_w , K , etc., at a temperature of 25°C., and if alkalinity or pH are determined at temperatures appreciably different, other graphs must then be prepared, taking into account the value of these constants at the temperatures used. Similarly, the presence of other salts—the ionic strength of the water—is important, as it too affects the constants. Moore states that these errors are compensating and that “generally for waters having temperatures from 15° to 25°C., dissolved salt contents of 500 p.p.m. or less, and pH values below 10, all corrections may be neglected and the graphs as shown may be used.” Within this category fall most natural surface waters. For other waters corrections are necessary, and the reader is referred to Moore’s original paper and other technical publications on the subject.

In most of our survey analyses carbon dioxide is not reported, but by using the reported alkalinity and pH the free CO_2 content can be determined for these waters from Figure 2. However, unless the alkalinity and pH have been determined at the time of sampling, the CO_2 content found is not that necessarily found in the natural water, but is the CO_2 content in the sample when testing is started.

Using these equations, the relationship between the various values can be graphically expressed in various ways. Several such charts prepared by E. E. Moore* are reproduced in Figures 2, 3, and 4. The basic data from which these graphs are plotted will be found in Table X.

Sulphides, Sulphites, and Sulphates

There is equilibrium at times in waters between sulphur and its compounds.

Waters containing dissolved sulphides, including hydrogen sulphide (H_2S), will readily lose H_2S if the pH of the water is lowered or if the temperature rises. If the pH of the water sample is high, oxidation will destroy sulphides and colloidal sulphur may be precipitated.

Surface waters containing sulphides are not common, although some industrially used ground waters may contain H_2S and other sulphides. It is difficult to determine free H_2S unless these waters are tested before they come into contact with air. The odour of H_2S may be quite noticeable in waters when the water contains barely 1 p.p.m. of the gas. Ordinarily, mention is merely made in the Water Survey Reports that H_2S is present, but occasionally a total sulphide or a dissolved sulphide has been determined.

If the pH of the water and the concentration of dissolved sulphide are known, the concentration of H_2S may be calculated from the equilibrium data.

Sulphites may be present in some waters but are not commonly found in natural supplies. Sewage contamination and industrial wastes, in particular waste liquor from pulp and paper mills, may cause their presence in surface waters.

Sulphate is a very important radical in water, since, when combined with the alkaline earths, it is the cause of non-carbonate or “permanent” hardness and scaling in piping, boilers, and condensers.

Sulphate is also a product of bacterial action by oxidation of other sulphur compounds, including H_2S . It is formed by oxidation of iron sulphides (pyrites) and may be in water from trade wastes and in drainage from mines. However, certain organisms found in the mud of waters low in oxygen are able to reduce sulphates to H_2S . In an unpolluted water sulphate is normally a relatively constant value and any appreciable change in sulphate concentration should be carefully considered. The determination is often useful in estimating the extent of mixing of waters from different sources.

The gravimetric determination of sulphate as barium sulphate (BaSO_4) is relatively accurate, provided care is taken to wash carefully the precipitated barium sulphate. Results by other analytical methods, such as turbidity measurements of the precipitated sulphate, must be accepted with caution, especially when small amounts of sulphate are present, because of the limitations in any turbidity measurement. Waters that have been treated with metaphosphate

* Journal of the American Water Works Association, vol. 31, pp. 51-56, 1939.

will appear to be high in sulphate unless special care is taken in analysis, since barium chloride precipitates the metaphosphate, which is then calculated as BaSO_4 . Treated waters may show high sulphate for this reason or because of the sulphate added as filter alum for coagulation and treatment of the water. Sulphites, if present, will cause error unless they are first determined and then oxidized and the sulphate so formed subtracted from the total sulphate found.

Halogens (Chloride, Bromide, Iodide, and Fluoride)

Chlorides are found in waters owing to pickup from chloride-containing rocks, from brine leakage, from deposits of NaCl , KCl , etc., or from pollution. High chloride contents are not commonly found in Canadian surface waters. Some ground waters, however, may normally contain very high quantities and still be potable. Although the amount of chloride is often reported as zero, it is zero only within the limits of accuracy of the analysis. Sufficient concentration of volumes of any water will usually show chlorides and many other elements not normally found. If pollution occurs, particularly if it is of animal origin, chlorides are normally present, since chlorides are excreted as waste by all higher living organisms; and any water showing a marked change in chlorides, or any water from an area not expected to be saline in nature showing a high chloride content, should be examined carefully for pollution.

Chlorides, especially when combined with alkaline earth salts, will markedly increase the corrosiveness of a water and cause "permanent" hardness. High chlorides in a water affect the value for residue on evaporation because some chlorides are deliquescent and others break down with loss of chloride.

Bromide and Iodide if present in a water will be reported in the usual analysis as chloride, but since they are seldom present in appreciable amounts few analysts consider them. They are found in some well waters and in seawater.

Fluorides were for many years not determined in water analyses. It is only within recent years that their importance in connection with decay of teeth has been suspected. For this reason fluoride determination is becoming a standard test in the Mines Branch laboratories. Although the non-distillation test is open to some criticism, it is believed satisfactory for survey purposes.

Fluorides in waters normally originate from contact with fluorspar or with rocks and soils containing varying amounts of fluorine. The quantity present in surface waters is usually small compared with that of the chlorides.

Nitrates, Nitrites, Ammonia, etc.

All common nitrates, nitrites, and nitrogen-containing compounds are soluble and do not occur to any extent in rocks or salts exposed to water. Most nitrates and nitrites found in surface waters, and to a large extent those formed in ground waters are due to the presence of vegetable or animal matter. All plant and animal matter contains nitrogen in various forms as amines, albuminoid ammonia, etc. What form they will have in water depends upon the extent of the bacterial or photosynthetic action occurring and upon its nature, that is, whether oxidizing or reducing. The decomposition of vegetation or animal waste may cause either oxidation of nitrogen compounds to nitrates or reduction to ammonia. Large amounts of nitrates usually indicate pollution of considerable extent at some earlier period which has since been oxidized. High nitrites are more indicative of recent pollution. Therefore, high nitrate or nitrite concentrations in a water should be carefully considered and all possibility of pollution investigated. There is a possibility of leakage of nitrogen from fertilizers or trade wastes causing high nitrogen contents in a water.

Ten to twenty p.p.m. of nitrates in water have recently been reported as producing the conditions of methemoglobinemia in infants (blue babies). When the nitrate is high (60 p.p.m. or greater) the condition becomes severe. Sodium nitrate, if present in sufficient quantity to

give a definite sodium nitrate-sodium hydroxide ratio, will act as an inhibitor of intercrystalline cracking (caustic embrittlement) in a boiler. Sodium nitrite is also an inhibitor of corrosion of iron by aqueous solutions, acting to some extent as a scavenger of residual oxygen.

Since nitrites should be determined at the time of sampling because of the changes that may occur in storage, only nitrates are normally determined in the Mines Branch laboratories, except in cases where a determination of ammonia or nitrite is indicated or desired. Nitrate values, unless nitrite is determined, normally include the nitrite since this is oxidized to nitrate before testing.

Most surface supplies so far studied are quite low in nitrogen compounds, which have little effect on the value of a water for most industrial uses.

Silica, Silicates

Normally, surface waters are said to show a silica range of 10 to 30 p.p.m., but many Canadian waters are in the range 4 to 8 p.p.m. Some ground waters, usually hot springs, contain as high as 65 p.p.m. silica.

Silica is dissolved to some extent by water, but its exact form in solution, and its relationship to other materials present is not definitely known. To what extent silicates enter into determinations such as alkalinity, how much silica is in the form of silicic acid or as various hydrated silica micelles, etc., is not too clear. Silica is considered to be present in either a soluble (crystalloidal) or insoluble (colloidal) form, but there are some indications of variations of each of these forms. There is evidence that the common analytical test using ammonium molybdate determines soluble silica in one form only and that long storage may change the proportion of this form. Storage possibly causes some aggregation and precipitation of colloidal silica with removal of certain other ions or, vice versa, the solution of colloidal silica.

With some clear waters, poor checks between total or gravimetric silica and colorimetric or soluble silica are obtained. This may be due in part to the effect of storage and test procedure as mentioned above. Dehydration of the silica with HCl and evaporation is normally carried out only once and in some cases this may account for the differences noted. Double dehydration has been employed at times by the Mines Branch, but has not always shown better correlation of gravimetric results with colorimetric silica. However, since most waters tested to date are low in total silica, the error is not considered sufficient in routine survey work to warrant expenditure of the extra time involved in continued dehydration. Very few analysts report whether silica is determined gravimetrically or colorimetrically; this seems to be quite important with some waters.

In order to balance some of the analyses it is sometimes necessary to include silica as a silicate ion, SiO_3^- . Some workers include only one-half the SiO_2 as silicate ion; others consider silica as already included in the balance calculation as alkalinity. In a few early analyses of low-mineralized water, sodium was not determined, and when calculating it from the analyses it was found that in order to obtain a figure similar to that found in the same water at other periods, a value of one-half the SiO_2 as silicate was required. It is apparent that there is still need for further clarification of the role played by silica in water, particularly in the low-mineralized waters found in many Canadian rivers, where even relatively small amounts of silica represent an appreciable percentage of the total solids present.

Silica has a detrimental effect in some industrial uses, particularly in high-pressure boiler operation. Silica in waters so used leads to the formation of very hard silicate scales and acts as a cementing agent for the softer, carbonate scales. It causes serious problems in steam turbines owing to silica build-up on the turbine blades. To prevent such trouble the silica should be removed from the feed water prior to its entrance to the boiler. Recent methods of treatment have produced waters with total solid content as low as 1 p.p.m., the silica being estimated at 0.01 p.p.m. There is need for a more sensitive method for detecting such traces of silica in steam and water.

Boron, Borates

Boron is of importance in the growth of plants. High boron content in waters has a deleterious effect on many crops, in particular on citrus crops, but it must usually exceed 0.75 p.p.m. before it affects even the most sensitive crops.*

Boron determinations are carried out in this survey only on waters that may be used in appreciable amounts for irrigation purposes, such as waters in Western Canada, and then only on periodic samples. To date, only very small amounts have been found. The determination as carried out is considered to be quite accurate, but care must be taken not to store the water for a long period in pyrex bottles or in contact with other boron-containing glass.

Dissolved Gases

Dissolved oxygen studies are preferably carried out as a separate project, as the per cent saturation of a surface water with oxygen or air is dependent upon many factors, such as depth of sampling, temperature, barometric pressure, wind conditions, amount of oxidizable matter present, and time of year. Dissolved oxygen tests are made at times in the field but must be interpreted with due consideration of the factors mentioned above.

The amount of dissolved oxygen in a water is very important in many uses. Too little oxygen means no fish, and a different type of micro-organism and plant growth from that found under normal oxygen conditions. In many waters a low oxygen content also indicates pollution by sewage or industrial waste, the normal oxygen having been used up in oxidizing nitrite, organic matter, and industrial waste compounds. A high oxygen content indicates the water to be suitable for most uses, but it raises problems of corrosion of metals, etc., in industry. Dissolved oxygen determinations are often carried out in connection with the use of high-pressure boilers, as they check the efficiency of the treatment equipment and the possibility of corrosion.

Carbon dioxide (CO₂) is present in water in three forms, namely, the bound CO₂ as in carbonates, the half-bound as in bicarbonates, and the free or dissolved CO₂ gas. The bound and half-bound CO₂ have already been discussed under alkalinity, page 54. The amount of free or "aggressive" carbon dioxide is dependent upon many factors, such as temperature, atmospheric pressure, the equilibrium with the carbonates, and pH.

Carbon dioxide may enter a water by contact with air, as in rainfall, by decomposition due to bacterial action on organic material such as leaves, and by contact with natural gases containing CO₂.

The free carbon dioxide must, therefore, be determined immediately after sampling, without excess aeration, and the amount found will be dependent upon the pH, alkalinity, temperature, etc., at the time of testing. It is normally not determined except on samples that can be tested in the field, but it may be calculated on other waters from the equilibrium referred to above using Figure 2, page 55. CO₂ values calculated on the basis of results obtained in the laboratory are seldom similar to the values present in the water in the natural state due to changes caused by storage. Even tests carried out in the field must take into account the possible loss of CO₂ by aeration of ground waters at pumps or, in the case of surface supplies, the depth of sampling.

The amount of free carbon dioxide in water is of major importance. Being acidic in water, as carbonic acid, it attacks iron, copper, and other metals and enters into the electro-chemical process of corrosion. It causes corrosion in steam lines and return condensate lines, where it is present owing partly to breakdown of carbonates in the boiler. It causes solution of carbonates, thus producing hardness in waters and removing protective scaling from piping and equipment.

Hydrogen sulphide. In some deep well waters dissolved H₂S gas is found in varying amounts and is very troublesome. When present in appreciable amount it makes a water unfit for domestic use. Since it is acidic in water, as sulphurous acid (H₂SO₃), it causes corrosion of metals, particularly iron, to form black rust (FeS). It reacts with many processing chemicals and

* Explanation and Interpretation of Analyses of Irrigation Waters, by L. V. Wilcox; Circular No. 784 (May 1948), U.S. Dept. of Agriculture, Washington, D.C.

causes discoloration and precipitation. Whenever free H_2S is found there is often present a high concentration of other sulphur compounds. There is a similar equilibrium here as with nitrogen or carbon dioxide, and a marked change in the amount of H_2S or other salts in this equilibrium may cause precipitation of sulphur, often as colloidal sulphur.

H_2S may be present from contact by the water with sulphide rocks (pyrites), coal, oil, or natural gas, and from decomposing sulphur-containing vegetation. Various bacteria may produce H_2S from sulphides, sulphates, or other sulphur compounds.

Simple aeration will remove H_2S from some waters, but with others more elaborate treatment is necessary.

Other Mineral Constituents

Many other elements and radicals, for example, phosphates, are normally found only in traces in water. Determination of these is not normal practice, but for special reasons may be carried out by standard procedures. Phosphate is usually found in waters only when it has been added for treatment, since phosphates in soils are only sparingly soluble.

A number of inorganic and organic elements and materials such as chromates, cyanides, and oil may be present in water polluted by industrial trade wastes. Only in special cases are analyses made for these constituents, when the standard procedures are used.

CALCULATED VALUES

Much information of assistance in interpreting the character of a water may be gained from a relatively complete analysis by calculation of ratios and other values.

Ratios

The calculation of various ratios of determined ions is of theoretical interest in research into interpretation of results and is of value in checking the accuracy of analyses or the constancy of a particular supply over a period of time. Some of the ratios determined in this survey from time to time are sodium to potassium, calcium to magnesium, residue on evaporation to sum of constituents, residue on evaporation or sum of constituents to conductivity, and soluble silica to total silica.

The calcium-to-magnesium ratio is of value in indicating any loss of calcium as a $CaCO_3$ precipitate from waters on long standing. In most surface waters the Ca:Mg ratio is about 2:1 and if it becomes nearer 1:1 the possibility of such precipitation is confirmed. Loss of calcium, of course, decreases the total hardness figure.

Some studies of the ratio of various ions to river flow have been made with interesting results.

Only the ratio sodium to total cations (per cent sodium), which is of value in assessing the suitability of a water for irrigation,* is reported in the Water Survey Reports.

To determine the per cent sodium of a water, the quantity of sodium ion in e.p.m. is divided by the sum of the quantities of calcium, magnesium, sodium, and potassium ions, all as e.p.m., and the result expressed as a percentage. In the sample analysis of Thompson River, page 37, per cent sodium is therefore $\frac{0.0783 \times 100}{0.7941} = 9.9$ per cent. This is a relatively low per cent sodium and the water would be suitable for irrigation purposes insofar as sodium content is concerned.

Hardness

Hardness is one of the most important calculated values. This has already been discussed on page 50.

* Explanation and Interpretation of Analyses of Irrigation Waters, by L. V. Wilcox; Circular No. 784 (May 1948), U.S. Dept. of Agriculture, Washington, D.C.

Incrustants and Calculated Formulæ

"Standard Methods" classifies silica, iron and aluminium oxides, and all combinations of calcium and magnesium, as *incrustating solids*, and sodium and other alkali combinations, as well as organic matter, as *non-incrustating solids*.

Corrosive compounds in waters are considered to include all acids, iron and aluminium sulphates, calcium chloride, calcium nitrate, magnesium sulphate (when in appreciable amount), magnesium chloride, and magnesium nitrate. Free CO₂ in appreciable amounts and dissolved oxygen when the pH is below 10 are also accelerators of corrosion.

Stabler* advocated some time ago the following formulæ for use in studying the character of a water. These formulæ are not used to any great extent and were designed especially for boiler water reactions. Other workers have from time to time devised somewhat similar formulæ to determine softening reactions, etc. As a matter of interest four of Stabler's formulæ are reproduced below:

1. Foaming Coefficient (*F*)

$F = 2.7 \text{ Na} + \text{K}$, where Na = p.p.m. Na; K = p.p.m. K. It is to be noted that this formula does not take into account the amount and character of any suspended or organic matter present, which may have a very important role in foaming and priming in boilers. This formula is said to represent approximately the "non-incrustating solids". Using the example given on page 37, *F* becomes $2.7 \times 1.8 + 0.6 = 5.46 = 5.5$ p.p.m. Non-incrustants as calculated from the hypothetical combination, page 39, are:

Na ₂ SO ₄	=	5.60
K ₂ SO ₄	=	0.18
KNO ₃	=	0.81
KF	=	0.31
		6.90 p.p.m.

2. Coefficient of Corrosion (in boilers) = (*C*)

$$C = 1.008 (\text{RH} + \text{RAI} + \text{RFe} + \text{RMg} - \text{RCO}_3 - \text{RHCO}_3)$$

where H = hydrogen ion concentration

Al = aluminium concentration in p.p.m.;

R = reacting value of ion: e.g., RFe = p.p.m. iron \times reacting weight or e.p.m. iron.

When *C* is positive the water is considered to be corrosive in boilers; when [*C* + 0.0503 Ca⁺⁺ (p.p.m.)] is negative the water is said to be non-corrosive; and when *C* is negative but (*C* + 0.0503 Ca⁺⁺) is positive corrosion may or may not occur. Corrosiveness of natural waters at ordinary temperature is estimated from the saturation index (*see below*).

3. Scaling Coefficient (*S*)

S (lbs. scale/1,000 gals. water evap.) = $0.00833 (\text{SM} + \text{CM}) + 0.3 \text{ RFe} + 0.142 \text{ RAl} + 0.168 \text{ RMg} + 0.492 \text{ RCa}$. SM = suspended matter, that is, all organic and inorganic matter removable by filtration; CM = colloidal matter—mostly silica (SiO₂), colloidal alumina (Al₂O₃), colloidal iron oxide (Fe₂O₃), and at times organic matter in colloidal form.

*The Mineral Analysis of Waters for Industrial Purposes and its Interpretation for the Engineer, by Herman Stabler; Eng. News, vol. 60, No. 14 (1908), p. 355.

RCa as used in the above formula should not exceed $(\text{RCO}_3 + \text{RHCO}_3 + \text{RSO}_4)$. Using the above analysis of Thompson River water:

$$\text{RCa} = 0.5689$$

$$\text{RCO}_3 + \text{RHCO}_3 + \text{RSO}_4 = 0 + 0.6523 + 0.1437 = 0.7960. \text{ Therefore, RCa does not exceed } (\text{RCO}_3 + \text{RHCO}_3 + \text{RSO}_4)$$

$$\begin{aligned} \text{Then } S &= 0.00833 (7.0 + 8.3) + 0.3 \times 0.001 + 0 + 0.168 \times 0.1316 + 0.492 \times 0.5689 \\ &= 0.1274 + 0.0003 + 0.0221 + 0.2799 = 0.4297 \text{ lbs./1,000 gals. water} = 43 \text{ p.p.m.} \end{aligned}$$

It is to be noted that no determination for aluminium was carried out and this is assumed zero in all these formulæ.

Where S is not >1 — very little scale

$S > 1$ but < 2 — little scale

$S > 2$ but < 4 — much scale

$S > 4$ — very much scale.

Therefore this water according to Stabler's formula should produce very little scale in a boiler.

4. Coefficient of Scale Hardness (H)

$H = \frac{HS}{S}$ where HS = hard scale in lbs./1,000 gals. and S is the above scaling coefficient.

$$H = \frac{HS}{S} = \frac{0.00833 \text{ SiO}_2 + 0.168 \text{ RMg} + 0.567 (\text{RCl} + \text{R SO}_4 - \text{RNa} - \text{RK})}{S}$$

The value in parenthesis must not exceed RSO_4 or RCa , nor should it be less than zero.

Using Thompson River analysis:

$$\begin{aligned} HS &= 0.00833 \times 8.3 + 0.168 \times 0.1316 + 0.567 (0 + 0.1437 - 0.0783 - 0.0153) \\ &= 0.0691 + 0.0221 + 0.567 (0.0501) = 0.1196 \text{ lbs./1,000 gals.} \end{aligned}$$

(Note that the value in parenthesis does not exceed RCa or RSO_4 and is not less than zero.)

$$\text{Therefore, } H = \frac{HS}{S} = \frac{0.1196}{0.4297} = 0.28$$

Soft scale is formed if H not > 0.25

Medium scale is formed if $H > 0.25$ but not < 0.5

Hard scale is formed if $H > 0.5$.

According to these formulæ this water will produce only a very small amount of a soft-to-medium scale when used as a boiler feed-water.

Various workers have developed other formulæ for determining these and other properties of waters.

Palmer Classification

Various methods of reporting and classifying waters have their merit for special purposes and for comparison of waters. That proposed by Chase Palmer¹, which is based on the reacting value of the constituents of the water and which is useful from a geological standpoint, has been used to some extent and is given as a typical example.

¹Dept. of the Interior, U.S. Geol. Survey, Bull. 479: The Geochemical Interpretation of Water Analyses, by Chase Palmer.

Most waters have two general properties, salinity and alkalinity, and it is on the relative proportions of these that their fundamental chemical character depends. Salinity is caused by salts in the water that are not hydrolyzed, and alkalinity by free alkaline bases produced by the hydrolytic action of water on solutions of bicarbonate and on solutions of salts of other weak acids. All positive radicals, hydrogen included, may participate in producing salinity, but the only negative radicals that do so are those of the actively strong acids, the principal negative radicals in natural waters being sulphate, chloride, and nitrate.

Palmer, therefore, divides the radicals into groups according to their chemical nature:

1. Alkalis or primary bases—sodium, potassium, and lithium. These occur together in nature, are chemically similar, decompose water, and form similar salts with acids, and cause no hardness.

2. Alkaline Earths—calcium, strontium, and magnesium. These secondary bases are comparatively similar in their chemical behaviour and are geologically associated. Many of their salts are sparingly soluble in water and cause hardness.

3. Hydrogen and the metals whose salts cause acidity in waters.

The acid radicals or negative ions (anions) fall into two groups:

(a) Strong acid radicals: Cl^- , SO_4^- .

(b) Weak acid radicals: HCO_3^- , CO_3^- , HBO_2^- .

On the basis of this grouping, Palmer then places all waters in five classes:

Class I. Value of strong acids (Cl , SO_4) less than value of alkalis (Na , K).

Class II. Value of strong acids equal to value of alkalis.

Class III. Value of strong acids greater than value of alkalis but less than alkalis plus alkaline earths.

Class IV. Value of strong acids equal to value of alkalis plus alkaline earths.

Class V. Value of strong acids exceeds value of alkalis plus alkaline earths.

These main classes may be subdivided according to salinity or alkalinity, that is, according to the nature of the salts formed by balancing up the various groups.

Primary salinity is caused by solution of strong acid salts of the alkalis such as NaCl , KCl , Na_2SO_4 , and K_2SO_4 ; secondary salinity by solution of strong acid salts of the alkaline earths, such as CaCl_2 , MgCl_2 , CaSO_4 , and MgSO_4 ; and tertiary salinity, by solution of strong acid salts of hydrogen, or of metals such as FeCl_2 , AlCl_3 , and $\text{Fe}_2(\text{SO}_4)_3$. Primary alkalinity is caused by solution of weak acid salts of the alkalis, such as Na_2CO_3 , NaHCO_3 , K_2CO_3 ; secondary alkalinity by solution of weak acid salts of the alkaline earths, such as $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$; and tertiary alkalinity by solution of hydrogen and certain metals as weak acid salts.

This is expressed graphically thus:

Bases	Acids	
	Strong Acids	Weak Acids
—	Cl , SO_4 , NO_3	CO_3 , HCO_3
Alkalis (Na , K , Li).....	Primary salinity	Primary alkalinity
Alk. earths (Ca , Mg , Sr).....	Secondary salinity	Secondary alkalinity
Metals (H , Fe).....	Tertiary salinity	Tertiary alkalinity

To illustrate the application of this classification, the analytical data on Thompson River are again used:

Base Analysis Radical	p.p.m.	e.p.m.	Corrected e.p.m.*	Formula per cent
Ca.....	11.4	0.56886	0.5740	35.78
Mg.....	1.6	0.13158	0.1328	8.27
Na.....	1.8	0.07826	0.0789	4.92
K.....	0.6	0.01535	0.0154	0.96
Fe.....	0.03	0.00107	0.0011	0.07
Total cations.....		0.7951	0.8022	50.0%
HCO ₃	39.8	0.65232	0.6466	40.30
CO ₃	0	0	0	0
SO ₄	6.9	0.14366	0.1423	8.87
Cl.....	0	0	0	0
NO ₃	0.5	0.00807	0.0080	0.50
F.....	0.1	0.00526	0.0053	0.33
Total anions.....		0.8093	0.8022	50.0%
Colloids.....				
SiO ₂	3.5			
Total concentration value =			1.6044 e.p.m.	100.0%

* The error between total cations and total anions is $0.8093 - 0.7951 = 0.0142$; one-half of this is proportioned to each, i.e., 0.0071 e.p.m. is proportionately taken from the anions and 0.0071 e.p.m. is proportionately added to the cations as above.

The per cent formula, which is the per cent calcium of the total concentration value, i.e., $\frac{0.5740 \times 100}{1.6044} = 35.78$, is now grouped into alkalis, alkaline earths, strong acids, and weak acids as follows:

Groups	Per cent
Alkalis { Na..... K..... }	5.88
Alkaline earths { Ca..... Mg..... Fe..... }	44.12
Strong acids { SO ₄ Cl..... NO ₃ F..... }	9.70
Weak acids { HCO ₃ CO ₃ }	40.30
Total concentration value.....	100.0

In this grouping the strong acids are greater than the alkalis but less than the sum of alkalis and alkaline earths, that is, the water is Class III.

Primary salinity is equal to twice the value of alkalis.....	11.76	Per cent
Secondary salinity is equal to twice the value of strong acids minus alkalis =		
2 (9.70 - 5.88).....	7.64	

There is no tertiary salinity.

Primary alkalinity is not present, since all alkalis are present as salinity.

Secondary alkalinity is equal to twice the total basic constituents minus the strong acids = $2(5.88 + 44.11 - 9.70) = 2 \times 40.30 = 80.62$ per cent, which is twice the weak acids.

Summarizing, this water according to Palmer is a Class III water with the following properties:

	<i>Per cent</i>
Primary salinity.....	11.76
Secondary salinity.....	7.64
Secondary alkalinity.....	80.60
	<hr/>
	100.00
Total salinity.....	19.40

Surface waters usually fall into one of the first three classes. Class IV is represented by sea-water and brines, and Class V by acid mine waters and waters of volcanic origin.

In the Water Survey Reports the Palmer classification of waters is reported occasionally, but no effort has been made to interpret this classification in terms of other factors such as geological formation and mineral deposits.

Saturation Index

The saturation index is defined as $\text{pH} - \text{pH}_s$ where pH is the pH of the water as determined, and pH_s , the pH of the water at the same temperature when saturated with CaCO_3 ; pH_s can be calculated if the alkalinity, calcium content, and other factors are known. It is important to realize that pH_s and the saturation index change markedly with temperature and with total dissolved solids or ionic activity.

The index is based on the work of Langelier, Larson and Buswell, and others on the fundamental chemical equilibria between alkalinity, pH, CaCO_3 , etc. The Langelier formula with the Larson-Buswell residue-temperature adjustment is

$$\text{pH}_s = \log. \frac{K_s}{K_2} - \log. \text{Ca}^{++} - \log. \text{alky.} + 9.30 + \frac{2.5 \sqrt{u}}{1 + 5.3 \sqrt{u} + 5.5 u}$$

where pH_s = pH when water is saturated with CaCO_3 .

K_s = activity product constant of CaCO_3 .

K_2 = activity constant for second dissociation of H_2CO_3 .

Ca^{++} = calcium in p.p.m.

Alky. = total alkalinity as p.p.m. CaCO_3 .

u = ionic strength = approximate residue on evaporation @ 105°C . (p.p.m.) $\times 0.00025$.

Various graphical and tabular methods have been developed for the determination of this pH_s for various waters. Different methods have been used in these laboratories but normally the scalar diagram developed by A. A. Hirsch* is used. A variation of this nomograph, which is also used in the Mines Branch laboratory, is reproduced in Figure 5. Some care must be taken to use methods that take into account the effect of temperature, ionic strength, and more recent values for the constants. The reader is referred to the original papers of Langelier, Larson and Buswell, and others for further information regarding saturation index or pH_s . The paper "Chemical Equilibria in Water Treatment", by W. F. Langelier, J.A.W.W.A., vol. 38, page 169, (1946), gives graphs for determination of pH_s and other values and is a recent survey of the subject.

Because temperature is of importance, it will be noted that in the reporting of results the temperature of analysis (i.e., at which pH was determined) is given. Therefore, the saturation index reported is always the index at this temperature, since the saturation index is the difference between the determined pH and the pH at saturation with CaCO_3 (pH_s) at the same temperature.

* Scalar Diagram for pH of Calcium Carbonate Equilibrium, by A. A. Hirsch; Journal of the American Water Works Association, vol. 35, No. 5 (May 1943).

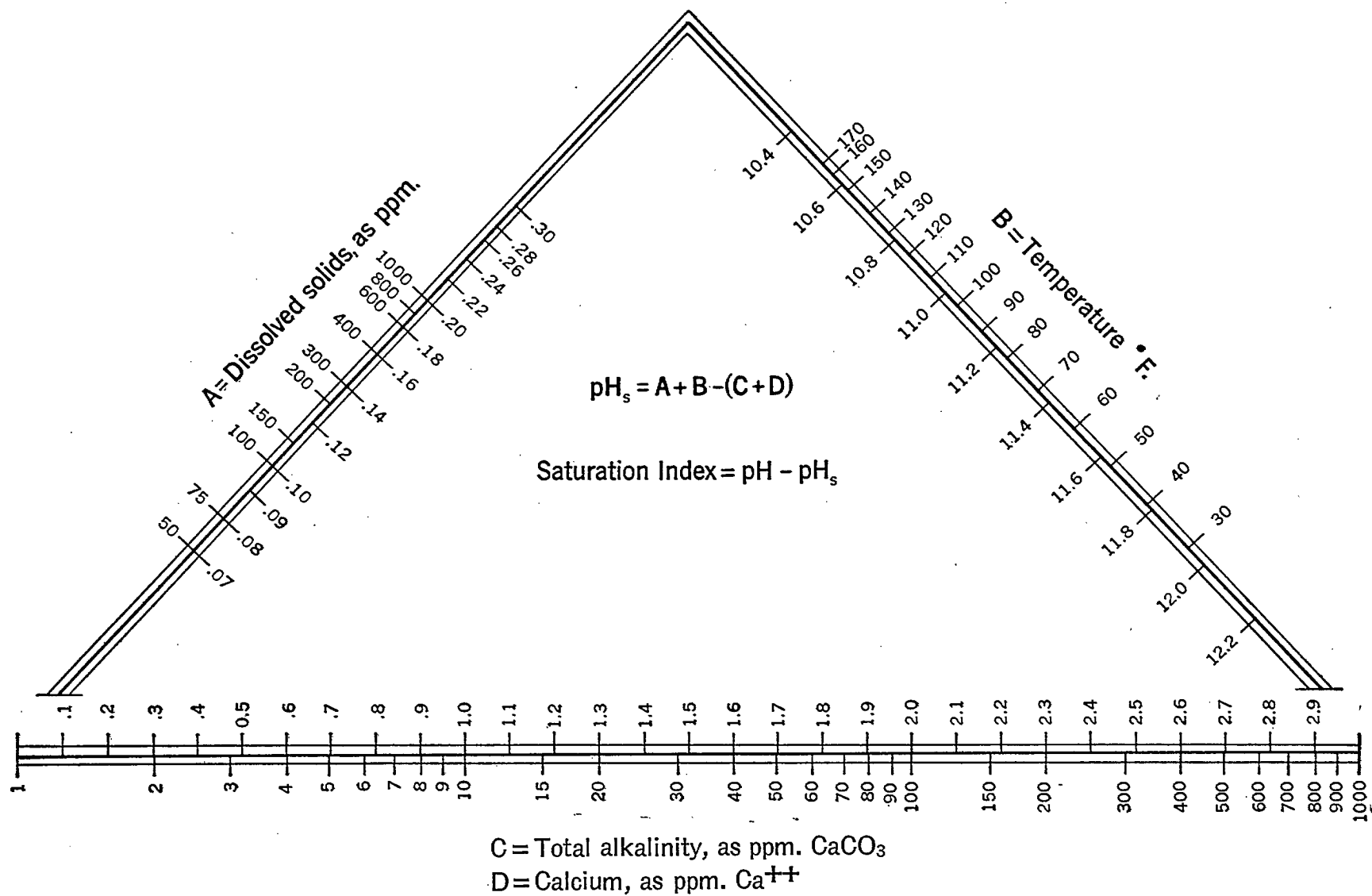


Figure 5. Diagram for determination of pH_s

Using this nomograph, Figure 5, the pH_s of the Thompson River water sample is determined:

Analysis:	pH.....	=	7.4
	Calcium.....	=	11.4 p.p.m.
	Total alkalinity.....	=	32.6 p.p.m. as $CaCO_3$
	Residue @ 105°C.....	=	56.2
	Temperature.....	=	21.5°C. = 70.7°F.

Reading from graph—

A =	0.07	C =	1.50
B =	11.35	D =	1.06
	<hr/>		<hr/>
	11.42		2.56

$$pH_s = 11.42 - 2.56 = 8.86$$

$$\begin{aligned} \text{Therefore: saturation index at } 21.5^\circ\text{C.} &= pH - pH_s \\ &= 7.4 - 8.9 = -1.5 \end{aligned}$$

This water is considered, therefore, to have a definite corrosive tendency, since if the pH is less than pH_s the index is negative, the water is undersaturated, and no protective coating of $CaCO_3$ will form. If the pH of a water is greater than pH_s the index is positive and the water is supersaturated with $Ca(HCO_3)_2$ or $CaCO_3$ with a natural tendency to deposit $CaCO_3$. The index has its greatest value in determining the corrosive property of a water. It is used also as a control test when addition of lime or filtering through limestone is used to raise the pH and content of $Ca(HCO_3)_2$ in a water so as to just form a slight scale and protect metal. It has proved of considerable value in piping protection, in protection against cooling waters, etc.

Opinion differs in regard to application of the index in practice and some workers prefer to use the so-called Stability Index*, which is $2 pH_s - pH$, based on the same pH_s and pH. One worker** claims from his experience that if the saturation index is -0.75 or less, the water is corrosive to iron; and if $+0.75$ or greater, it is definitely scale-forming; but that between these two limits, although the tendency to corrode or form scale is present in varying degrees, the results may not be definite because of other factors such as organic contaminants, high sodium alkalinity, and suspended matter.

SUMMARY

This report outlines in some detail the aim, scope, and method of procedure of the present survey of major water supplies available for industrial use in Canada.

Some discussion of the chemical results to be published in future reports is included to assist in the interpretation of those reports. In assessing any water for an industrial or other use as regards quality, many factors must be taken into account. A knowledge of the meaning of the various determinations normally made or calculated in water analyses, some of their limitations, and the possibility that other factors not normally determined may be of importance, must be kept in mind.

The chemical analyses and data obtained from a survey of the nature of that now under way can be put to so many uses by different readers that it is impossible to attempt to interpret the results for all. However, with the basic principles herein described, and a tabulation of rather complete analyses in other reports, it is hoped that the use of the data will be broadened to assist many readers of diversified interest.

It is not always possible in our present state of knowledge to place a definite limit on the amount of any radical permissible in a water for a particular use. From experience and research certain limits have been set by other workers, but no attempt has been made to outline these limits. It is hoped this work and future studies will aid in establishing such limits more accurately.

* A new Index for Determining the Amount of Calcium Carbonate Scale formed by a Water, by J. W. Ryznar. Journal of the American Water Works Association, Vol. 36, No. 472 (1944).

** Private communication.

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Canada Mines Branch
Report # 833