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Standard Guide for Displaying the Results of Chemical Analyses of Ground Water for Major Ions and Trace Elements—Diagrams for Single Analyses[1]

This standard is issued under the fixed designation D 5738; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide covers the category of water-analysis diagrams that use pictorial or pattern methods (for example, bar, radiating vectors, pattern, and circular) as a basis for displaying each of the individual chemical components that were determined from the analysis of a single sample of natural ground water (see Terminology).

1.2 This guide on single-analysis diagrams is the second of several standards to inform the professionals in the field of hydrology with the traditional graphical methods available to display ground-water chemistry.

NOTE 1—The initial guide described the category of water-analysis diagrams that use two-dimensional trilinear graphs to display, on a single diagram, the common chemical components from two or more complete analyses of natural ground water.

1.2.1 A third guide will be for diagrams based on data analytical calculations that include those categories of water analysis graphs where multiple analyses are analyzed statistically and the results plotted on a diagram (for example, the box, and so forth).

1.3 Numerous methods have been developed to display, on single-analyses diagrams, the ions dissolved in water. These methods were developed by investigators to assist in the interpretation of the origin of the ions in the water and to simplify the comparison of analyses, one with another.

1.4 This guide presents a compilation of diagrams from a number of authors that allows for transformation of numerical data into visual, usable forms. It is not a guide to selection or use. That choice is program or project specific.

NOTE 2—Use of tradenames in this guide is for identification purposes only and does not constitute endorsement by ASTM.

1.5 *This guide offers an organized collection of information or a series of options and does not recommend a specific course of action. This document cannot replace education or experience and should be used in conjunction with professional judgment. Not all aspects of this guide may be applicable in all circumstances. This ASTM standard is not intended to represent or replace the standard of care by which the adequacy of a given professional service must be judged, nor should this document be applied without consideration of a project's many unique aspects. The word "Standard" in the title of this document means only that the document has been approved through the ASTM consensus process.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 596 Practice for Reporting Results of Analysis of Water[2]

D 653 Terminology Relating to Soil, Rock, and Contained Fluids[3]

D 1129 Terminology Relating to Water[2]

D 5754 Guide for Displaying the Results of Chemical Analyses of Ground Water for Major Ions and Trace Elements—Trilinear Diagrams for Two or More Analyses[2]

3. Terminology

3.1 *Definitions*—Except as listed as follows, all definitions are in accordance with Terminology D 653.

3.1.1 *anion*—an ion that moves or would move towards an anode; thus nearly always synonymous with negative ion.

3.1.2 *cation*—an ion that moves or would move towards a cathode; thus nearly always synonymous with positive ion.

3.1.3 *equivalent per million (epm)*—for water chemistry, an equivalent weight unit expressed in English terms, also expressed as milligram-equivalent per kilogram. When the concentration of an ion, expressed in parts per million (ppm), is multiplied by the equivalent weight (combining weight) factor (see explanation of equivalent weight factor) of that ion, the result is expressed in epm.

3.1.3.1 *Discussion*—For a completely determined chemical analysis of a water sample, the total epm value of the cations will equal the total epm value of the anions (chemically balanced). The plotted values on the water-analysis diagrams described in this guide can be expressed in percentages of the total epm (although all illustrations are in milliequivalent per litre) of the cations and anions of each water analysis. Therefore, in order to use the diagrams, analyses must be converted from ppm to epm by multiplying each ion by its

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 04.08.

equivalent weight factor and determining the percent of each ion of the total cation or anion.

3.1.4 *equivalent weight factor*—the equivalent weight factor or combining weight factor, also called the reaction coefficient, is used for converting chemical constituents expressed in ppm to epm and mg/L to meq/L (see explanation of epm and meq/L). To determine the equivalent weight factor, divide the formula weight of the solute component into the valence of the solute component:

$$(\textit{equivalent weight factor}) = \frac{(\textit{valence solute component})}{(\textit{formula weight solute component})} \tag{1}$$

Then to determine the equivalent weight (meq/L) of the solute component, multiple the mg/L value of the solute times the equivalent weight factor, as follows:

$$(\textit{meq/L solute component}) = (\textit{mg/L solute component}) \times (\textit{equivalent weight factor}) \tag{2}$$

For example, the formula weight of Ca^{2+} is 40.10 and the ionic charge is two (as shown by the 2 +), and for a value of 20 mg/L Ca, the equivalent weight value is computed to be 0.9975 meq/L;

$$(0.9975\ \text{meq}/L\ Ca) = (20\ \text{mg}/L\ Ca) \times \frac{(2)}{(40.10)} \tag{3}$$

3.1.4.1 *Discussion*—Many general geochemistry publications and water encyclopedias have a complete table of equivalent weight factors for the ions found in natural ground water **(1, 2)**.[4]

3.1.5 *grains per U.S. gallon* (gpg)—for water chemistry, a weight-per-volume unit, also, for irrigation water, can be expressed in tons per acre-foot (ton/acre-ft). The weight (grains or tons) of solute within the volume (gallon or acre-foot) of solution and solute. A grain is commonly used to express the hardness of water where one grain is equal to 17.12 ppm $CaCO_3$.

3.1.6 *milliequivalent per litre* (meq/L)—for water chemistry, an equivalent weight unit expressed in metric terms, also expressed as milligram-equivalent per litre. When the concentration of an ion, expressed in mg/L, is multiplied by the equivalent weight (combining weight) factor (see explanation of equivalent weight factor) of that ion, the result is expressed in meq/L.

3.1.6.1 *Discussion*—For a completely determined chemical analysis of a water sample, the total value of the cations will equal the total value of the anions (chemically balanced). The plotted values on the water-analysis diagrams described in this guide are expressed in percentages of the total meq/L of the cations and anions of each water analysis. Therefore, in order to use the diagrams, analyses must be converted from mg/L to meq/L by multiplying each ion by its equivalent weight factor and determining the percent of each ion of the total cation or anion.

3.1.7 *milligrams per kilogram* (mg/kg)—for water chemistry, a weight-per-weight unit expressed in metric terms. The number of milligrams of solute (for example, sodium (Na)) per kilogram of solution (water) and solute. For example, a 10 000 mg/kg solute is the same as 1 % solute in the total 100% solute and solution. The mg/kg unit is equivalent to ppm according to Matthess **(3)**.

3.1.8 *milligrams per litre* (mg/L)—for water chemistry, a weight-per-volume unit expressed in metric terms. The weight in milligrams (10^{-3} g) of the solute within the volume (litre) of solute and solution. The weight can be also expressed in micrograms (10^{-6} g). The use of the mg/L unit is the worldwide standard for the analysis and reporting of water chemistry.

3.1.8.1 *Discussion*—The ppm and mg/L values of the constituents in natural ground water are nearly equal (within anticipated analytical errors) until the concentration of the dissolved solids reaches about 7000 mg/L. For highly mineralized waters, a density correction should be used when computing ppm from mg/L **(1)**.

3.1.9 *natural ground water*—as defined for this guide, is water positioned under the land's surface, that consists of the basic elements, hydrogen and oxygen (H_2O), and numerous major dissolved chemical constituents, such as calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), carbonate (CO_3), bicarbonate (HCO_3), chloride (Cl), and sulfate (SO_4), and has not been significantly influenced by human development.

3.1.9.1 *Discussion*—Other major constituents, in special cases, can include aluminum (Al), boron (B), fluoride (F), iron (Fe), nitrate (NO_3), and phosphorus (PO_4). Minor and trace elements that can occur in natural ground water vary widely, but can include arsenic (As), copper (Cu), lead (Pb), mercury (Hg), radium (Ra), and zinc (Zn). In addition, natural ground water may contain dissolved gases, such as hydrogen sulfide (H_2S), carbon dioxide (CO_2), oxygen (0_2), methane (CH_4), ammonia (NH_3), argon (Ar), helium (He), and radon (Rn). Also maybe included are neutrally charged mineral species, such as silicate (SiO_2), naturally occurring organics, such as tanic acids, colloidal materials, and particulates, such as bacteria viruses and naturally charged pollen spores.

3.1.9.2 *Discussion*—Most of the natural ground water is a part of the hydrologic cycle, that is the constant circulation of meteoric water as vapor in the atmosphere as a result of evaporation from the earth's surface (land and ocean), liquid and solid (ice) on and under the land as a result of precipitation from the atmosphere, and as liquid returned to the ocean from the land. A very small amount of the ground water may be magmatic water originating from rocks deep within the crust of the earth. Other ground water is connate in that it is trapped in sediments and has not actively moved in the hydrologic cycle for a period measured in geologic time.

3.1.9.3 *Discussion*—While moving through the hydrologic cycle, chemical elements in the water are exchanged with other ions and dissolved into and precipitated out of the water, depending upon reactions with air and other gases, rock minerals, biological agents, hydraulic pressure, and the ambient temperature. The chemical composition of natural ground water ranges from that similar to distilled water with a minor amount of dissolved solids to a brine with at least 100 000-mg/L dissolved solids (natural occurring brine have been

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[4] The boldface numbers in parentheses refer to a list of references at the end of the text.

analyzed with more than 300 000-mg/L dissolved chemical solids) **(4)**.

3.1.10 *parts per million*—for water chemistry, a dimensionless ratio of unit-of-measurement per unit-of-measurement expressed in English terms. One part per million is equivalent to 1 mg of solute to 1 kg of solution. For example, if the total weight of the solution and solute (1 million ppm) has 99 % solution and 1 % solute, this is the same as 990 000 ppm solution and 10 000 ppm solute in the 1 million parts.

3.1.11 *water analysis*—a set of chemical ions as analyzed from a water sample. In this guide, the water analysis normally includes the common constituents as found in natural ground water (see 3.1.9; *natural ground water*).

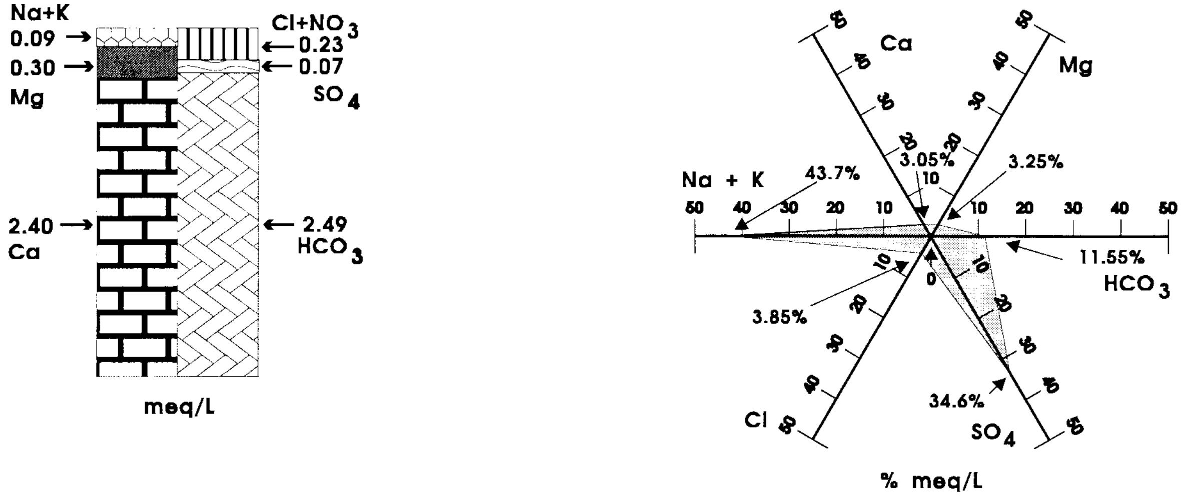
3.1.12 *water-analysis diagram*—the phrase, as used in this guide, is for the graphical plotting methods used for displaying a single water-quality analysis. These systems use various types of graphical displays that form characteristic patterns of the plotted individual cations and anions of the analysis. The pattern of the one analysis is then compared with the patterns formed by the plotting of other analyses. This method can be utilized to assist in the scientific interpretation of occurrence of cations and anions in natural ground water, for example, the interrelationship of a number of water samples within the studied area. Simpler types of the diagrams (for example, bars) can be used to display single ion values, such as Cl^- or Na^+.

4. Summary of Guide

4.1 This guide includes descriptions of the water-analysis diagrams that pictorially display common chemical components of a single water analysis from a natural ground-water source.

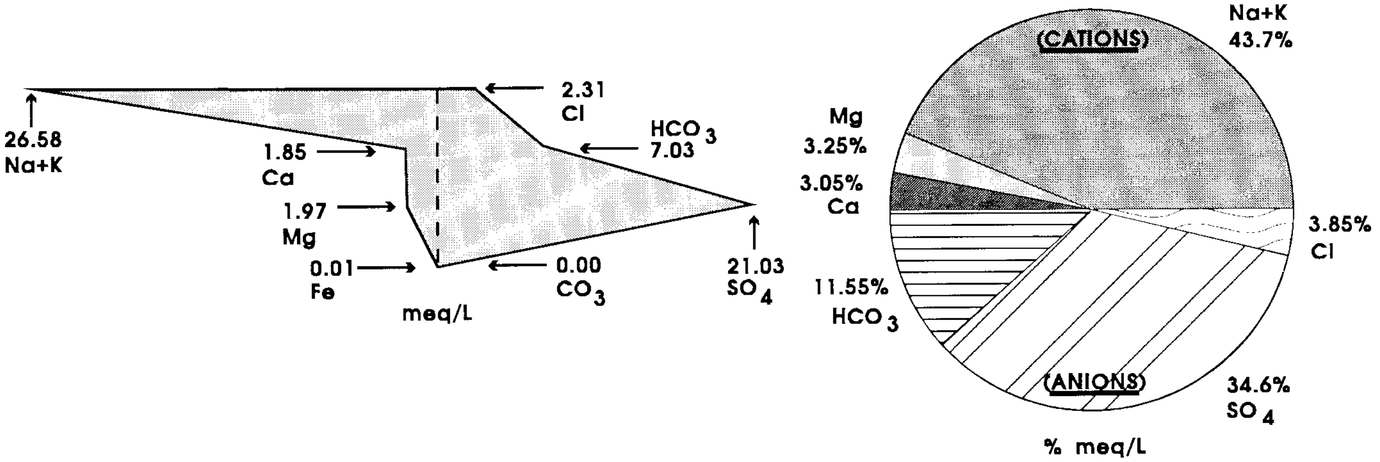
4.1.1 The significance and use of the four distinct types of diagrams (bar, radiating, pattern, and circular) (see Fig. 1) are described.

4.2 The minimum required chemical constituents from each water analysis for inclusion on the more commonly used diagrams are listed.



(*a*) Bar Diagram

(*b*) Radiating Vector Diagram



(*c*) Pattern Diagram

(*d*) Circle Diagram

FIG. 1 Examples of the Four Types of Single-Analysis Diagrams

4.3 The recommended analytical accuracy or chemical balance of the minimum required chemical constituents is defined.

4.4 Calculations required for the preparation of an analysis for plotting on a diagram are described.

4.5 Descriptions and comprehensive illustrations are given for the following water-analysis diagrams:

4.5.1 *Bar Diagrams*:

4.5.1.1 Hintz/Grünhut bar diagram **(5)**,

4.5.1.2 Rogers bar diagram **(6, 7)**,

4.5.1.3 Collins bar diagram **(8)**,

4.5.1.4 Renick bar diagram **(9)**,

4.5.1.5 Preul bar diagram **(10)**,

4.5.1.6 Single-ion bar diagram **(3)**, and

4.5.1.7 Carlé bar diagrams **(11)**.

4.5.2 *Radiating Vector Diagrams*:

4.5.2.1 Tickell radial diagram **(12)**,

4.5.2.2 Dalmady radial diagram **(13)**,

4.5.2.3 Maucha 16-vector radial diagram **(14, 15)**,

4.5.2.4 Maucha six-vector radial diagram **(16)**,

4.5.2.5 Girard four-axis diagram **(17)**,

4.5.2.6 Frey four-axis diagram **(18)**,

4.5.2.7 Colby kite diagram **(19)**,

4.5.2.8 Rónai starred diagram **(20)**, and

4.5.2.9 EPA vector diagram (7.7.2 on GEOBASE 6.0).

4.5.3 *Pattern Diagrams*:

4.5.3.1 Stiff pattern diagram **(21)**,

4.5.3.2 Dulas baseline diagram **(22)**,

4.5.4 *Circular Diagrams*:

4.5.4.1 Carlé circular diagram **(23)**,

4.5.4.2 Pie diagram **(1)**,

4.5.4.3 Tolstichin cyclical diagram **(24)**,

4.5.4.4 Disk diagram **(24)**, and

4.5.4.5 Udluft circular diagram **(25, 26)**.

4.6 Automated procedures (computer-aided graphics) for basic calculations and the construction of the water-analysis diagrams are identified.

4.7 Keywords

4.8 A list of referenced documents is given for additional information, and

4.9 A bibliography (non-referenced documents) is given for further sources of information in Appendix X1.

5. Significance and Use

5.1 Each year, many thousands of water samples are collected and the chemical components are determined from natural ground-water sources.

5.2 An understanding of the relationships between the similarities and differences of these water analyses are facilitated by displaying each separate analysis as a pictorial diagram. This type of diagram allows for a direct comparison between two or more analyses and their displayed ions.

5.3 This guide presents a compilation of diagrams that allows for transformation of numerical data into visual, usable forms. It is not a guide to selection or use. That choice is program or project specific.

5.4 The single sample water-analysis diagrams described in this guide display the following; (1) the ppm or mg/L concentrations of the cations and anions on bars, circles, or baseline diagrams; (2) the epm or meq/L percentages of the cation and anion weights on bars, double bars, circles, radiating vectors, or kitelike shapes and; (3) a combination of (1) and (2) on circles **(1, 3, 25, 27, 28, 29)**.

5.5 The classification of the composition of natural ground water is an early use of the single sample water-analysis diagram.

NOTE 3—Palmer, in 1911, developed a tabular system for the classification of natural water. Rogers, in a 1917 study of oil-field waters, presented the Palmer classification on a graphical display that had three vertical bars **(6, 7, 29)**.

5.6 The origin of the water may be postulated by the amount and the relationship of the cations and anions in a water sample that is plotted on the diagram. Patterns visually indicate water types and origins.

5.7 Comparison of the visual similarity or dissimilarity of diagrams for different water analyses that are from separate locations allows the analyst to evaluate if the samples may be from the same water source or not.

5.8 Numerous interpretive methods are possible from the examination of a series of the single sample water-analysis diagrams.

NOTE 4—For example, by arranging the diagrams at the point of origin as represented on a geologic cross section or on an areal map, the hydrochemical changes can be visualized as the water travels through the hydrologic regime, the amount of mixing that has taken place with water from a different origin, and the effects of ambient conditions, such as air, temperature, rock, and man-induced contaminants, on the water.

NOTE 5—It should be noted that for many hydrochemical research problems involving the interpretation of the origin, chemical reactions, and mixing of natural water, the single sample water-analysis diagram is only one segment of several analytical methods needed to understand condition.

6. Selection and Preparation of Data for Plotting on Single-Analysis Diagrams

6.1 In most cases, raw data needs to be transformed before it can be plotted in a uniform manner on the diagram.

6.2 *Minimum Data Requirements*—Many of the basic water-analysis diagrams require water analyses that have a minimum number of major ions determined, although on several diagrams a minimum of one ion can be plotted and compared with similarly plotted diagrams.

NOTE 6—The constituents commonly used on the diagrams are the cations calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K); and the anions bicarbonate (HCO_3), carbonate (CO_3), sulfate (SO_4), and chloride (Cl). If, in special circumstances, some other ions, such as dissolved iron (Fe^{2+}) and ammonia (NH_4^+), exceed the conventional group described above, and all water analyses for the study include these constituents, they can replace or be combined with the ion with which they are most similar. If the major anions and cations do not balance within a reasonable percent, normally 0 to ± 10 %, the analysis cannot be used **(1, 27)**.

NOTE 7—Natural potable waters normally contain relatively few dissolved constituents in concentrations greater than 1 mg/L. The maximum recommended dissolved solids for drinking water by the U.S. Public Health Service is 500 mg/L. The World Health Organization guidelines recommend a maximum of 1000 mg/L dissolved solids **(30)**.

6.3 *Recommended Accuracy for Chemical Balance*—The chemical balance or chemical equilibrium of a complete analysis (all major ions determined) is calculated by converting the ions from mg/L to meq/L values and adding the cations together and the anions together. The computation for percent balance is as follows, with zero as the optimum percentage value (percentage is determined by multiplying the computed value times 100);

$$\% \, Chemical \, Balance \, (\pm) = \frac{Total \, Cations - Total \, Anions \, (\text{meq}/L)}{Total \, Cations + Total \, Anions \, (\text{meq}/L)} \times 100 \quad (4)$$

Recommended Chemical Balance For Use of Analyses on Water-Analysis Diagrams

Dissolved Solids	*Chemical Balance*
0 to 100 mg/L	Within ± 5 %
101 to 250 mg/L	Within ± 3 %
Greater than 250 mg/L	Within ± 2 %

NOTE 8—Minor amounts of ions such as fluoride (F), nitrate (NO_3), iron (Fe), and barium (Ba), may occur in natural ground water, but normally do not significantly influence the chemical balance. If any of these ions (for example, NO_3) occur in amounts that alter the chemical balance, they can be included in the computations for construction of water-analysis diagrams. Other constituents may occur in minor amounts in a colloidal or suspended state, such as silica (SiO_2), iron hydroxide (Fe), and aluminum compounds (Al), and are not considered in the chemical balance because they are not dissolved constituents.

NOTE 9—In a study of the Delmarva Peninsula, Hamilton, Shedlock, and Phillips used 10 % as the error limit for the ionic charge balance of analyses with a complete set of major ions (nitrate was excluded as a major ion) **(31)**. In addition, there may be circumstances where the ionic balance is greater than 10 % due to analytical error. If so, specify the circumstances.

6.4 *Required Calculations for Diagram Construction*:

6.4.1 *Type of Plot Units*—The single water-analysis diagrams include plot methods that require no additional computations to the original constituent determinations (values in ppm or mg/L units); conversion to equivalent weights (ppm to epm or mg/L to meq/L); ion percentage of the total equivalent weight (epm to % epm or meq/L to % meq/L); and to the plot percentages determined from the principle of ion combinations. Variations in the expression of plot units include the Hintz/Grunhut bar diagram where values are given in milligrams per kilogram (mg/kg) and milliequivalents per kilogram (meq/kg) **(5)**.

6.4.2 *Scale of the Plots*:

6.4.2.1 Most of the diagrams use direct scale methods where the length of a line, vector, or bar represents the ion value in ppm (or mg/L) or epm (or meq/L) or % epm (or % meq/L) units.

6.4.2.2 Some circular diagrams (for example, pie, Tolstichin, Udluft) use the length of the arc of the circle to form pie-shaped sectors and to represent the percentage equivalent weight of the ions **(24, 26)**.

6.4.2.3 The diameter of the circular pie diagram can be varied and scaled to represent the total constituent concentration of the analysis.

6.4.2.4 Several of the plot methods (circular, Rónai) use area, for example, square inches (in.^{2}) or square centimetres (cm^2), to represent the concentration of the individual ions. This circular diagram uses the area of concentric circles to represent the ion concentration in mg/L of the selected constituents **(20)**.

NOTE 10—Most of the single-analysis diagrams (excluding the line diagrams, for example, Maucha radiating vector **(14, 15, 16)**) have enclosed two-dimensional areas to represent the individual ions and, in reality, are representations of the concentrations. These patterned areas (for example, Collins bar diagram **(8)**) emphasize the variation in ion concentrations to assist in the pictorial comparison and interpretation of the analyses. The actual ion concentration is determined directly from an accompanying line scale, therefore, the determination of the area represented by an ion is unnecessary.

6.4.3 *Equivalent Weight Factors*—The factors (see 3.1.4) used for converting the most common ions (used on the water-analysis diagrams) to meq/L from mg/L or epm from ppm values are as follows:

Cations		*Anions*	
Calcium.................	0.04990	Bicarbonate..............	0.01639
Magnesium............	0.08229	Carbonate................	0.03333
Sodium.................	0.04350	Sulfate.....................	0.02082
Potassium..............	0.02558	Choloride................	0.02821

6.4.4 *Determining Ion Percentages*—The percentage values used for plotting on some of the single water-analysis diagrams are determined by multiplying times 100 the number derived from dividing the total meq/L or epm value of the cations and anions into the individual cation or anion value. For example, the number derived from dividing the total ion value (Ca + Mg + Na + K + HCO_3 + CO_3 + SO_4 + Cl) divided into the meq/L or epm value of Ca is multiplied times 100 to give the percentage of Ca in the total ions (by weight):

$$\% \, Ca = \frac{meq/L \, Ca}{meq/L \, \, (Anions + Cations)} \times 100 \quad (5)$$

6.4.4.1 This percentage is the plot value for Ca on some of the single-analysis diagrams (Fig. 1, (*b*) and (*d*)). This procedure of computation is followed for each of the remaining cations (Mg and (Na + K)) and for each of the anions (Cl, SO_4, and (HCO_3 + CO_3)) for the diagrams.

6.4.5 *Example of Computations Using an Actual Chemical Analysis*—An example of the computations required to prepare a complete chemical analysis for plotting on standard water-analysis diagrams is given as follows:

6.4.5.1 *Chemical Analysis*—The following is the chemical analysis that is used as an example for demonstrating the steps needed for the plotting of constituent values.

Chemical Constituents of Ground-Water Sample as Determined by Laboratory Analyses (after Fetter, **(32)**):

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	CO_3^{-}	SO_4^{2-}	Cl^{-}
	Laboratory Determined Value							
mg/L	23	4.7	35	4.7	171	0	1.0	9.5
	Multiplied by							
Equivalent Weight Factor	0.04990	0.08229	0.04350	0.02558	0.01639	0.03333	0.02082	0.02821
	Results							
meq/L	1.15	0.39	1.52	0.12	2.80	0	0.02	0.27
	Plot Value (Ion Percentage)							
Percent	36.2	12.2	47.8	3.8	90.6	0	0.7	8.7

6.4.5.2 *Example of meq/L Computation*:

$$1.15 \text{ meq}/L \text{ Ca} = 23 \text{ mg}/L \, Ca \times 0.04990 \, (conversion \, factor) \quad (6)$$

6.4.5.3 *Chemical Balance*—The chemical balance of the analysis is checked as follows:

$$97\ \%\ (balance) = \frac{3.09\ (anions)}{3.18\ (cations)} = \frac{2.80+0+0.02+0.27\ (anions)}{1.15+0.39+1.52+0.12\ (cations)} \times 100 \qquad (7)$$

6.4.5.4 *Cation*—Plot values (percentage of each cation constituent) for the cation are determined by dividing the total cation amount in meq/L into the meq/L amount for each cation.

NOTE 11—Plot values are rounded to a whole number for illustration.

6.4.5.5 *Example of Plot Value (Cation Percentage) Computation*:

$$36.2\ \%\ Ca = \frac{1.15\ \text{meq}/L\ Ca}{3.18\ meq/L\ cations} \times 100 \qquad (8)$$

$$12.2\ \%\ Mg = \frac{0.39\ \text{meq}/L\ Mg}{3.18\ \text{meq}/L\ cations} \times 100 \qquad (9)$$

$$51.6\ \%\ Na + K = \frac{1.52\ \text{meq}/L\ Na + 0.12\ \text{meq}/L\ K}{3.18\ \text{meq}/L\ cations} \times 100 \qquad (10)$$

6.4.5.6 *Anion*—Plot values (percentage of each anion constituent) for the anion are determined by dividing the total anion amount in meq/L into the meq/L amount for each anion.

6.4.5.7 *Example of Plot Value (Anion Percentage) Computation*:

$$90.6\ \%\ HCO_3 + CO_3 = \frac{2.80\ \text{meq}/L\ HCO_3 + 0\ \text{meq}/L\ CO_3}{3.09\ \text{meq}/L\ anions} \times 100 \qquad (11)$$

$$0.7\ \%\ SO_4 = \frac{0.02\ \text{meq}/L\ SO_4}{3.09\ \text{meq}/L\ anions} \times 100 \qquad (12)$$

$$8.7\ \%\ Cl = \frac{0.27\ \text{meq}/L\ Cl}{3.09\ \text{meq}/L\ anions} \times 100 \qquad (13)$$

NOTE 12—Dissolved Fe (Fe^{+2} and FE^{+3}) can be a larger component in some aquifers of terrestrial origin than Na + K (for example, coals, iron bog ores, and deltaic deposits). The Fe usually occurs in the deposits as an iron carbonate ($FeCO_3$) that dissolves to Fe and CO_3 in the water or an iron sulfate (FeSO4) that dissolves to Fe and SO_4 in the water.

7. Water-Analysis Diagrams

7.1 *Introduction*—This guide is an attempt to clearly describe many of the diagrams that have been developed for displaying a single water-quality analysis of natural ground water. Four distinct types of single-analysis diagrams (bar, radiating vector, pattern, and circular) (see Fig. 1) are presented in the following sections of this guide.

7.1.1 An outline of pictorial diagrams by Matthess describes a number of the plotting systems developed for the display of the chemical composition of a single analysis from natural waters **(3)**.

7.1.2 In the description by Matthess is stated "the pictorial form (for example, diagrams of representative ground water) can be presented in cartographic form, to facilitate comparison of regional or facies variations in the water" **(3)**.

7.1.3 Matthess also stated "it is however difficult, or even impossible, to represent the analyses of several ground waters of quite different geochemical origins clearly on one diagram."

NOTE 13—A number of other excellent publications are available for the geochemistry of natural ground water, most of those are referred to in the text and listed in the bibliography. Two of those publications are by Hem **(1)** and Zaporozec **(24)**.

NOTE 14—The criteria for the selection of an analysis and the computations required for preparing the analysis for plotting on many of the single-analysis diagrams is described in Section 6.

7.2 *Bar Diagrams*—Bar diagrams are those where the ion values are represented by the length of symboled bars that extend vertically or horizontally from a zero base (Fig. 1 (*a*)).

7.2.1 *Hintz/Grünhut Bar Diagram*— Hintz and Grünhut, for a study of mineral waters (spa) in 1907, presented a horizontally oriented two-bar diagram that uses meq/kg units for plotting the ion values (see Fig. 2) **(5)**.

7.2.1.1 On the diagram, the cations Na, Ca, and Mg are arranged from left to right on the upper bar. The anions Cl, SO_4, and HCO_3 are from left to right on the lower bar.

7.2.1.2 In addition, the total concentration in mg/kg is shown as a solid line above the bars and the free CO_2 content is inserted as an extension to the anion bar **(3, 5)**.

7.2.2 *Rogers Diagram*—Rogers, in 1917, developed one of the earlier methods for displaying the chemical constituents of natural ground water on a pattern graph **(6)**.

7.2.2.1 The graphical display presented by Rogers is a vertically oriented triple-bar diagram (see Fig. 3). This diagram uses the system as proposed by Palmer **(29)** to simplify the determination of the geochemical classification of natural ground water.

7.2.2.2 On the diagram (see Fig. 3), the left bar represents the 50 % reacting value for the anions (acids), the right bar represents the 50 % reacting value for the cations (bases), and the central bar shows the properties of reaction that result from the proportions of acids and bases.

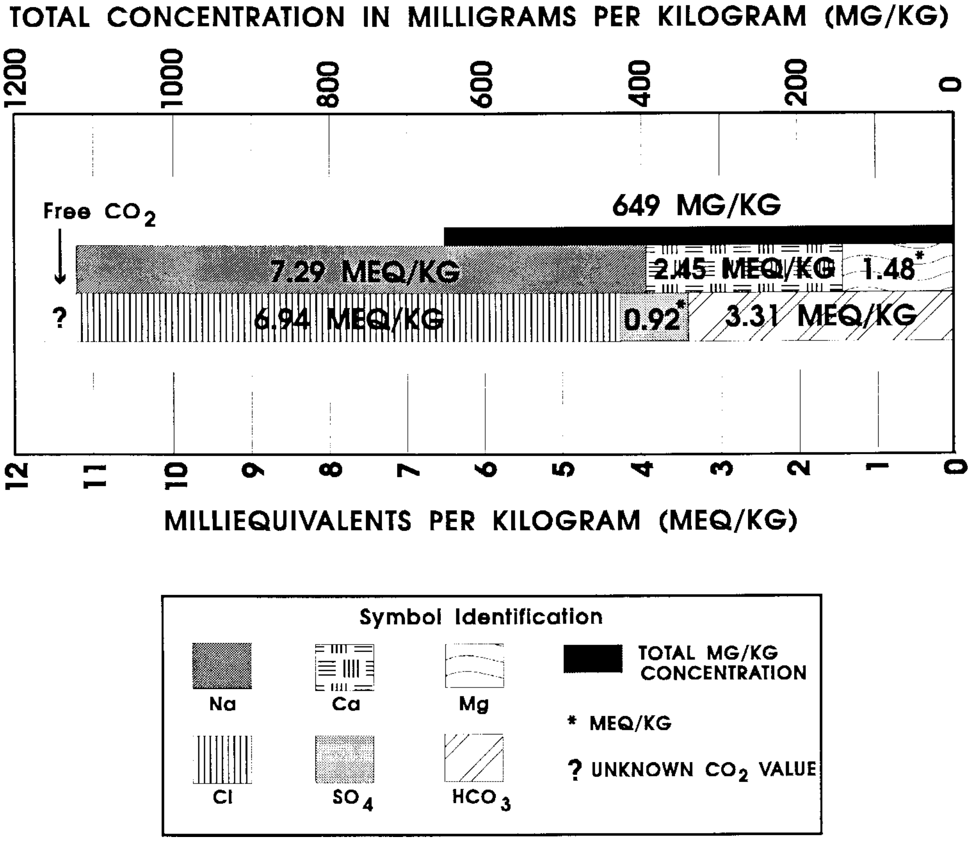
7.2.2.3 The acids are arranged with the strong acids (Cl and SO_4) at the bottom of the left column and the weak acids (HCO_3 and CO_3) at the top of the column. The bases are arranged with the alkalies (Na and K) at the bottom of the right column and the alkaline earths (Ca and Mg) at the top of the column.

7.2.2.4 The primary salinity is due to the balance between equal values of the alkalies (Na and K) and strong acids (Cl and SO_4), the amount determined by the smaller (in this case strong acids) of the two components. The 22.3 % strong acids combines with an equal amount of alkalies to form 44.6 % primary salinity in the total composition.

7.2.2.5 The primary alkalinity is the result of combining the remainder of the alkalies (41.8 − 22.3 % = 19.5 % Na and K) with an equal amount of the weak acids (HCO_3 and CO_3). Therefore the primary alkalinity is equal to 39 % of the total composition.

7.2.2.6 The secondary alkalinity is the result of combining the remainder of the weak acids (27.7 − 19.5 % = 8.2 % HCO_3 and CO_3) with the alkaline earths (Mg and Ca). Therefore the secondary alkalinity is equal to 16.4 % of the total composition.

7.2.2.7 If the strong acids had exceeded the alkalies, the remainder of the strong acids would have combined with the alkaline earths, creating secondary salinity. This water would be permanently hard. Rogers stated that "the writer has found this distinction one of the most valuable features of Palmers'



NOTE 1—Analysis selected from Ref **(1)**.

FIG. 2 Hintz/Grünhut Bar Diagram (3)

classification for by it all waters are separated into two important group."

NOTE 15—Clarke stated later that the Palmer method was limited as "it takes no account of the silica in natural waters and is of little use in the study of mineral springs and mine waters" **(33, 34)**.

7.2.2.8 Symbols shown on the Rogers Diagram are contrasting patterns for ease of distinguishing the individual ions. Various colors also can be used to represent the ions.

7.2.3 *Collins Diagram*—Collins, in 1923, published a pictorial technique that has two vertical bars, one for cations and the other for anions in epm units (see Fig. 4) **(8)**.

7.2.3.1 Collins states "the method used in the U.S. Geological Survey is like others that have been published ...," thus saying that this was not the first use of this type of diagram.

7.2.3.2 The left bar, in meq/L, represents the 50 % reacting value for the cations and the right bar represents the 50 % reacting value for the anions.

7.2.3.3 The meq/L values of the ions are determined by comparison with an accompanying scale. For example, the combined reacting value of all represented ions for analysis Number 1 is equal to about 10.5 meq/L (5.25 times two) of dissolved solids.

7.2.3.4 For project reports, the analysis numbers are used as a cross-reference index to an accompanying table of detailed source identifications and chemical constituent values.

7.2.3.5 Symbols shown on the Collins bar diagram are contrasting patterns for ease of distinguishing the individual ions. Various colors also can be used to represent the ions.

7.2.3.6 Primarily, the diagram is designed to compare one analysis with another and to the originating geologic formations.

7.2.3.7 The Collins diagrams can be placed on areal maps and geologic cross sections to visualize the similarities and differences throughout the area of study.

7.2.3.8 Langelier and Ludwig, in 1942, demonstrated a method of comparing related pairs of analyses by use of the Collins diagram. The first diagram of the pair extends upward from a central horizontal zero (0) line and the second extends downward from the 0 line directly below the first diagram **(35)**.

7.2.3.9 Other variations of the Collins Bar Diagram include single-ion bars and horizontal orientation of the diagram.

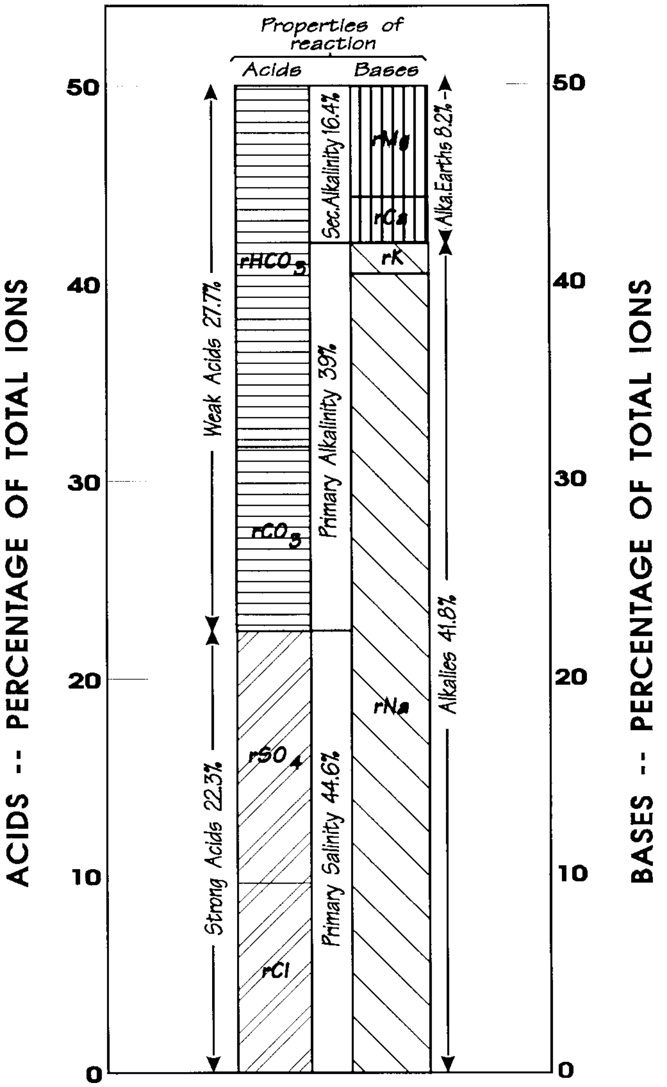
7.2.4 *Renick Diagram*—Renick, in 1924, developed a vertical double-bar diagram (see Fig. 5) similar to Collins **(8, 9)**.

7.2.4.1 The diagram is arranged with the following ions and combinations of ions; cations Ca, Mg, and Na + K and anions HCO_3 + CO_3, SO_4, and Cl + NO $_3$.

7.2.4.2 The left bar, in meq/L units, represents the 50 % reacting value for the cations and the right bar represents the 50 % reacting value for the anions.

7.2.4.3 In addition, the diagram includes a third column, the length of which represents the sampling depth, in feet or metres, for the ground water.

7.2.4.4 Symbols shown on the diagram are contrasting patterns for ease of distinguishing the individual ions. Various colors also can be used to represent the ions.



NOTE 1—Adapted from Ref **(6)**.

FIG. 3 Rogers Diagram/Palmers Classification

7.2.5 *Preul Bar Graph*—Preul, in 1958, developed a bar graph (see Fig. 6) that has six vertical columns to represent the most important components **(10)**.

7.2.5.1 Each column, for example, SO_4, Cl, HCO_3, NO_3, Fe, and Mn, has an individual mg/L scale.

7.2.5.2 Depending upon the intended use of the water or purpose of the project, a critical concentration is established for each ion and a horizontal center line is placed on the diagram to show those ions above the critical concentration.

7.2.5.3 These diagrams are commonly placed on maps at the points of origin of the water samples.

7.2.5.4 A single pattern is used on the diagram for ease of distinguishing the diagram from other backgrounds. A color can be used as a pattern to emphasize the diagram.

7.2.6 *Single-Ion Bar Diagram*—Matthess, in 1982, demonstrated the use of single-ion bar diagrams (see Fig. 7) placed at the points of origin on a map as a method for aiding the visual comparison of Cl concentrations within the studied area **(3)**.

7.2.6.1 In Matthess's example, the lengths of the bars represent the mg/L concentrations of Cl in the sampled waters.

7.2.6.2 Contrasting patterns are used to quickly distinguish the various levels of ion concentrations, for example, 50 to 100 mg/L from 100 to 150 mg/L.

7.2.6.3 Triangular-shaped designs were used by Matthess to represent ion concentrations greater than 200 mg/L.

7.2.6.4 Any ion of interest can be illustrated for visual comparison by the method.

7.2.6.5 Any combination of contrasting symbols or colors can be used to emphasize the bars or other designs on maps or other illustrations.

7.2.7 *Carlé Bar Diagrams*—Carlé, in 1950, demonstrated two types of bar diagrams where the anions and cations are in one vertical or horizontal bar (see Fig. 8) **(11)**.

7.2.7.1 The anions are at the top or left end of the bar. The cations are at the bottom or right end of the bar.

7.2.7.2 The scale of the vertical bar is shown by Carlé in g/kg (grams per kilogram) or weight-per-weight units.

7.2.7.3 The scale of the horizontal bar is shown by Carlé in meq/L percentages, where 100 % equals the total anion and cation concentration.

7.2.7.4 Symboled patterns are used to distinguish the individual anions and cations. Colors may be used for the same purpose.

7.3 *Radiating Vector Diagrams*—Those diagrams are where the ion values are represented by the plot distance on a line or the length of lines or bars radiating from a central point (Fig. 1(*b*)).

7.3.1 *Tickell Radial Diagram*—Tickell, in 1921, proposed a diagram (see Fig. 9) with six lines radiating out at 60° angles from the origin **(12)**.

7.3.1.1 Each line represents a single or combined anion or cation scaled in meq/L percentage units.

7.3.1.2 The six radial lines of the Tickell diagram are the alkali ions Na + K, alkaline earth ion Ca, alkaline earth ion Mg, carbonate species $CO_3 + HCO_3$, sulfate ion SO_4, and chloride ion Cl.

7.3.1.3 The length of each line represents 50-meq/L percentage units from the central origin of the diagram.

7.3.1.4 The percentage of each ion is based on 100 % total ions, for example, cation SO_4 is 34.6 % of the total anion and cation meq/L.

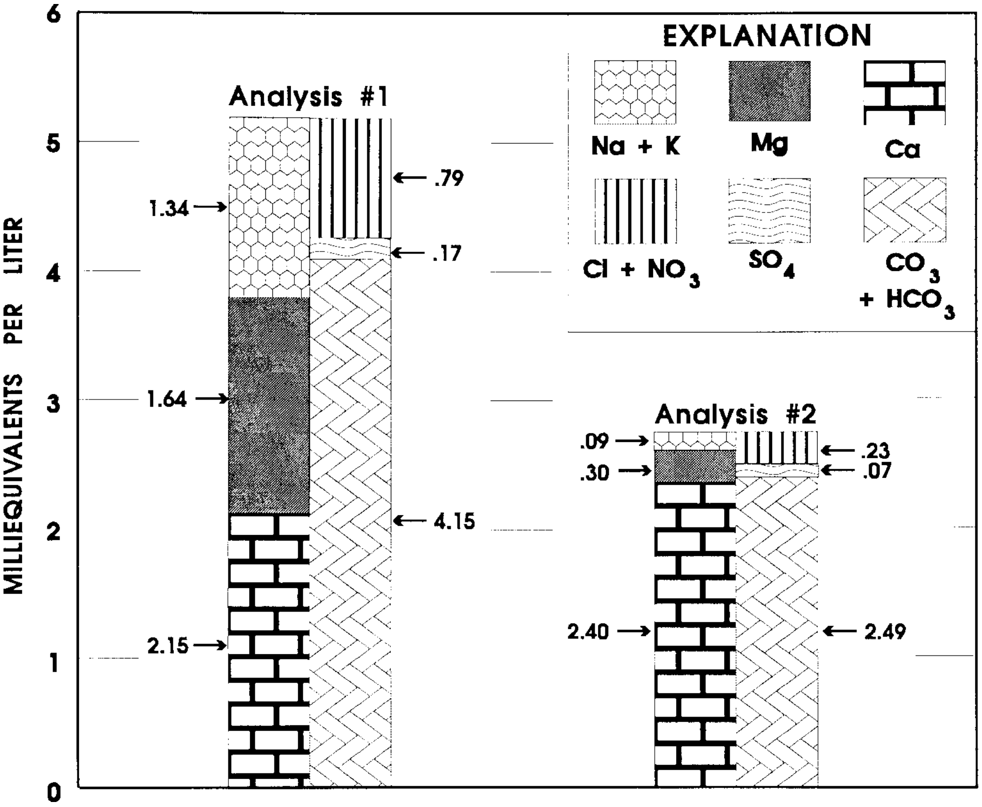
7.3.1.5 The plot positions on the ion lines are interconnected (for example, the 34.6 % position of SO_4 to the 11.55 % position of HCO_3), the total shape of which gives a characteristic pictorial representation of the water analysis.

7.3.1.6 The area enclosed by interconnecting the ion plot positions is filled with a pattern or color to emphasize the shape formed by the analysis.

7.3.1.7 In the original version of the diagram, Tickell combined the Ca and Mg on one line and reserved the sixth line for plotting the total meq/L concentration of the analysis or for any other constituent or parameter of interest to the study.

7.3.2 *Dalmady Radial Diagram*—Dalmady, in 1927, presented a modified version of the Tickell diagram (see Fig. 10) also with six lines radiating out at 60° angles from the origin **(13)**.

7.3.2.1 Dalmady's modification represented the ions by wide bars that extend from the central origin of the diagram



NOTE 1—Adapted from Ref **(1)**.

FIG. 4 Collins Bar Diagram

along the lines to the plot positions of the meq/L percentage value of the ions. The plot positions on the ion lines were not interconnected as was done for the Tickell diagram.

7.3.2.2 The six radial lines of the Dalmady diagram are the same as the Tickell diagram and are the alkali ions Na + K, alkaline earth ion Ca, alkaline earth ion Mg, carbonate species CO_3 + HCO_3, sulfate ion SO_4, and chloride ion Cl.

7.3.2.3 The length of each line represents 50-meq/L percentage units from the central origin of the diagram.

7.3.2.4 The percentage of each ion is based on 100 % total ions, for example, cation SO_4 is 34.6 % of the total anion and cation meq/L.

7.3.2.5 The total shape of the ion bars gives a characteristic pictorial representation of the water analysis.

7.3.3 *Maucha 16-Vector Radial Diagram*— Maucha, in 1932, developed an intricate 16-vector radial system (see Fig. 11) for illustrating meq/L percentages of the primary four anions and four cations for natural ground water (there are eight nonion vectors) **(3, 14, 15)**.

7.3.3.1 Maucha started with a regular eight-sided polygon constructed to give an area of 200 mm^2 (axial length of 8.082 mm). This polygon was divided into sectors by the 16 vectors radiating at angles of 22.5° from the center of the polygon. Each of the 16 sectors of the polygon had areas of 12.5 mm^2.

7.3.3.2 A vertical line (formed by nonion Vectors A and E) separates the polygon (and diagram) into two halves. The anions SO_4, Cl, HCO_3, and CO_3 are on four vectors on the left half and cations K, Na, Ca, and Mg on four vectors on the right half of the diagram. The eight intermediate vectors (alternating with the ion vectors) are labeled A, B, C, D, E, F, G, and H and are, necessary to complete the characteristic shape of Maucha's diagram.

7.3.3.3 Each ion vector is scaled in 100-meq/L percentage units, where, on the original diagram, 100 mm is equal to 100 %.

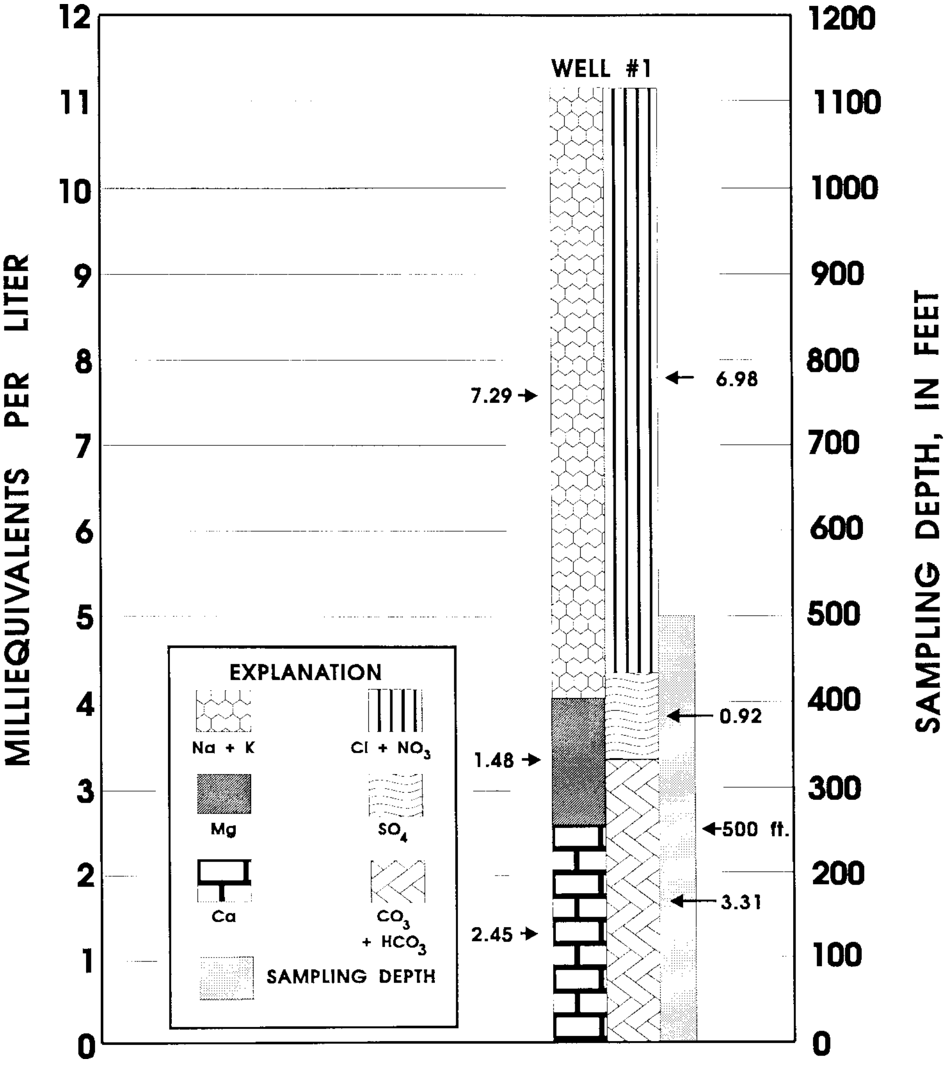
7.3.3.4 The plot position of an individual anion or cation is determined by computing the percentage included in the total anions (100 %) or cations (100 %). For example, on Maucha's original diagram, Na would be 87.4 % of the total cations and would be plotted 87.4 mm from the center of the diagram (see Fig. 11).

7.3.3.5 The plot position of each individual ion is connected by lines to the two adjacent vectors at the position where they intersect the polygon. For example, the plot position of Na at 87.4 % (87.4 mm on the original diagram) is connected to Vector Line B and Vector Line C at the point where they intersect the polygon.

7.3.3.6 Assuming the diagram is constructed according to Maucha's original specifications, the area in square millimetres of the two triangles formed (center of diagram to ion plot position to intersection of vector line with polygon and back to center) corresponds to the ion percentages. For example, the two triangles formed by Na (see Fig. 11) would have an area of 87.4 mm^2.

7.3.3.7 The area enclosed by the series of lines produces a distinctive pattern and can be emphasized by filling in with a pattern or color.

7.3.4 *Maucha Six-Vector Radial Diagram*— Maucha, in



NOTE 1—Adapted from Ref **(3)**. Analysis selected from Ref **(1)**.

FIG. 5 Renick Diagram

1949, adopted a simple six-vector radial diagram (see Fig. 12), that he attributed to Telkessy (unknown reference), for graphically displaying the meq/L values of the major ion groups **(1, 16, 22, 24)**.

7.3.4.1 The six vectors radiate outward at 60° angles from the central point of the diagram.

7.3.4.2 The length of each vector represents the individual ion value in meq/L (or epm units). An accompanying meq/L unit scale allows for the determination of the value of each ion or of combined ions.

7.3.4.3 These six-vector radial diagrams give a characteristic pictorial representation of the water analysis.

7.3.4.4 The diagrams can be compared, one with another, or positioned at the relative sample location on an areal map for the visual relationship of water analyses of a ground-water study.

7.3.5 *Girard Four-Axis Diagram*—Girard, in 1935, presented a four-vector radial diagram (see Fig. 13) for graphically displaying the meq/L concentrations of the major ion pairs from water analyses **(3, 17)**.

7.3.5.1 The four vectors radiate outward at 90° angles from the central point of the diagram.

7.3.5.2 The length of each vector represents the individual ion value in meq/L units. A meq/L unit scale can accompany the diagram to allow for the determination of the value of each ion.

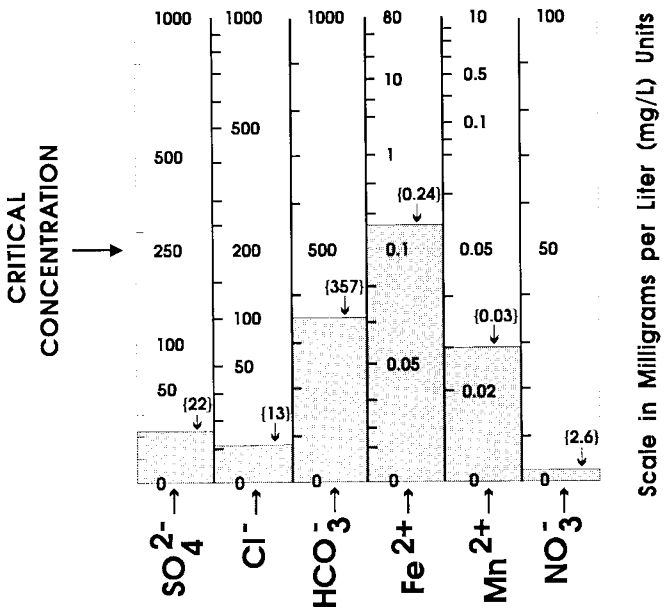
7.3.5.3 The following ion pairs are plotted on separate axes; Ca and HCO_3, SO_4 and Mg, Cl and Na, and H and CO_3. Normally, the H and CO_3 concentrations are nearly zero and do not show on the diagram.

7.3.5.4 The plot positions of the cations (Ca, Mg, Na, and H) are connected by solid lines and the anions (HCO_3, SO_4, Cl, and CO_3) by dashed lines.

7.3.5.5 The diagram also may be plotted in mg/L values or meq/L percentages.

7.3.5.6 These four-vector radial diagrams give a characteristic pictorial representation of the water analysis. The diagrams can be compared, one with another, for the visual relationship of water analyses of a ground-water study.

7.3.6 *Frey Four-Axis Diagram*—Frey, in 1933, presented a



NOTE 1—Each ion bar has its own scale. Also, ion values are given in brackets **(22)**.

NOTE 2—Adapted from Ref **(3)**.

FIG. 6 Preul Bar Diagram

four-axis radial diagram (see Fig. 14) for graphically displaying the reconstituted salts of a water analysis by plotting the meq/L percent of the combined ions (See Table 1 and Table 2 for analyses and order of combination) **(3, 18)**.

7.3.6.1 The system, that distinguishes the three water facies, alkaline, earth, and chlorine, is described by Frey as to permit the differentiation between psuedochloride waters and the real chloride waters.

7.3.6.2 The four axes radiate outward at 90° angles from the central point of the diagram.

7.3.6.3 The length of each axis is determined by the percentage of the combined ion value. A scale for the percentage of the meq/L values can accompany the diagram (as shown on Fig. 14) to allow for the determination of the combined ions, however, Frey included only the actual values on the diagram.

7.3.6.4 For the alkaline and earth water facies, the diagram has the alkaline carbonates ((Na + K)CO_3) on the right *x*-axis, earth carbonates ((Ca + Mg + Fe)CO_3) on the upward *y*-axis, alkaline sulfates ((Na + K)SO_4) on the left *x*-axis, and earth sulfates ((Ca + Mg)SO_4) on the downward *y*-axis.

NOTE 16—When the chemical character of the water is of the alkaline or earth facies, the ion distribution allows for three plot values to be determined. Lines are drawn between the three plotted points to form a triangular-shaped area (the third side of the triangle is the *x*- or *y*axis).

NOTE 17—The enclosed area formed by the combined ion triangle for alkaline and earth waters can be filled-in with a pattern or color to emphasize the water type.

NOTE 18—The elongation of the triangle along one of the axes determines the water quality type.

NOTE 19—A triangle elongated to the right is a sodium bicarbonate (Na_2CO_3) type, to the left is a sodium sulfate (Na_2SO_4) (analysis Number 1 on Fig. 14), to the top is a calcium bicarbonate ($CaCO_3$), and to the bottom is a calcium sulfate ($CaSO_4$) type water.

NOTE 20—For the alkaline and earth water facies, the second triangle on analysis Number 1 of Fig. 14 supplies additional information on chloride concentration to the user of the diagram and does not assist in determining the classification of the water.

NOTE 21—For the alkaline and earth facies, the chlorides are exclusively alkalines and are shown by plotting the alkaline chlorides on both the positive *x* and negative *y* axes. The triangle is formed by the *x* and *y* axes and by connecting the plot points together with a line. When the chloride is abundant to the point of being predominant, the water would be of the class determined by the combined ion triangle and the additional statement chloride content exaggerated. The total meq/L percentage sum of the three combined ion values and one alkaline chloride value is 100 %.

7.3.6.5 For the chlorine water facies, the diagram has the alkaline chlorides ((Na + K)Cl) on the *x*-axis to the right and the earth chlorides ((Ca + Mg)Cl) on the *x*-axis to the left. To complete the chlorine triangle, the total of the (Na + K)Cl and (Ca + Mg)Cl percentages is plotted on the negative *y* axis (see analysis Number 2 on Fig. 14).

NOTE 22—On Fig. 14, the earth carbonates (Ca + Mg)CO_3 plot on the positive *y* axis and the earth sulfates (Ca + Mg)SO_4) on the negative *y* axis.

7.3.6.6 The order of ion combination and the resultant plot values, as given in Table 2, is required as a guide for the construction of the Frey diagram.

7.3.6.7 These four-axis radial diagrams present an easily interpreted pictorial method for the chemical classification of water.

7.3.7 *Kite Diagram*—Colby, Hembree, and Rainwater, in 1956, presented a four-axis pattern diagram (Fig. 15) that radiates from a central point and was named a kite diagram because of its general shape **(3, 19, 24)**.

7.3.7.1 The kite diagram has the four ionic groups plotted on the axes. The ions Ca + Mg are on the upward *y* axis, Na + K on the downward *y* axis, SO_4 + Cl + NO_3 on the left *x* axis, and CO_3 + HCO_3 on the right *x*-axis.

7.3.7.2 The axes are in epm or meq/L units with the zero (0) at the central point. The total diagram can be scaled to correspond to the range of ion values for the project.

7.3.7.3 The kite figure is formed by connecting lines to plot positions on the four axes.

7.3.7.4 The diagrams can be compared, one with another, or positioned at the relative sample locations on an areal map for the visual relationship of water analyses from a ground-water study.

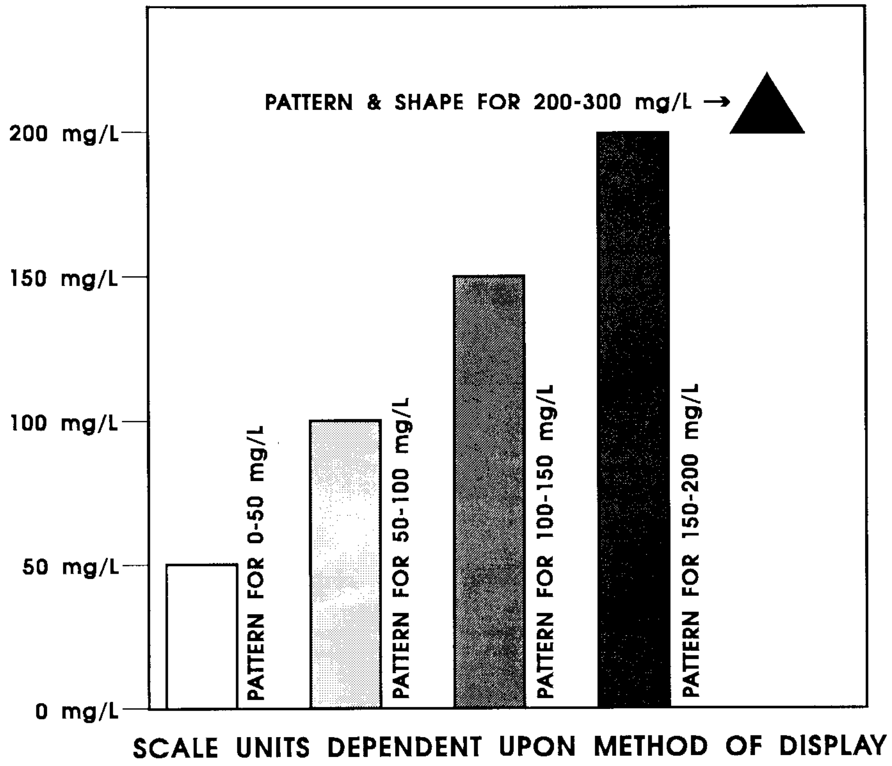
7.3.8 *Rónai Starred Diagram*—Rónai, in 1958, presented an eight-vector diagram (see Fig. 16) that represents the individual ions as right isosceles triangles where the area of the triangles are proportional to the meq/L concentrations. The plot was named a "starred diagram" because of its general shape **(20, 24)**.

7.3.8.1 The area and related size of the Rónai diagram is proportional to the total meq/L concentration of the anions and cations.

7.3.8.2 Individual anion and cation values are in meq/L units.

7.3.8.3 The area represented by the meq/L concentration of each ion is proportional to the total anion or cation area.

7.3.8.4 The meq/L concentrations of the ions are plotted on the four vertical positive and negative *y* axes and the horizontal positive and negative *x* axes that radiate from a central point. The cations are above and the anions below the *x*-axis.



NOTE 1—Adapted from Ref **(3)**.

FIG. 7 Example of Single Ion Diagrams

NOTE 23—The ions are plotted individually, where the upper vertical axis has Ca to the left and Mg to the right, the left horizontal has Na + K above and Cl below the line, the lower vertical has HCO_3 to the left and SO_4 to the right, and the right horizontal axis is for optional ions, but, for illustration, has Fe above and NO_3 below the line.

7.3.8.5 The four remaining axes radiate at 45° angles from the center of the diagram.

NOTE 24—To complete the starred-shaped diagram, lines are drawn at right angles (90°) from the ion plot points to the adjacent 45° axes to create right isosceles triangles, for example, from the upper vertical Ca axis to the upper left 45° axis.

7.3.8.6 The unit size of the area enclosed by each of the ion right isosceles triangles represents the meq/L concentrations of the individual ions.

7.3.8.7 Using the ion concentrations shown on Fig. 16, the unit plot distance for Ca along the upper *y* ion axis from the center of the diagram is determined using the following basic mathematics.

$$Ca\ plot\ distance = \sqrt{\frac{Ca\ meq/L}{meq/L\ plot\ unit} * 2} \tag{14}$$

or:

$$6.90\ plot\ \ units = \sqrt{\frac{23.38\ meq/L\ (Ca)}{1.0\ (units\ per\ meq/L)} * 2} \tag{15}$$

NOTE 25—The meq/L plot unit is determined by the user and can be millimetres, centimetres, inches, tenths of inches, and so forth. For this example, assume 1.0 meq/L equals one square unit on the diagram. Therefore, the area of the Ca right isosceles triangle is equal to 23.38 square units.

7.3.8.8 Using the total meq/L concentration shown on Fig. 16 (232 meq/L), the unit size of each individual Rónai diagram is determined using the following computation.

$$Unit\ length\ of\ each\ side\ of\ \ square = \sqrt{\frac{Anion\ or\ cation\ total\ meq/L}{meq/L\ plot\ unit} * 8} \tag{16}$$

or:

$$30.46\ plot\ \ units = \sqrt{\frac{116\ meq/L\ (total\ anions\ or\ cations)}{1.0\ (units\ per\ meq/L} * 8} \tag{17}$$

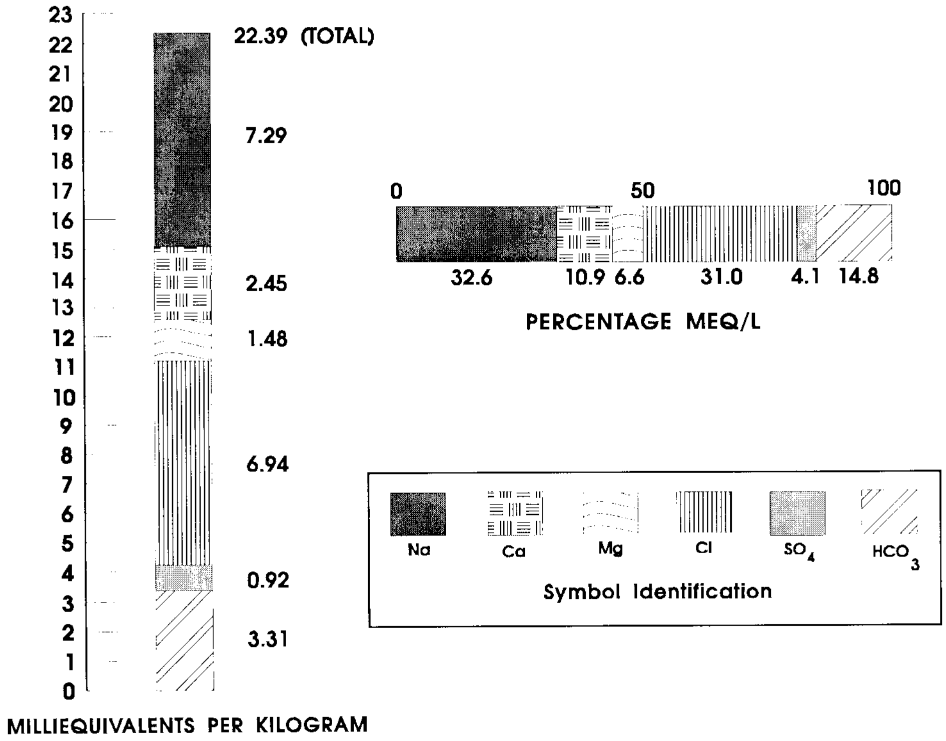
NOTE 26—The unit area of the total diagram is based on the sum of eight right isosceles triangles. Each of these triangles has an area that represents either the total anions or total cations, which is 116 square plot units. Therefore, the total area of the square diagram is 928 units (8 × 116). Each side of the square is 30.46 plot units (square root of 928). The outer boundary of the diagram is the 100 % meq/L line as shown on Fig. 16.

7.3.8.9 The percentage lines (25, 50, and 75 % meq/L) shown on Fig. 16 are not required for diagram construction, however, they assist in the interpretation of the water quality data. These lines are computed by the formula in 7.3.8.7.

NOTE 27—For example, the 25 % line is 0.25 times 116 or 29 meq/L. The plot distance of the 25 % line from the center of the diagram along a *X* or *Y* axis is the square root of ((29 divided by 1.0) × 2) or 7.62 plot units.

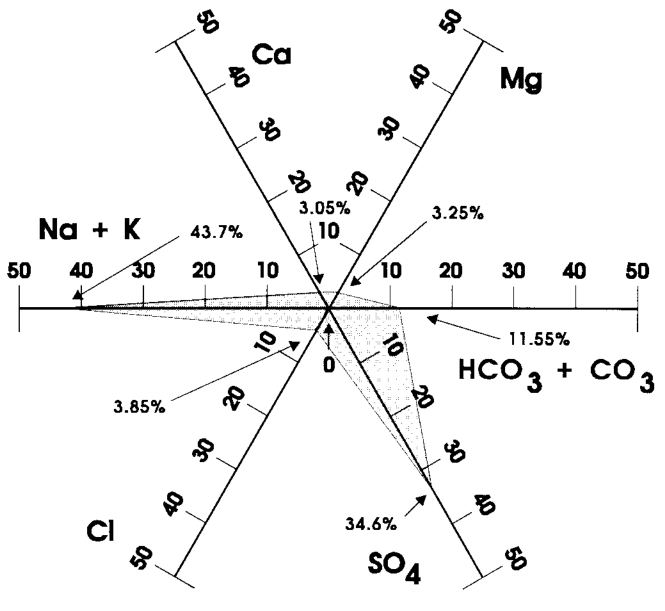
7.3.8.10 The triangles can be filled-in with colors or patterns to represent each ion and emphasize the starred pattern.

7.3.8.11 These eight radiating axes starred diagrams give a



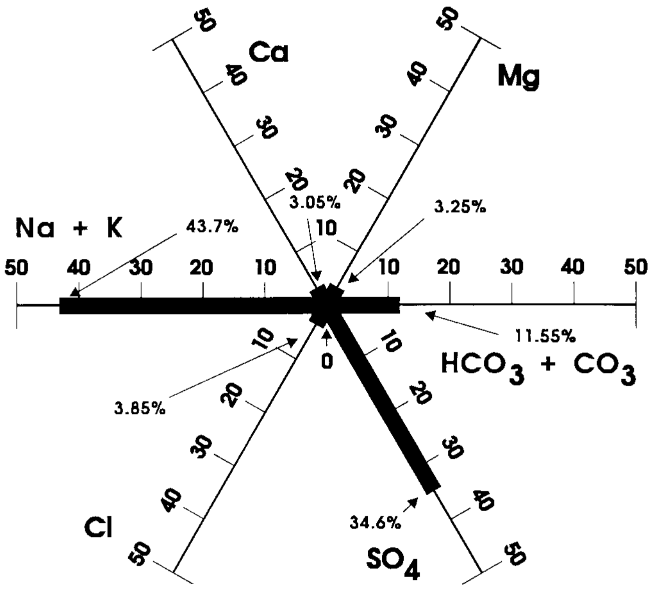
NOTE 1—Analysis selected from Ref **(1)**.

FIG. 8 Two Bar Diagrams Discussed by Carlé (11)



NOTE 1—Scale of diagram = percentage (%) of total meq/L (100 %).
NOTE 2—Adapted from Ref **(24)**. Analysis selected from Ref **(1)**.

FIG. 9 Tickell Radial Diagram



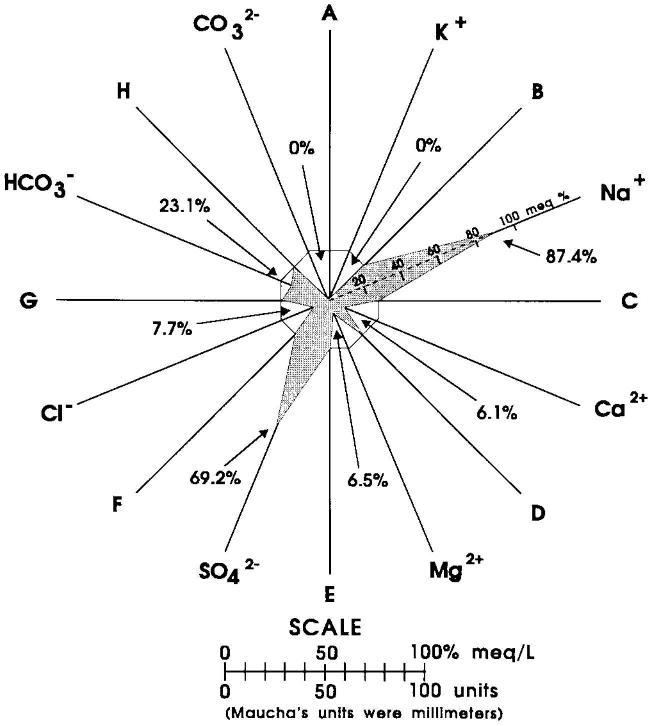
NOTE 1—Scale of diagram = percentage (%) of total meq/L (100 %).
NOTE 2—Adapted from Ref **(24)**. Analysis selected from Ref **(1)**.

FIG. 10 Dalmady Radial Diagram

characteristic pictorial representation of the water analysis. The diagrams can be compared, one with another, for the visual relationship of water analyses of a ground-water study.

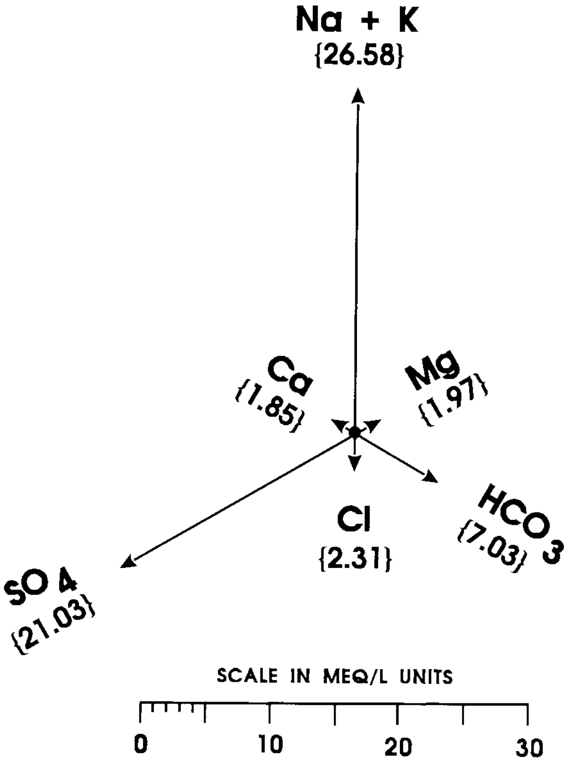
7.3.9 *EPA Pattern Diagram*—The EPA pattern diagram (see Fig. 17) is a plot of the meq/L percentages of ions on five vectors that radiate from a central point (see 7.7.3 on GEOBASE 6.0).

7.3.9.1 The scale of each of the five vectors is 100-meq/L percentage units.



NOTE 1—Adapted from Ref **(3)**. Analysis selected from Ref **(1)**.

FIG. 11 Maucha 16-Vector Radial Diagram



NOTE 1—Adapted from Ref **(24)**. Analysis selected from Ref **(1)**.

FIG. 12 Maucha Six-Vector Radial Diagram

7.3.9.2 The meq/L percentages of the anions (or cations) are determined by dividing the total meq/L anions (or cations) into each individual meq/L anion (or cation) value.

7.3.9.3 The cation meq/L percentages are plotted on the upper part of the diagram with the combined Na + K plotted on the vector that radiates at a 30° angle to the left of a vertical axis and the Ca + Mg on the vector that radiates 30° to the right.

7.3.9.4 The anions meq/L percentages are plotted on the lower half, with the HCO_3 on the vector that radiates at a 30° angle to the left of the vertical axis, the Cl on the vector that radiates 30° to the right, and SO_4 on the vertical vector.

7.3.9.5 The plot positions on the vectors are connected by lines and the enclosed area shaded or colored to form a distinctive pattern.

7.3.9.6 These five-vector radial diagrams give a characteristic pictorial representation of the water analysis. The diagrams can be compared, one with another, for the visual relationship of water analyses of a ground-water study.

7.4 *Pattern Diagrams*—Pattern diagrams are those where the ion values are represented by the length of lines extending at right angles in both directions from a horizontal or vertical line (see Fig. 1(*c*)).

7.4.1 *Stiff Diagram*—Stiff, in 1951, developed a pattern diagram system (see Fig. 18) with horizontal ion lines for graphically presenting analytical data of oil field waters. This diagram is widely used in the study of potable ground water **(1, 2, 3, 21, 22, 24, 27, 28, 32, 36, 37, 38)**.

NOTE 28—Stiff's intentions were to use the diagrams to identify various geologic formations by distinct patterns caused by the chemical makeup of the water. In addition, Stiff used the diagram to trace salt water leaking from a brine pit as it moved in a fresh water aquifer. Also, by examining the diagrams of water sampled over a period of time from an oil well, he was able to distinguish a leak of water of a different composition into the casing of the well.

7.4.1.1 The basic diagram consists of a central vertical line that has no scale and four horizontal ion axes that are scaled in meq/L units.

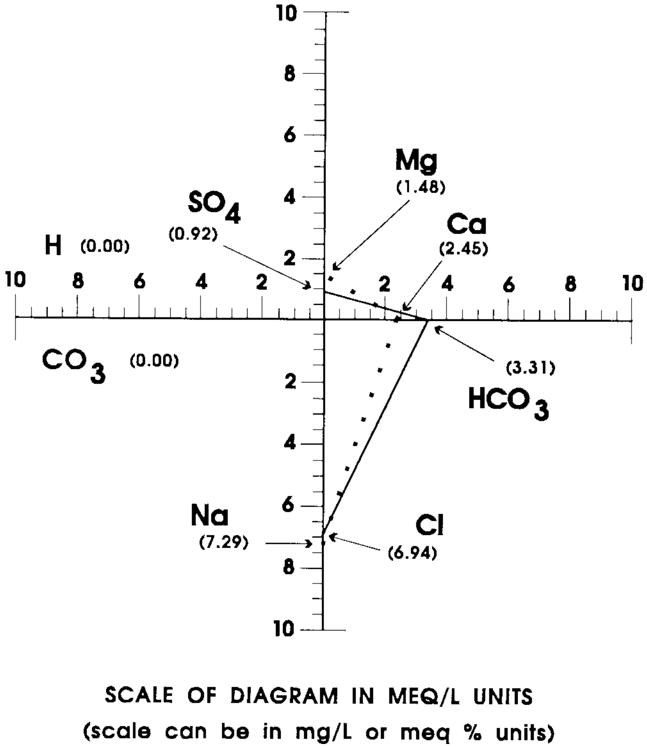
7.4.1.2 The central vertical line of the diagram is the zero axis, with the cations plotted on four horizontal axes to the left and the anions on four horizontal axes to the right of the zero axis.

7.4.1.3 Multiple meq/L scales may be used on the diagram when some of the ions have exaggerated concentrations.

NOTE 29—Brines may have a large amount of Na and Cl in comparison to the other major ions. The use of a common scale would either give very long axes for Na and Cl or very short axes for the other ions. A convenient method of designing the diagram so that the shape is manageable is to use multiple scales. For example, on equal length axes, scale the Na and Cl at 100 meq/L and the other ions at 10 meq/L. This multiple-scaled diagram should be used for all analyses of a ground-water project to allow for a less confusing visual comparison.

7.4.1.4 The diagrams for a project should be accompanied with an explanation of the ion arrangement and the meq/L scale of the horizontal axes.

7.4.1.5 Concentrations of other ions of interest to a particular study, for example, selenium (Se), can be shown on the diagrams by use of additional horizontal axes.



NOTE 1—Adapted from Ref **(3)**. Analysis selected from Ref **(1)**.

FIG. 13 Girard Four-Axis Diagram

7.4.1.6 The outer ends of the horizontal axes may be connected by lines to produce a distinctive enclosed area (see Fig. 18). This area may be filled in with a symbol or color to emphasize the pattern.

7.4.1.7 The diagrams can be compared, one with another, or positioned at the relative sample locations on an areal map or a geologic section for displaying the visual relationship of water analyses from a ground-water study.

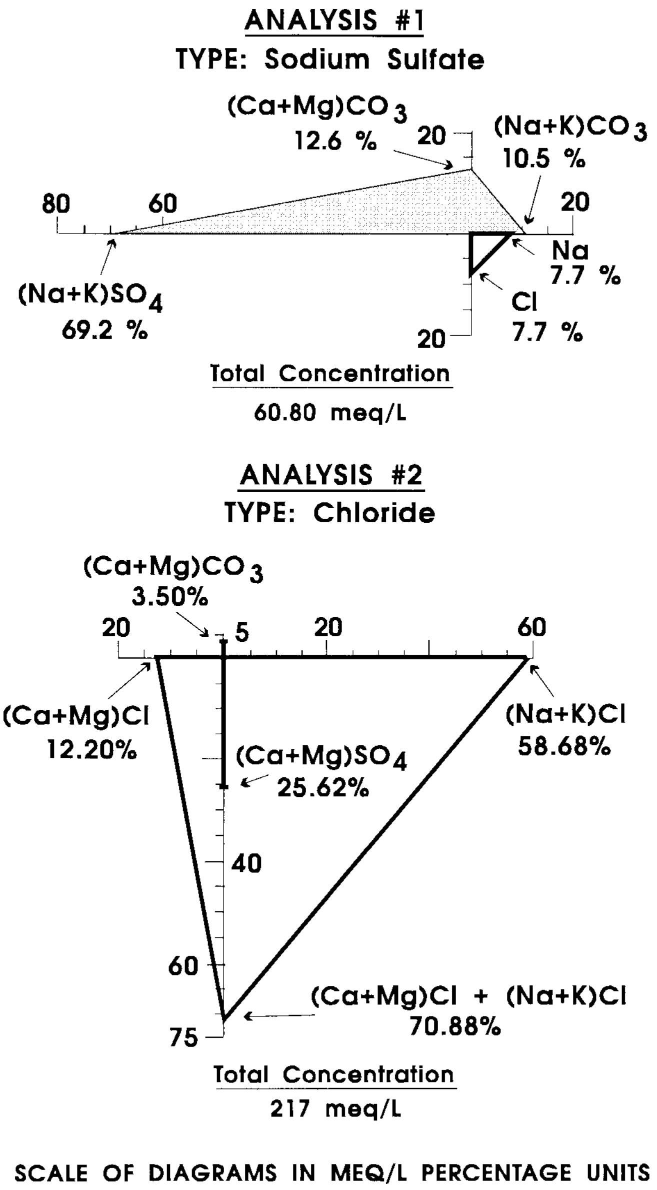
7.4.1.8 The Stiff pattern diagram basically is used as support for evaluating scientific interpretations of the hydrology of ground-water aquifers. This diagram and modifications of the diagram is one of the more common methods used in the United States by the hydrologic profession for illustrating a single chemical analysis by a pattern.

7.4.2 *Dulas Baseline Diagram*—Dulas, in 1977, presented a water quality illustration (see Fig. 19) with vertical component lines that was identified as a baseline diagram. The purpose of this diagram is to easily make a judgment, through a visual method, about the suitability of the analyzed water for drinking **(22)**.

7.4.2.1 Dulas' basic diagram consists of a central horizontal line that has no scale, six vertical water quality component axes that are scaled in ppm (epm) units, and a vertical specific conductance axis that is in micromhos at 25°C.

7.4.2.2 The water quality components selected for display on the original diagram were dissolved solids, Na + K, SO $_4$, Cl, NO$_3$, total hardness, and the specific conductance.

7.4.2.3 Each of these components has a baseline or maximum recommended concentration (for example, NO$_3$ is 45 ppm) when used for drinking water. This baseline is shown by the horizontal line of the diagram.



NOTE 1—Adapted from Ref **(18)**. Analysis Number 1 selected from Ref **(1)**. Analysis Number 2 from Ref **(18)**.

FIG. 14 Frey Four-Axis Diagram

TABLE 1 Analyses on Frey Diagram (See Fig. 14)

Constituent	Analysis Number 1^A		Analysis Number 2^B	
	meq/L	% meq/L	meq/L	% meq/L
Na,K	26.58	43.70	63.67	29.34
Ca	1.85	3.05	10.98	5.06
Mg	1.97	3.25	33.85	15.60
Cl,F,NO$_3$	2.34	3.85	76.90	35.44
SO$_4$	21.03	34.60	27.80	12.81
HCO$_3$,CO$_3$	7.03	11.55	3.80	1.75
TOTAL	60.80	100.00	217	100.00

^{A}Analysis Number 1 selected from Ref **(1)**.

^{B}Analysis Number 2 selected from Ref **(18)**.

7.4.2.4 Each water quality component shown on the diagram has an individual scale factor, which is given in an accompanying table on Fig. 19.

7.4.2.5 The baseline diagram emphasizes those components

TABLE 2 Order of Combination of Percentage Reacting Values for Frey Diagram (See Fig. 14)

Order of Combination	Analysis Number 1[A]	Analysis Number 2[A]
Na,K + Cl	3.85 + 3.85 = 7.70 %	29.34 + 29.34 = 58.68 %
Remaining Na,K	43.70−3.85 + 39.85 %	29.34−29.34 = 0.00 %
Remaining Cl	3.85−3.85 = 0.00 %	35.44−29.34 = 6.10 %
Mg + Cl	0.00 + 0.00 = 0.00 %	6.10 + 6.10 = 12.20 %
Remaining Mg	3.25−0.00 = 3.85 %	15.60−6.10 = 9.50 %
Remaining Cl	0.00−0.00 = 0.00 %	6.10−6.10 = 0.00 %
Ca + Cl	0.00 + 0.00 = 0.00 %	0.00 + 0.00 = 0.00 %
Remaining Ca	3.05−0.00 = 3.05 %	5.06−0.00 = 5.06 %
Remaining Cl	0.00−0.00 = 0.00 %	0.00−0.00 = 0.00 %
Na,K + SO_4	34.60 + 34.60 = 69.20 %	0.00 + 0.00 = 0.00 %
Remaining Na,K	39.85−34.60 = 5.25 %	0.00−0.00 = 0.00 %
Remaining SO_4	34.60−34.60 = 0.00 %	12.81−0.00 = 12.81 %
Ca + SO_4	0.00 + 0.00 = 0.00 %	5.06 + 5.06 = 10.12 %
Remaining Ca	3.05−0.00 = 3.05 %	5.06−5.06 = 0.00 %
Remaining SO_4	0.00−0.00 = 0.00 %	12.81−5.06 = 7.75 %
Mg + SO_4	0.00 + 0.00 = 0.00 %	7.75 + 7.75 = 15.50 %
Remaining Mg	3.25−0.00 = 3.25 %	9.50−7.75 = 1.75 %
Remaining SO_4	0.00−0.00 = 0.00 %	7.75−7.75 = 0.00 %
Ca + CO_3[B][C]	3.05 + 3.05 = 6.10 %	0.00 + 0.00 = 0.00 %
Remaining Ca	3.05−3.05 = 0.00 %	0.00−0.00 = 0.00 %
Remaining CO_3	11.55−3.05 = 8.05 %	1.75−0.00 = 1.75 %
Mg + CO_3[B]	3.25 + 3.25 = 6.50 %	1.75 + 1.75 = 3.50 %
Remaining Mg	3.25−3.25 = 0.00 %	1.75−1.75 = 0.00 %
Remaining CO_3	8.05−3.25 = 5.25 %	1.75−1.75 = 0.00 %
Na,K + CO_3	5.25 + 5.25 = 10.50 %	0.00 + 0.00 = 0.00 %
Remaining Na,K	5.25−5.25 = 0.00 %	0.00−0.00 = 0.00 %
Remaining CO_3	5.25−5.25 = 0.00 %	0.00−0.00 = 0.00 %

[A] Analysis Number 1 selected from Ref **(1)**; Analysis Number 2 from Ref **(18)**.

[B] $CaCO_3$ and $MgCO_3$ are combined under $CaCO_3$ on Frey Diagram.

[C] CO_3 and HCO_3 are combined under CO_3 on Frey Diagram.

that exceed the maximum concentration by the extension of the representative vertical line above the horizontal baseline.

7.4.2.6 Those water quality components that are less than the baseline criteria are shown by the vertical lines that extend below the baseline.

7.4.2.7 The end of the line (either above or below baseline), corresponds to the analyzed value of the component. This value can be determined by comparison with accompanying table of scale factors.

NOTE 30—The baseline diagram, as illustrated on Fig. 19, was designed for evaluating water quality components related to drinking water. Similar diagrams could be constructed to visually examine components and ions that may be of interest to a project, for example, a ground-water pollution study.

7.5 *Circular Diagrams*—The circular diagrams are those where the outer border is a circle and the ion concentrations are represented by appropriately sized subdivisions of the circle (Fig. 1(*d*)).

7.5.1 *Carlé Circular Diagram*— Carlé, in 1954, presented a method where selected elements of an analysis are portrayed in separate eccentric circles (see Fig. 20) and where the area of the circles represent the ionic concentration. This use of the area allows for a wide range of element values to represented by moderately sized circles **(23)**.

7.5.1.1 The example given, Fig. 20, has three components plotted in mg/L units; dissolved solids, Cl, and HCO_3.

7.5.1.2 The circle area of a component is determined by setting each 10-mg/L value of the component equal to one unit or one cm^2, for example, a Cl of 13 mg/L is equal to 1.3 cm^2.

7.5.1.3 The radius (r) of the circle that represents a component is equal to the square root of the surface area (F) of the circle divided by pi (π) (3.1416) or 0.6383 cm for a 1.3-cm^2 circle. The equation is as follows:

$$r = \sqrt{F/\pi} \tag{18}$$

or:

$$0.6383(r) = \sqrt{1.3(F)/3.1416(\pi)} \tag{19}$$

NOTE 31—The unit used for the surface area (F) and radius (r) of the circle can be any convenient system of measurement, for example, inch or millimetre. Also, the circle sizes can be adjusted by using smaller or larger ion concentrations to represent one unit of circle surface area. For example, one unit of circle area can be set equal to 1-mg/L or to 100- mg/L component concentration. When all of the original circles and the matching scale circle are drafted using the selected unit of measurement, the unit value can be deleted and the circle diagrams and related scale circle reduced or enlarged as needed for publication.

7.5.1.4 On Fig. 20, the dissolved solids creates the largest circle and lesser valued elements form smaller circles within the circles of the greater-valued elements. The lesser-valued circles are placed at the lower edge of the greater-valued circles.

7.5.1.5 Each element may be emphasized by a fill-in pattern or color with the lowest-valued circle unimpeded by the patterns of greater-valued circles.

7.5.2 *Pie Diagram*—The traditional pie diagram (see Fig. 21) is circular with scaled cation pie-shaped sectors positioned in the upper half and anion sectors in the lower half of the circle **(2, 3, 24, 28)**.

7.5.2.1 The size of the pie sectors within the circle represent the percent of the individual ion meq/L of the total (anion + cation) meq/L concentration (a 3.6° arc of the circle equals 1 % meq/L of the total concentration).

7.5.2.2 The radius and area of each circle is directly related to the dissolved solids meq/L concentration for the analysis (see explanation under 7.5.1.2 and 7.5.1.3).

7.5.2.3 Each ion sector may be identified with a symbol or a color to emphasize the ion concentrations for the constituents.

7.5.2.4 The diagrams can be compared, one with another, or positioned at the relative sample locations on an areal map for the visual relationship of water analyses from a ground-water study.

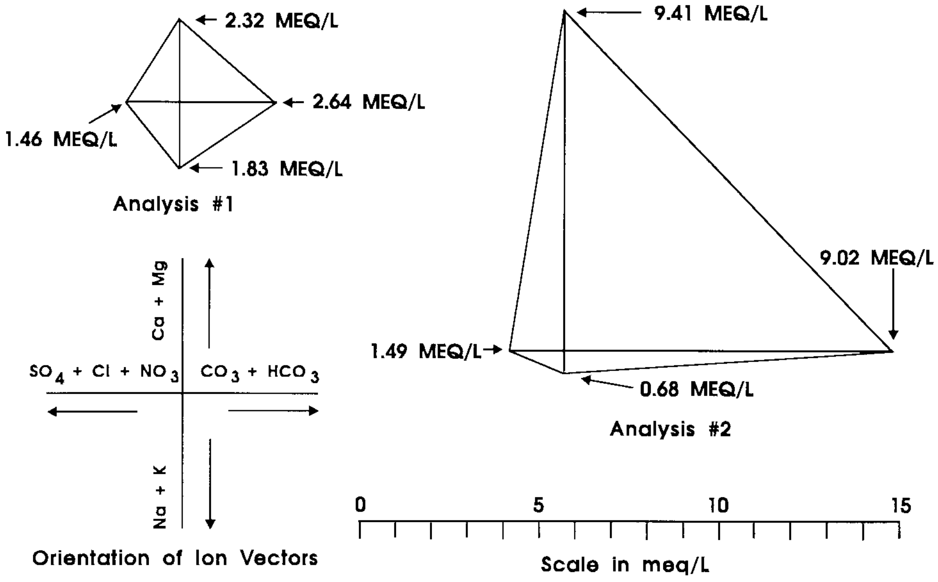
7.5.2.5 A variation in the pie diagram is where the diameter of the circle is scaled directly to the mg/L concentration of the dissolved solids, for example, one scale unit equals 500 mg/L and two units equals 1000 mg/L **(24, 28)**.

7.5.3 *Tolstichin Cyclical Diagram*—Tolstichin, in 1937, presented a cyclical diagram (Fig. 22) for visually illustrating the ions of a water quality analysis. This diagram consists of two overlying circles of different diameters, each divided into pie-shaped sectors **(24)**.

7.5.3.1 The smaller circle overlies the center of the larger circle and represents the total anion concentration (100 %) in percent meq/L.

7.5.3.2 The outer large circle represents the total cation concentration in percent meq/L.

7.5.3.3 The circle size is independent and does not represent any of the components of the analysis.



NOTE 1—Adapted from Ref **(19)**. Analyses from Ref **(1)**.

FIG. 15 Kite Pattern Diagram

7.5.3.4 The percent meq/L of each ion is given by the size of the pie-shaped sector in the appropriate anion or cation circle, where one percent of an ion equals a 3.6° arc of the circle.

7.5.3.5 Each sector may be filled-in with a pattern or color to visually identify the ions.

7.5.3.6 The diagrams can be compared, one with another, or positioned at the relative sample locations on an areal map for the visual relationship of water analyses from a ground-water study.

7.5.4 *Disk Diagram*—The disk diagram (see Fig. 23), described by Zaporozec in 1972 and originating in Czechoslovakia, consists of a circle divided into twelve pie-shaped equal-sized sectors **(24)**.

7.5.4.1 The disk diagram allows for as many as twelve ion concentrations of an analysis to be shown on one illustration.

7.5.4.2 The cations meq/L percentages are plotted in the six sectors of the upper half and the anions meq/L percentages in the six sectors of the lower half of the diagram.

7.5.4.3 An individual cation value is determined as a meq/L percentage of the total cation meq/L concentration and an anion value as a meq/L percentage of the total anion meq/L.

7.5.4.4 The radius of the circle is scaled in meq/L percentage units, with 0 % at the center and 100 % at the circumference. A percentage scale for the radius can accompany the diagram.

7.5.4.5 Unused sectors are empty. The arrangement of the ion sectors should remain constant when a number of "disk" diagrams are constructed from a series of analyses of a ground-water project.

7.5.4.6 The diameter and area of the circle has no direct meaning concerning ion concentrations.

7.5.4.7 The pie-shaped sector that is assigned to an individual ion is shaded or colored from the center (0 %) out to the arc that represents the total meq/L percentage of that ion. The radius is segmented at 20 % intervals to assist in plotting the ion percentages.

7.5.4.8 The diagrams can be compared, one with another, for the visual relationship of water analyses of a ground-water study.

7.5.5 *Udluft Circular Diagram*—Udluft, in 1953 and 1957, presented a circular diagram segmented in grads (400 grads is 400 new degrees, see sketch on Fig. 24) that Matthess described as "a complex circular diagram for illustrating comprehensive water analyses and chemical peculiarities" **(2, 25, 26)**.

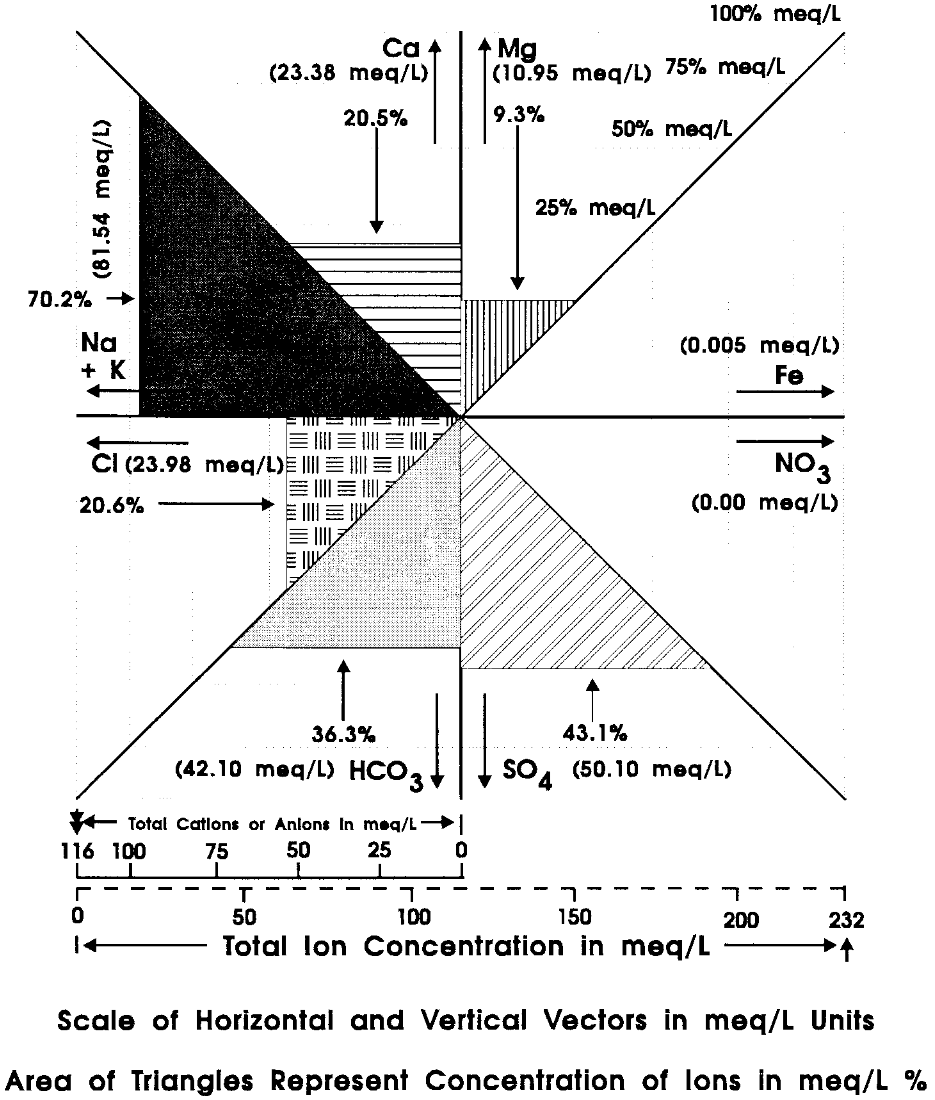
7.5.5.1 Individual cation plot values are determined as meq/L percentages (0 to 100 %) of the total cation meq/L concentration and anion plot values as meq/L percentages (0 to 100 %) of the total anion meq/L.

7.5.5.2 The diagram has the cation meq/L percentage segment (100 % cations or 200 grads or 200 new degrees) in the upper half and the anion meq/L percentage segment (100 % anions or 200 grads or 200 new degrees) in the lower half. Two grads (two new degrees) equals one percent of the anions or of the cations.

7.5.5.3 Anions and cations, with concentrations of 0.51 % or greater, are plotted as pie-shaped sectors. For example, a cation that is 50 % of the total cation meq/L concentration would have a sector that consists of one half of the upper cation segment of the diagram or 100 new degrees.

7.5.5.4 Ions with concentrations of 0.01 to 0.50 % meq/L are represented by scaled spokes that radiate into the sectors of related cations or anions. For example, on Fig. 24, Li^+ is shown by a spoke that is scaled to be 0.37 % meq/L in length.

7.5.5.5 The area of the circular diagram is scaled to represent the dissolved solids concentration in mg/L. For example, the large circle, with a radius of 53.21 units, has an area of 8896 $units^2$ that represents the total concentration of 8896 mg/L (see explanation under 7.5.1.2 and 7.5.1.3).



NOTE 1—Adapted from Ref **(24)**. Analysis selected from Ref **(24)**.

FIG. 16 Rónai Starred Diagram

7.5.5.6 The species CO_2 and SiO_2 (see Fig. 24), and other constituents, such as HBO_2, that do not contribute to the ionic balance, are shown at the center of the diagram as concentric circles with a true area relationship.

NOTE 32—The inner circle, with a radius of 5.2 units and an area of 85 units^2, represents SiO_2 with a 85-mg/L concentration. The second circle, with a radius of 11.2 units and an area of 394 units^2, represents SiO_2 (85 mg/L) + CO_2 (309 mg/L) for a total concentration of 394 mg/L.

7.5.5.7 The diagram allows for plotting temperatures in °C of ground water by circles placed outside the total concentration circle.

NOTE 33—On Fig. 24, the three circles represent a temperature of 60°C or greater and less than 80°C for a known temperature of 65°C. Each circle is therefore equal to 20°C.

7.5.5.8 Radioactive constituents, such as radon and radium, can be shown by scaled arcs.

NOTE 34—Matthess gives examples of these constituents by placing the radium outside the total concentration circle with the arc projecting upward from the 0 % line on the left side of the diagram. The radon arc is projected downward from the 0 % line outside and to the left of the circle identified as CO_2. These constituents are scaled in 10^{-7}-mg/kg units.

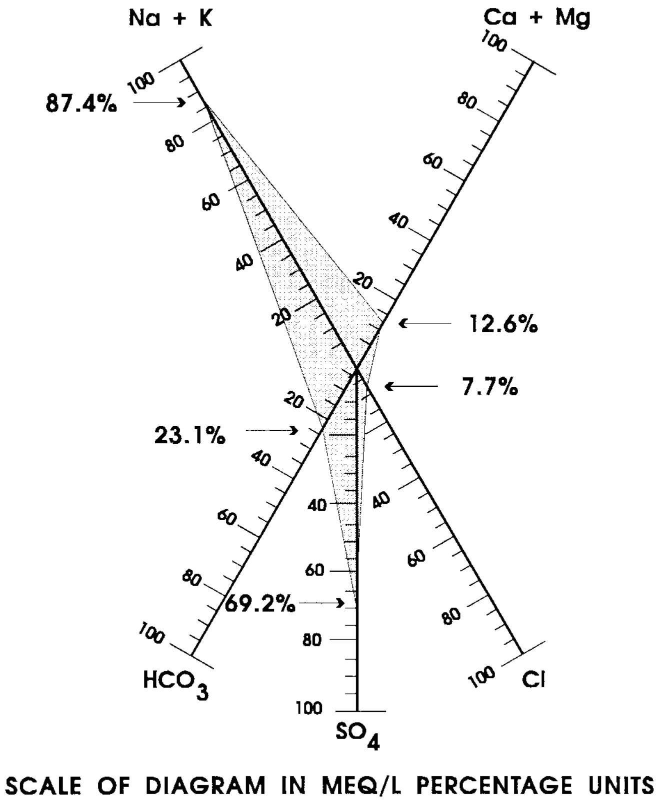
7.5.5.9 Each sector may be filled-in with a pattern or color to visually identify the ions.

7.5.5.10 The diagrams can be compared, one with another, for the visual relationship of water analyses from a ground-water study.

7.6 Numerous published resource evaluation and research studies are available where "water-analysis diagrams" were used to assist in the interpretation of the ground-water geochemistry.

7.7 *Automated Procedures for Single-Analysis Pattern Diagrams*:

NOTE 35—Literature searches and verbal inquires found computerized procedures for the Collins, Stiff, Tickell, Disk, Maucha Radial, Pie, and EPA diagrams. Although procedures for the other pattern diagrams discussed in this guide are probably available, none could be found. Additional sources of computerized procedures can be added in the



NOTE 1—Adapted from GEOBASE. Analysis selected from Ref **(1)**.

FIG. 17 EPA Pattern Diagram

subsequent publication of this guide.

7.7.1 The Stiff and Collins diagrams were automated in 1966 for use with computerized ground-water quality files and a line printer **(36, 37)**.

7.7.2 A relational ground-water database with an extensive collection of ground water, geology, and areal map procedures (GEOBASE 6.0) for desktop computers is available from Earthware of California. Included in this program package are routines for the display of the Collins, Stiff, Tickell, Disk, Maucha, Pie, and EPA diagrams.[5]

7.7.3 A package of software (ROCKSTAT) from Rockware Scientific Software contains routines for the plotting of water-analysis diagrams on a desktop computer. Included is a version of the Stiff diagram.[6]

7.7.4 A package of six water-quality diagrams is available through documentation from the USGS **(39)**. Included in the package are versions of the Stiff and Pie diagrams.[7]

7.7.5 A graphics package called PLOTCHEM^{EM} includes a version of the Stiff, Collins, Pie, and radial diagrams where water quality data may be entered directly or from a separate ASCII file.[8]

8. Keywords

8.1 chemical ions; geochemical classification; ground water; pattern diagram; water-analysis diagram

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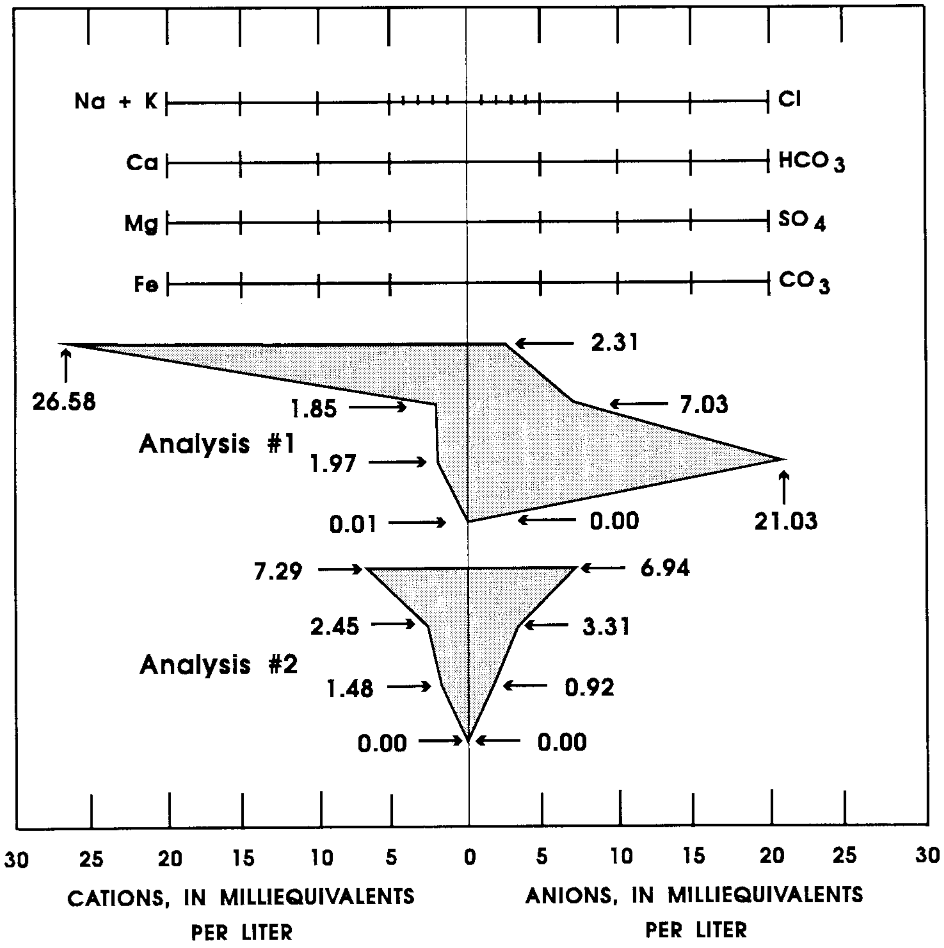
[5] For further information contact: Earthware of California, 30100 Town Center Drive #196, Laguna Niguel, CA 92677.

[6] For further information contact: Rockware Scientific Software, 4251 Kipling St., Suite 595, Wheat Ridge, CO 80033.

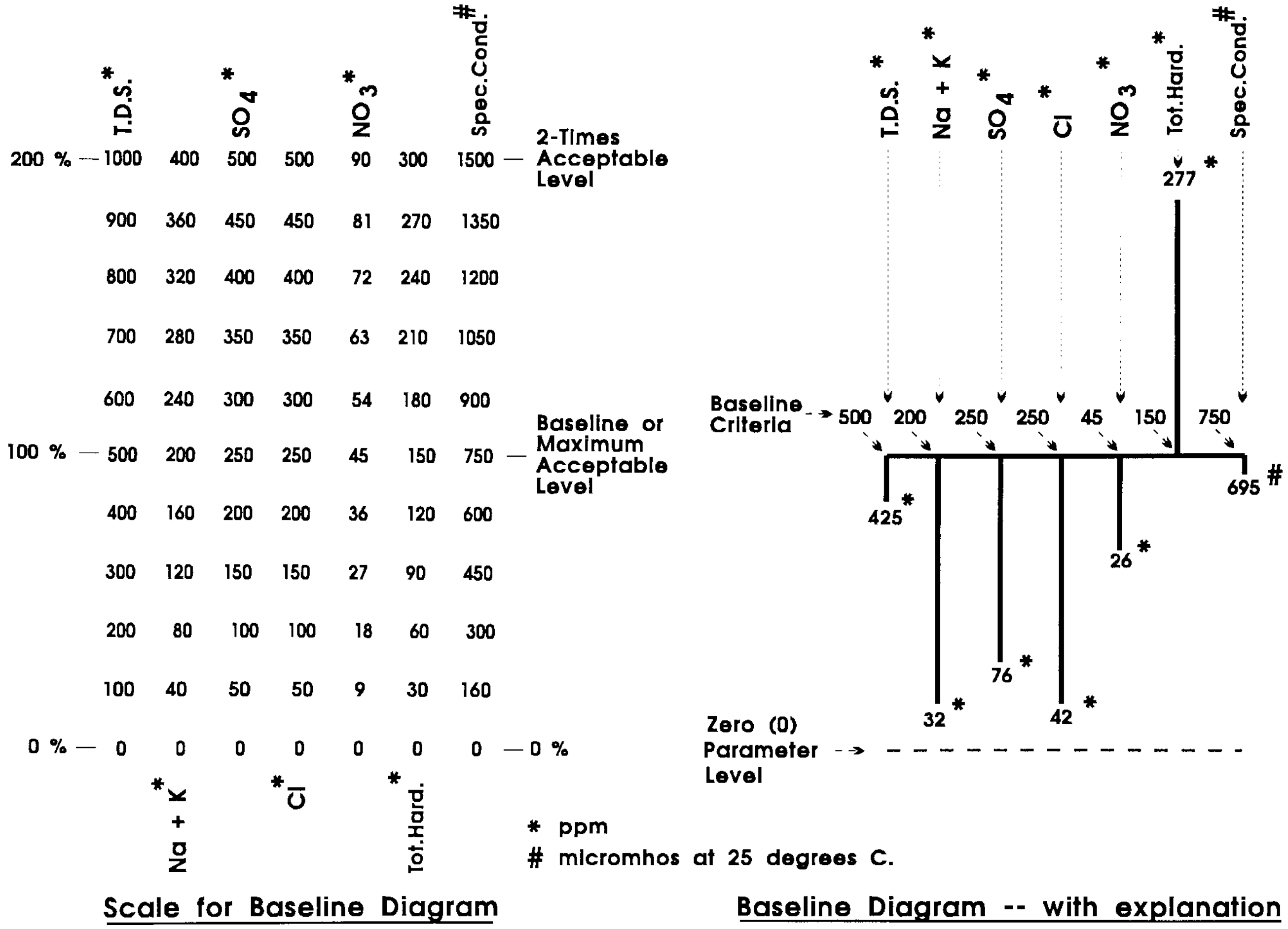
[7] For further information contact: USGS Books and Reports Sales, Federal Center, Box 25425, Denver, CO 80225.

[8] For further information contact: Scientific Software Group, P. O. Box 23041, Washington, DC 20026-3041.



NOTE 1—Adapted from Ref **(1)**. Analyses selected from Ref **(1)**.

FIG. 18 Stiff Pattern Diagram



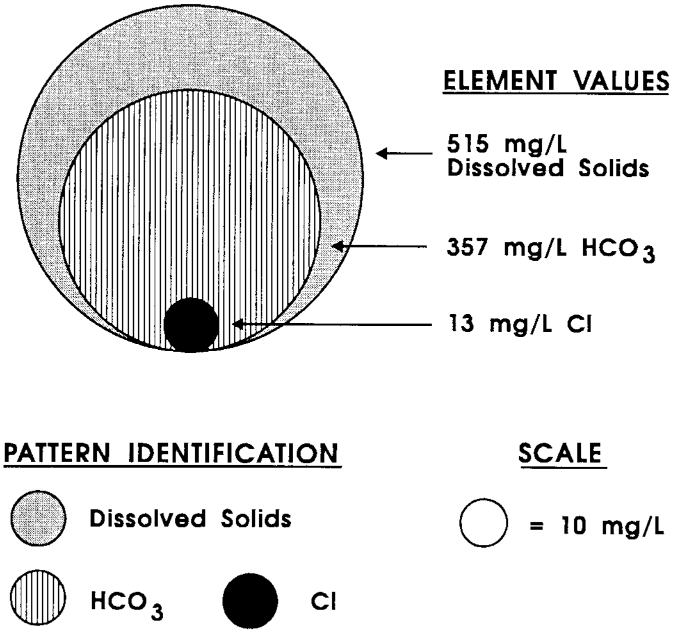
Scale for Baseline Diagram

	T.D.S.*	Na + K*	SO$_4$*	Cl*	NO$_3$*	Tot.Hard.*	Spec.Cond.#	
200 %	1000	400	500	500	90	300	1500	2-Times Acceptable Level
	900	360	450	450	81	270	1350	
	800	320	400	400	72	240	1200	
	700	280	350	350	63	210	1050	
	600	240	300	300	54	180	900	
100 %	500	200	250	250	45	150	750	Baseline or Maximum Acceptable Level
	400	160	200	200	36	120	600	
	300	120	150	150	27	90	450	
	200	80	100	100	18	60	300	
	100	40	50	50	9	30	160	
0 %	0	0	0	0	0	0	0	0 %

Baseline Diagram -- with explanation

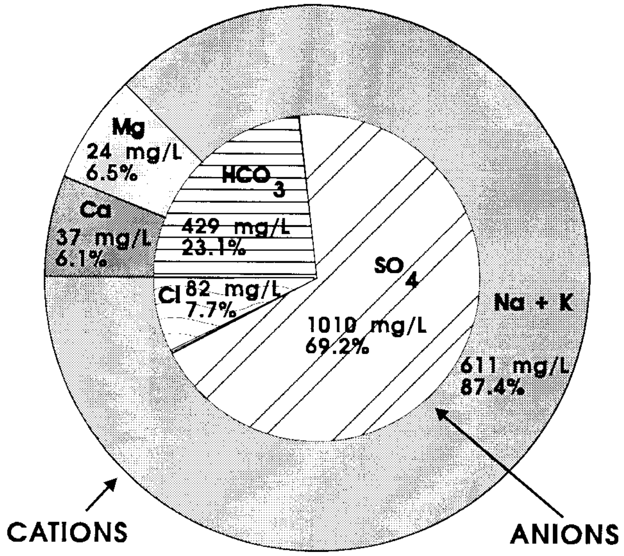
Note 1—Adapted from Ref (22).

FIG. 19 Baseline Diagram



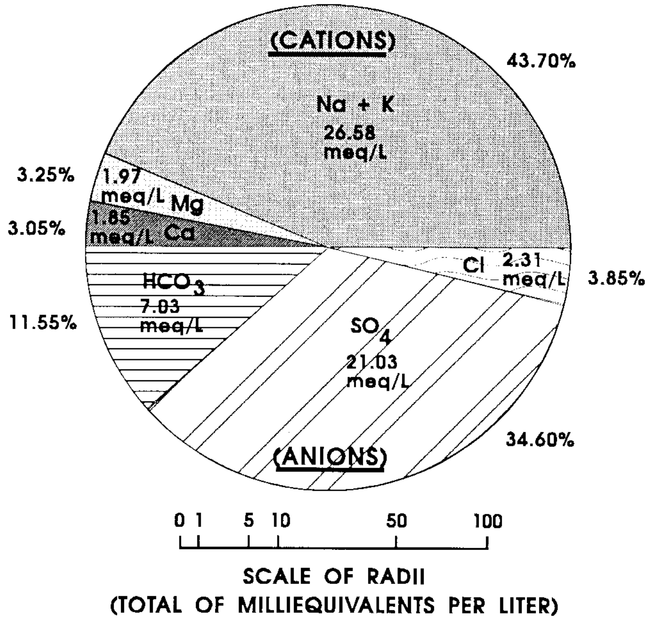
NOTE 1—Adapted from Ref **(3)**. Analysis selected from Ref **(3)**.

FIG. 20 Carlé Circular Diagram



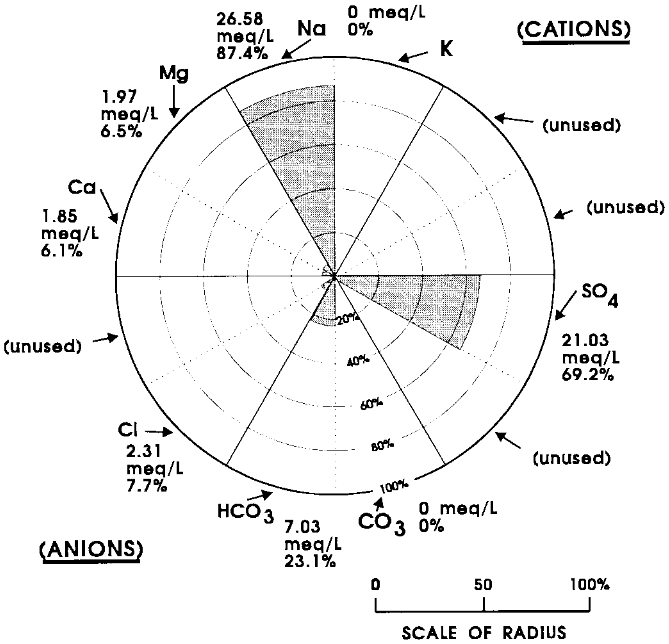
NOTE 1—Adapted from Ref **(24)**. Analysis selected from Ref **(1)**.

FIG. 22 Tolstichin Cyclical Diagram



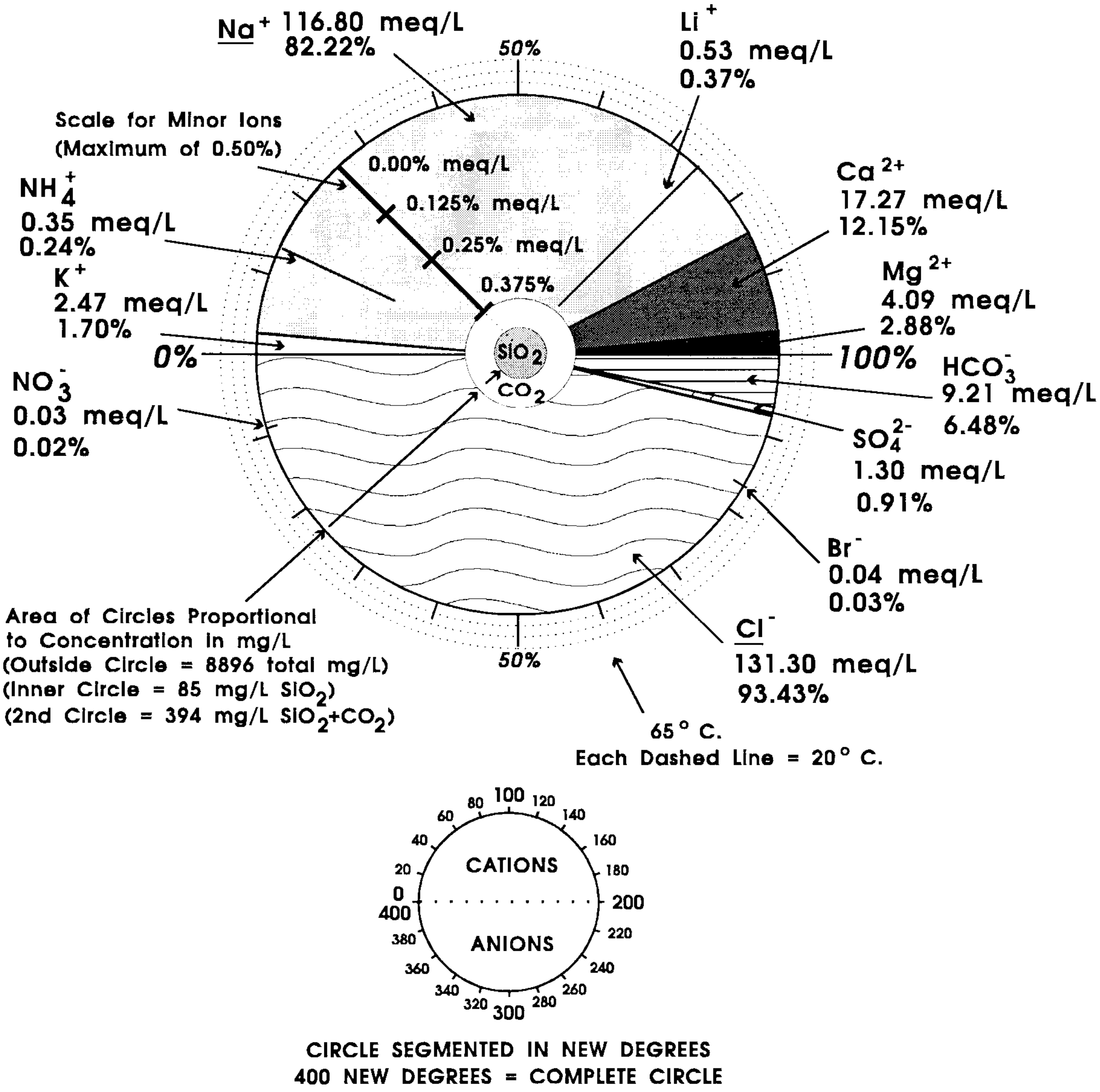
NOTE 1—Adapted from Ref **(1)**. Analysis selected from Ref **(1)**.

FIG. 21 Pie Diagram



NOTE 1—Adapted from Ref **(24)**. Analysis selected from Ref **(1)**.

FIG. 23 Disk Diagram



NOTE 1—Adapted from Ref **(3)**. Analysis selected from Ref **(25)**.

FIG. 24 Udluft Circular Diagram

APPENDIX

(Nonmandatory Information)

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