



Designation: D 5738 – 95 (Reapproved 2000)

Standard Guide for Displaying the Results of Chemical Analyses of Ground Water for Major Ions and Trace Elements—Diagrams for Single Analyses¹

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 Water²

D 653 Terminology Relating to Soil, Rock, and Contained Fluids³

D 1129 Terminology Relating to Water²

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 Analyses²

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

¹ This guide is under the jurisdiction of ASTM Committee D18 on Soil and Rock and is the direct responsibility of Subcommittee D18.21 on Ground Water and Vadose Zone Investigations.

Current edition approved July 15, 1995. Published August 1995.

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

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

litre) of the cations and anions of each water analysis. Therefore, in order to use the diagrams, analyses must be converted from ppm to ep_m by multiplying each ion by its 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 ep_m and mg/L to meq/L (see explanation of ep_m and meq/L). To determine the equivalent weight factor, divide the formula weight of the solute component into the valence of the solute component:

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

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:

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

For example, the formula weight of Ca²⁺ 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;

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

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 CaCO₃.

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 Matthes (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 (H₂O), and numerous major dissolved chemical constituents, such as calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), carbonate (CO₃), bicarbonate (HCO₃), chloride (Cl), and sulfate (SO₄), 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 (NO₃), and phosphorus (PO₄). 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 (H₂S), carbon dioxide (CO₂), oxygen (O₂), methane (CH₄), ammonia (NH₃), argon (Ar), helium (He), and radon (Rn). Also maybe included are neutrally charged mineral species, such as silicate (SiO₂), naturally occurring organics, such as tannic 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 to seawater.

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

amount of dissolved solids to a brine with at least 100 000-mg/L dissolved solids (natural occurring brine have been 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.

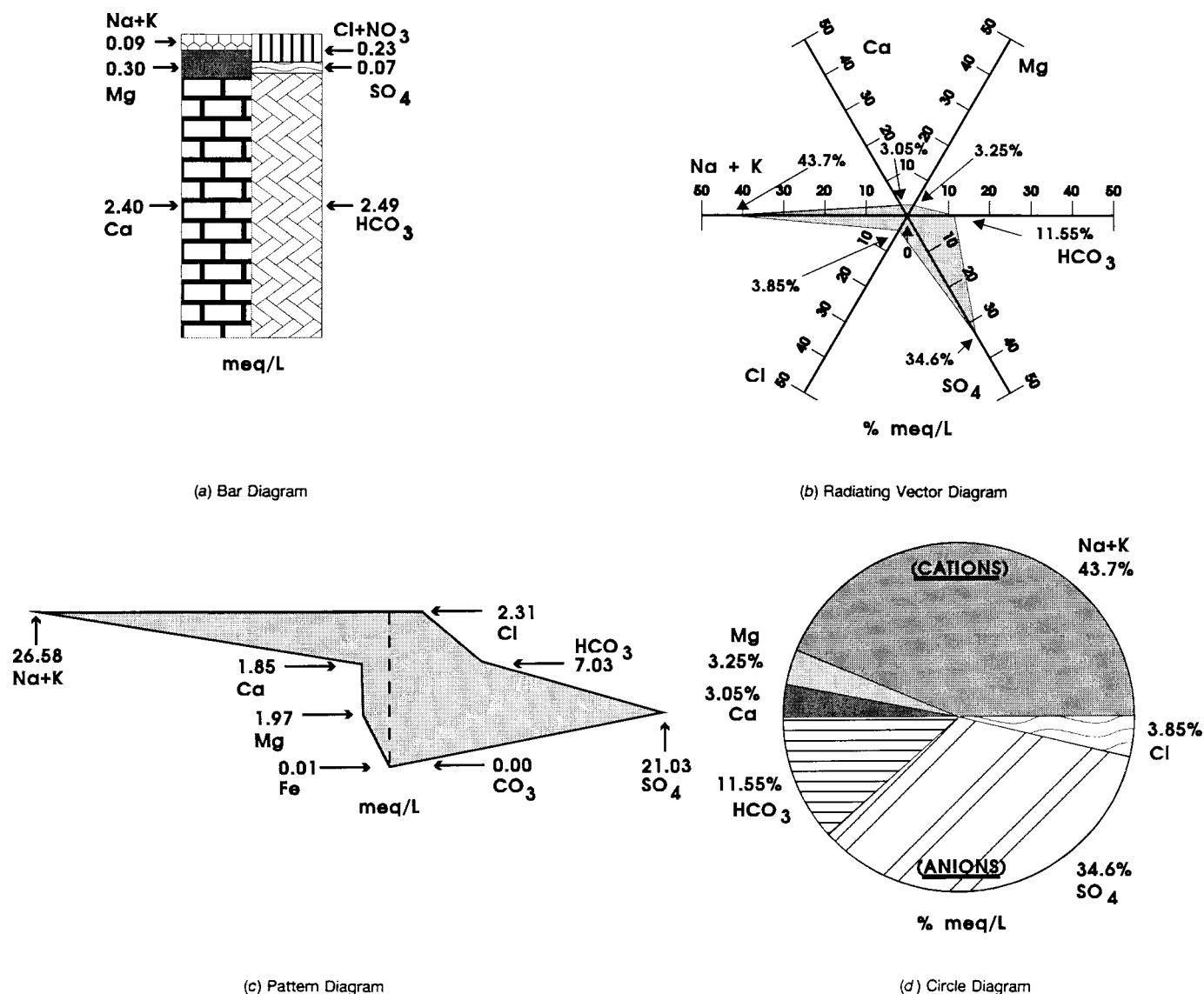


FIG. 1 Examples of the Four Types of Single-Analysis Diagrams

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

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 $\pm 10\%$, 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);

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

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

Dissolved Solids	Chemical Balance
0 to 100 mg/L	Within $\pm 5\%$
101 to 250 mg/L	Within $\pm 3\%$
Greater than 250 mg/L	Within $\pm 2\%$

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 epn or mg/L to meq/L); ion percentage of the total equivalent weight (epn to % epn 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 epn (or meq/L) or % epn (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 epn 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	Chloride.....	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 epn value of the cations and anions into the individual cation or anion value. For example, the number derived from dividing the total ion value ($\text{Ca} + \text{Mg} + \text{Na} + \text{K} + \text{HCO}_3 + \text{CO}_3 + \text{SO}_4 + \text{Cl}$) divided into the meq/L or epn value of Ca is multiplied times 100 to give the percentage of Ca in the total ions (by weight):

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

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 ($\text{HCO}_3 + \text{CO}_3$)) 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:

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

(6)



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

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

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*:

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

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

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

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*:

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

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

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

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 ($FeSO_4$) 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 Matthes 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 Matthes 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 Matthes 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 symbolized 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.

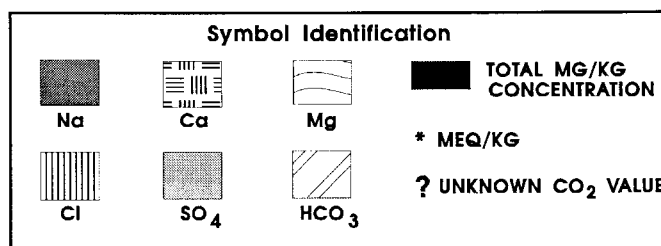
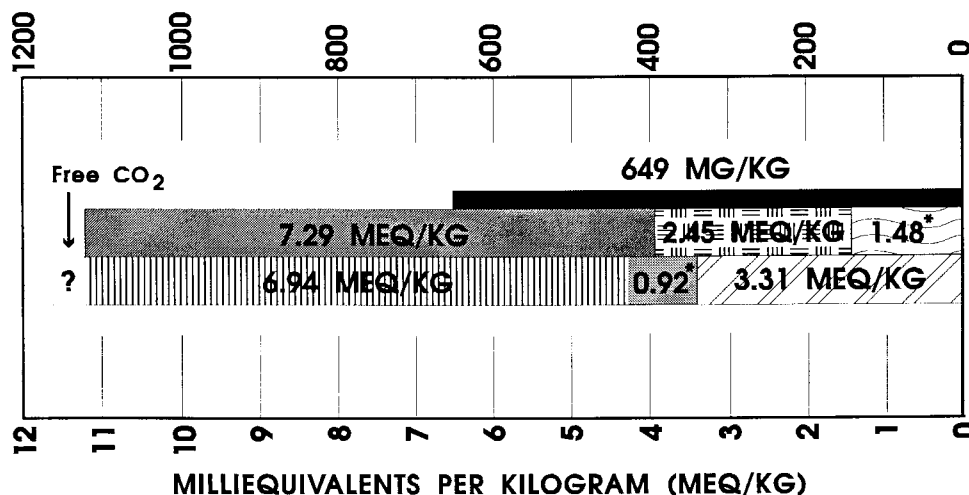
7.2.2.3 The acids are arranged with the strong acids (Cl and SO_4) at the bottom of the left column and the weak acids (HCO_3 and CO_3) at the top of the column. The bases are arranged with the alkalies (Na and K) at the bottom of the right column and the alkaline earths (Ca and Mg) at the top of the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

TOTAL CONCENTRATION IN MILLIGRAMS PER KILOGRAM (MG/KG)



NOTE 1—Analysis selected from Ref (1).
FIG. 2 Hintz/Grünhut Bar Diagram (3)

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’ 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.

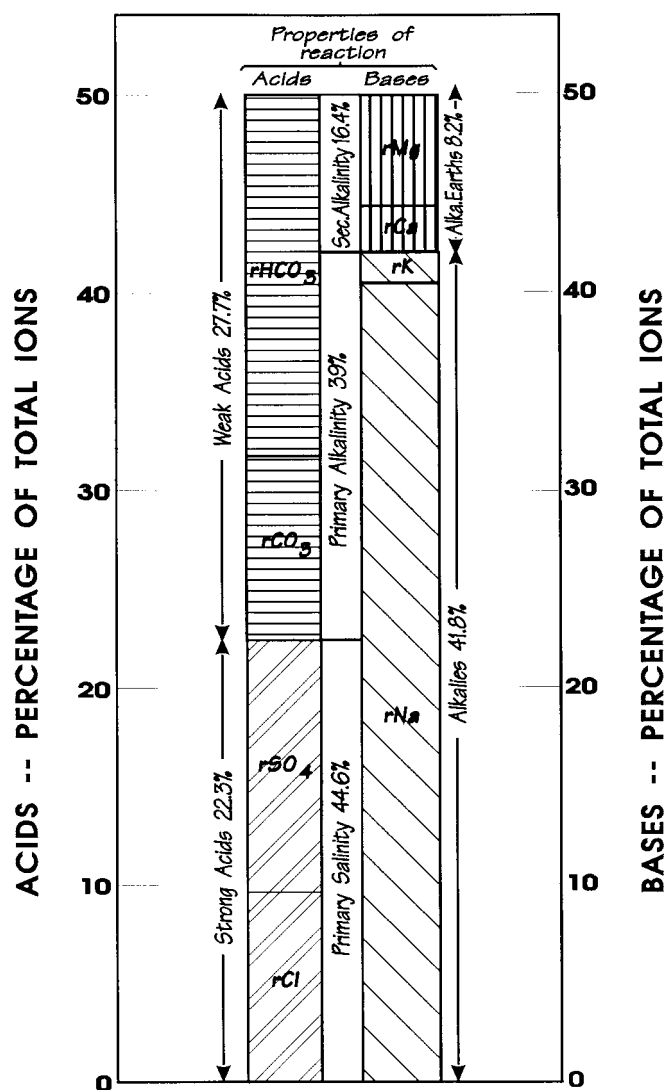
7.2.3.6 Primarily, the diagram is designed to compare one analysis with another and to the originating geologic formations.

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).



NOTE 1—Adapted from Ref (6).

FIG. 3 Rogers Diagram/Palmers Classification

7.2.4.1 The diagram is arranged with the following ions and combinations of ions; cations Ca, Mg, and Na + K and anions $\text{HCO}_3 + \text{CO}_3$, SO_4 , and $\text{Cl} + \text{NO}_3$.

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.

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 Symbolized 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 $\text{CO}_3 + \text{HCO}_3$, 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 in the