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Standard Guide for Displaying the Results of Chemical Analyses of Groundwater for Major Ions and Trace Elements—Trilinear Diagrams for Two or More Analyses¹

This standard is issued under the fixed designation D5754; 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 two-dimensional trilinear graphs as a technique for displaying the common chemical components from two or more complete analyses of natural groundwater (see Section 3) on a single diagram. This category includes not only trilinear-shaped diagrams but also the diamond- or parallelogram-, rectangular-, or square-shaped graphs that have trilinear subdivisions.

1.2 This guide is the first of several documents to inform professionals in the field of hydrology with the traditional graphical methods available to display groundwater chemistry.

NOTE 1—Subsequent guides are planned that will describe the other categories of diagrams that have been developed to display groundwater chemical analyses.

(1) A guide for diagrams based on data analytical calculations will include those categories of water analysis graphs in which one analysis is plotted on each diagram (for example, the pattern, bar, radial, and circle diagrams).

(2) A guide for statistical diagrams will include those categories of water analysis graphs in which multiple analyses are analyzed statistically and the results plotted on the diagram (for example, the box, etc.).

1.3 Numerous methods have been developed to display the ions dissolved in water on trilinear diagrams. These diagrams are valuable as a means of interpreting the physical and chemical mechanisms controlling the composition of water.

1.4 The most commonly used trilinear methods were developed by Hill (1-3),² Langelier and Ludwig (4), Piper (5, 6), and Durov (7-13). These techniques are proven systems for interpreting the origin of the ions in natural groundwater and for facilitating the comparison of results from a large number of analyses.

NOTE 2—The use of trade names in this guide is for identification

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² The boldface numbers in parentheses refer to the list of references at the end of this guide.

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:³

D596 Guide for Reporting Results of Analysis of Water
D653 Terminology Relating to Soil, Rock, and Contained Fluids

D1129 Terminology Relating to Water

3. Terminology

3.1 Definitions:

3.1.1 Except as listed as follows, all definitions are in accordance with Terminology D653.

3.1.2 *anion*—an ion that moves or would move toward an anode; the term is thus nearly always synonymous with *negative ion*.

3.1.3 *cation*—an ion that moves or would move toward a cathode; the term is thus nearly always synonymous with *positive ion*.

3.1.4 *equivalent per million (epm)*—for water chemistry, an equivalent weight unit expressed in English terms and also expressed as milligram-equivalent per kilogram. When the concentration of an ion, expressed in parts per million (ppm),

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

is multiplied by the equivalent weight (combining weight) factor (see *equivalent weight factor*) of that ion, the result is expressed in ep_m.

3.1.4.1 Discussion—

(1) For a completely determined chemical analysis of a water sample, the total ep_m value of the cations will equal the total ep_m 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 ep_m (although all illustrations are in milliequivalent per litre) of the cations and anions of each water analysis. In order to use the diagrams, analyses must therefore 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.

(2) 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 milliequivalent per litre (meq/L) of the cations and anions of each water analysis. In order to use the diagrams, analyses must therefore be converted from milligram per litre (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.

3.1.5 *equivalent weight factor*—also called the combining weight factor and reaction coefficient, this is used for converting chemical constituents expressed in ppm to ep_m and mg/L to meq/L (see *equivalent per million* and *milliequivalent per litre*). To determine the equivalent weight factor, divide the formula weight of the solute component into the valence of the solute component:

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

To then determine the equivalent weight (meq/L) of the solute component, multiply the mg/L value of the solute component times the equivalent weight factor, as follows;

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

$$\times (\text{equivalent weight factor})$$

For example, the formula weight of Ca²⁺ is 40.10 and the ionic charge is 2 (as shown by the 2 +), and the equivalent weight value is computed to be 0.9975 meq/L for a value of 20 mg/L Ca:

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

3.1.5.1 *Discussion*—Many general geochemistry publications (14) and water encyclopedias (15) have a complete table of equivalent weight factors for the ions found in natural groundwater.

3.1.6 *grains per U.S. gallon (gpg)*—for water chemistry, a weight-per-volume unit; also, for irrigation water, it 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. A grain is commonly used to express the hardness of water, where one grain is equal to 17.12 ppm CaCO₃.

3.1.7 *hydrochemical facies*—as described by Back (16), the diagnostic chemical character of water solutions in aquifers. These facies reflect the effects of chemical processes in the lithologic environment and the contained groundwater flow patterns. Freeze and Cherry (17) state, “Hydrochemical facies are distinct zones that have cation and anion concentrations describable within defined composition categories.” The definition of a composition category is commonly based on subdivisions of the trilinear diagram, as described by Back (16, 18).

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

3.1.9 *milligrams per kilogram (mg/kg)*—for water chemistry, a weight-per-weight unit expressed in metric terms. The number of mg of solute (for example, Na) per kg of solution (water). For example, if the total weight of the solution (one million mg/kg) has 99 % solvent and 1 % solute, this is the same as 990 000 mg/kg solution and 10 000 ppm solute in the 1 000 000 mg/kg of solution.

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

3.1.10.1 *Discussion*—The ppm and mg/L values of the constituents in natural groundwater are nearly equal (within anticipated analytical errors) until the concentration of the dissolved solids reaches approximately 7000 mg/L. A density correction should be used when computing ppm from mg/L (14) for highly mineralized waters.

3.1.11 *natural groundwater*—as defined for this guide, 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).

3.1.11.1 Discussion—

(1) In special cases, other major constituents can include aluminum (Al), boron (B), fluoride (F), iron (Fe), nitrate (NO₃), and phosphorus (PO₄). Minor and trace elements that can occur in natural groundwater vary widely, but they can include arsenic (As), copper (Cu), lead (Pb), mercury (Hg), radium (Ra), and zinc (Zn). In addition, natural groundwater 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). Neutrally charged mineral species such as silicate (SiO₂), naturally occurring organics such as tannic acids and colloidal materials, and particulates such as bacteria viruses and naturally charged pollen spores.

(2) Most natural groundwater is part of the hydrologic cycle, which 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 liquid returned to the ocean from the land. A very small amount of the groundwater may be magmatic water originating from rocks deep within the crust of the earth. Other groundwater is connate in that it is trapped in sediments and has not moved actively in the hydrologic cycle for a period measured in geologic time.

(3) 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 on reactions with air and other gases, rock minerals, biological agents, hydraulic pressure, and ambient temperature. The chemical composition of natural groundwater ranges from that similar to distilled water with a minor amount of dissolved solids to a brines, with at least 100 000 mg/L dissolved solids (19). (Naturally occurring brine has been analyzed with more than 300 000 mg/L dissolved chemical solids.)

3.1.12 *parts per million (ppm)*—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 (1 000 000 ppm) has 99 % solvent and 1 % solute, this is the same as 990 000 ppm solvent and 10 000 ppm solute in the 1 000 000 parts of solution.

3.1.13 *water analysis*—a set of data showing the concentration of chemical ions as analyzed from a water sample. In this guide, it normally includes the common constituents as found in natural groundwater (see 3.1.11).

3.1.14 *water analysis diagram*—as used in this guide, a graphical display method for multiple water analyses. This method can be used to assist in scientific interpretation of the occurrence of cations and anions in natural groundwater. The method consists of various combinations of triangular-shaped cation and anion diagrams and diamond- or square-shaped integrated cation and anion diagrams. The sides of the diagrams are divided into equal parts (commonly fifty 2 % or ten 10 % segments) for representing the percentage of each of the cations or anions within the total cation or anion concentration (100 %). The plotted positions of the cations and anions on the diagrams offer an indication of the origin of a water sample, chemical composition of the water (hydrochemical facies), and interrelationship of a number of water samples within the studied area.

4. Summary of Guide

4.1 This guide includes descriptions of the water analysis diagrams that graphically display common chemical components of multiple sets of water analyses from natural groundwater sources.

4.1.1 The historical development of four of the more commonly used diagrams (1-13) is described in Section 1.

4.1.2 Other less commonly known methods of graphically displaying multiple sets of water analyses are described briefly.

4.2 The minimum required chemical constituents from each water analysis for inclusion on the four 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 Detailed descriptions and applications for the following more commonly used water analysis diagrams are given:

4.5.1 Hill geochemical pattern diagram,

4.5.2 Langelier and Ludwig water classification diagram,

4.5.3 Piper water analysis diagram, and

4.5.4 Durov water classification diagram.

4.6 Automated procedures (computer-aided graphics) for basic calculations and the placement of analysis plot symbols onto computer-generated water analysis diagrams are described.

4.7 A list of references is cited and provided for additional information.

4.8 A bibliography (non-referenced documents) is provided for further sources of information.

5. Significance and Use

5.1 Many thousands of water samples are collected each year and the chemical components are determined from natural groundwater sources.

5.2 A single analysis can be interpreted easily regarding composition and geochemical type; however, it is difficult to comprehend all of the factors of similarities, interrelationships, and differences when large numbers of analyses are being compared.

5.3 One of the methods of interpreting the implication of these chemical components in the water is by displaying a number of related water analyses graphically on a visually summarizing water analysis diagram.

5.4 The water analysis diagrams described in this guide display the percentages of the individual cation and anion weights of the total cation and anion weights on graphs shaped as triangles, squares, diamonds, and rectangles.

NOTE 3—The concentration of dissolved solids determined for each analysis is not evident by the plotted location. Scaled symbols, usually circles, can represent the amount of dissolved solids for each analysis plotted on the diagrams.

5.5 Classification of the composition of natural groundwater is a major use of water analysis diagrams.

NOTE 4—Palmer (20) developed a tabular system for the classification of natural water. Hill (1) classified water by composition using two trilinear and one diamond-shaped diagrams of his own design combined. Back (21) improved the classification techniques for determining the hydrochemical facies of the groundwater by a modification of the Piper diagram.

5.6 The origin of the water or degree of mixing may be postulated by examination of the placement and relationship of the cations and anions from different water samples that are plotted on the diagrams.

5.7 Numerous interpretive methods are possible from the examination of water analysis diagrams. For example, it is reasonable to hypothesize the path that the groundwater has

traveled while in the hydrologic regime, the amount of mixing that has occurred 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 water analysis diagram is only one segment of several analytical methods necessary to understand the condition.

6. Documentation

6.1 Introduction:

6.1.1 An outline of graphical plots by Hem (14) describes the trilinear plotting systems developed to display the chemical composition of natural waters. Hem’s summary states, “All trilinear plotting techniques are, in a sense, descendants of the geochemical classification scheme of Palmer” (20).

NOTE 6—The publication by Hem (14) offers an overview of the geochemistry of natural waters and was used throughout this guide as a source of information. A number of other excellent publications are available for the geochemistry of natural groundwater; most of those are referred to in the text and listed in the bibliography.

6.1.2 The earliest reference to the use of trilinear plots to study groundwater was by Emmons and Harrington (22) for the study of mine water composition. Their method was designed principally to examine some of the less common ions that are found in the mineralized waters associated with mines, not with potable groundwater.

NOTE 7—Earlier uses of the trilinear diagram, attributed to Goldschmidt (23), were in the study of the geochemistry of metamorphic rocks in Norway. Brownlow (24) has numerous examples of the use of trilinear diagrams in the study of igneous and metamorphic rocks. Bumb, et al (25) presented a trilinear diagram designed by the U.S. Department of Agriculture, Soil Conservation Service, that delineates the basic soil texture classification.

6.1.3 The first documented use of the cation and anion trilinear diagrams that incorporated a combined cation/anion diamond-shaped diagram for assisting in the interpretation of quality data for potable groundwater was by Hill (1) (Fig. 1). Developed from work performed by Palmer (20), Hill’s diagram provides a graphical representation of the chemical characteristics of different natural waters and mixtures of these waters.

6.1.4 Langelier and Ludwig (4) developed a rectangular graph without the trilinear plots (Fig. 2) that they described as an adaptation of the trilinear method of Hill (1). They changed the outward form of the diagram in order to permit the use of standard triangular graph paper.

6.1.5 Piper (5, 6) developed a method (Fig. 3) similar to Hill’s independently. He describes the graphical procedure as “an effective tool in segregating analytical data for critical study with respect to sources of the dissolved constituents in waters, modifications in the character of a water as it passes through an area, and related geochemical problems.”

NOTE 8—The method developed by Piper was distributed originally as an unpublished document to his coworkers in the Ground Water Branch of the Water Resources Division (WRD), U.S. Geological Survey (USGS), on Oct. 5, 1942. Because of Piper’s influence and his promotion of the technique, the trilinear form that he identified as the water analysis

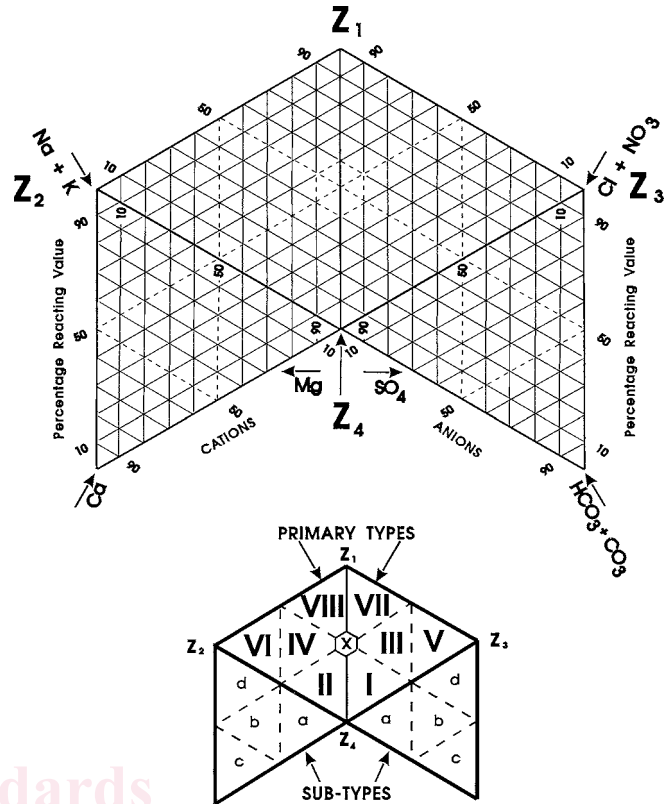


FIG. 1 Geochemical Pattern Diagram (Adapted from Refs (1) and (4))

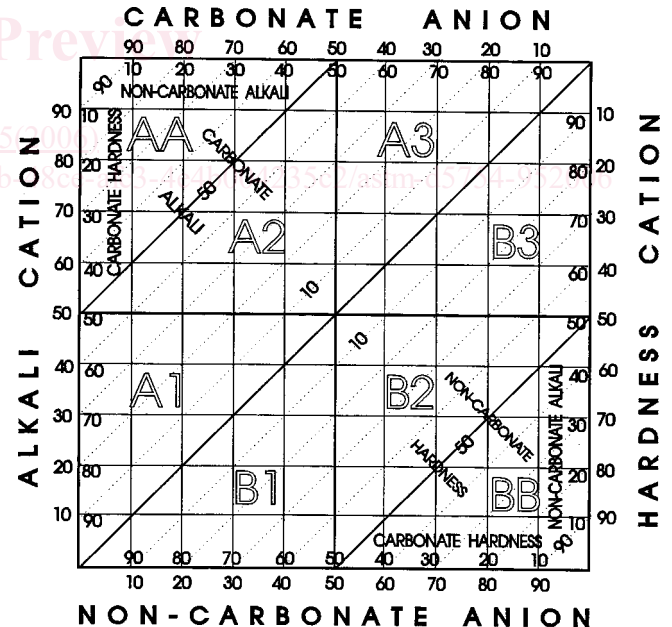


FIG. 2 Water Classification Diagram (Adapted from Ref (4))

diagram became used widely and known subsequently as the Piper diagram (Fig. 3).

6.1.6 Durov developed a series of diagrams (7-13) similar to those of Hill, Langelier and Ludwig, and Piper that provides the percentage of cations and anions on individual trilinear

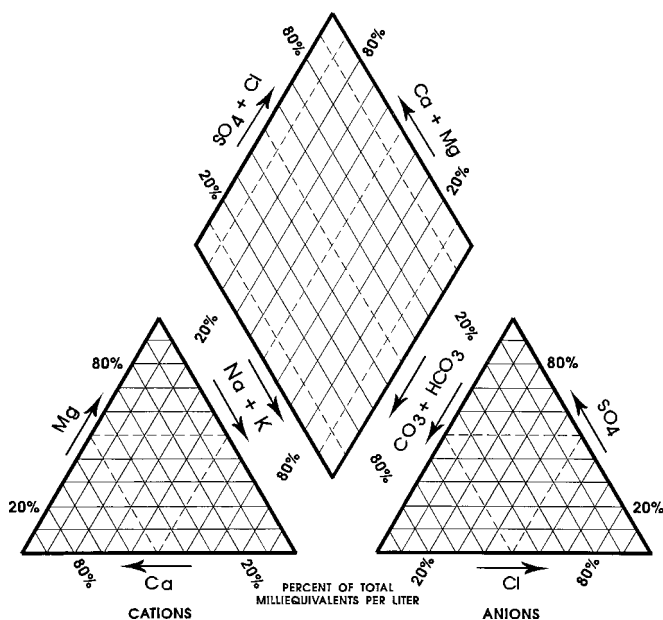


FIG. 3 Water Analysis Diagram (Adapted from Refs (5) and (6))

diagrams, and the intersection of lines extended from the cation and anion diagrams to a square gives the major-ion type of the water (Fig. 4). However, in addition, Durov extended the cation and anion lines to two rectangles adjacent to the square to provide for the representation of two other parameters, for example, dissolved solids, pH, specific conductance, etc. (described by Freeze and Cherry (17)).

6.1.7 Other researchers developed graphical display methods that are similar to those described above.

6.1.7.1 Käss (26) developed a square four-coordinate diagram in which the alkaline earths are compared with the alkalis on the vertical axis, while the anions chloride, sulfate, and hydrogen carbonate (bicarbonate) appear on the horizontal axis (Fig. 5a). The analysis is represented on the diagram by a horizontal line, the length of which corresponds to the percentage of sulfate content (27).

6.1.7.2 Water-type diagrams were developed by Tolstichin (Fig. 5b) (28) and Furtak and Langguth (Fig. 5c) (29) that designate a number for the water type, depending on where the

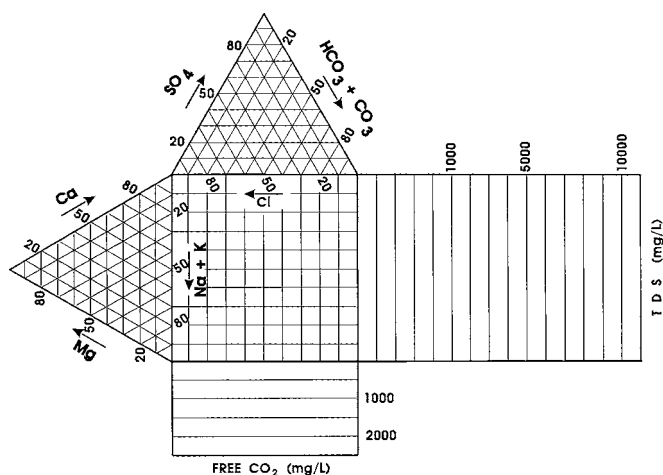


FIG. 4 Water Classification Diagram (Adapted from Ref (7))

analysis plots on the diagram (27). For example, for the example analysis (Table 1), the water type numbers are 11 for the Tolstichin diagram and 98 for the Furtak and Langguth diagram (classified as a Ca-HCO₃ water).

6.1.7.3 Schwille (30) devised a hardness triangle to compare total hardness, carbonate hardness, and noncarbonate hardness (Fig. 5d) (27). In German hardness or meq/L units (one German unit in degrees = 17.8 mg/L hardness), the scale of the diagram is determined by the highest hardness value to be plotted. The plot symbol can represent the sampling category (for example, aquifer unit, lithology, etc.). Equal symbols can be enclosed by lines and the enclosed areas filled in with a pattern to emphasize a particular category. In addition, other ion values (for example, Cl and SO₄) for each analysis can be plotted on scaled rectangular diagrams that are positioned parallel to the sides of the triangular hardness diagram. Fig. 5d demonstrates the technique of plotting the individual ions.

6.1.7.4 Filatov (31) proposed a two-point system with cation and anion equilateral triangles having a common side (Fig. 6a), thus forming a diamond-shaped diagram (described by Hem (14)). Each triangle is divided into ten segments. The segments are of three different sizes. Each segment is identified by the predominate ion or ions. Areas with no predominate ion are classified as mixed.

NOTE 9—The diagram is scaled with each side representing 50 % of the total ions (cations plus anions), so that a cation or anion plot position would be computed, for example, as follows:

$$\% \text{ Ca} = \frac{\text{Ca meq/L units}}{(\text{Ca} + \text{Mg} + \text{Na} + \text{Cl} + \text{SO}_4 + \text{HCO}_3) \text{ meq/L units}} \quad (4)$$

Filatov presented an anion coefficient that identifies mixed waters numerically (see Analysis 3 in Table 2). Anion coefficients that are in the range from 0.5 to 1.0 units plot in the mixed area of the diagram. The same is true with cation coefficients. The anion computation is as follows:

$$\text{anion coefficient} = \frac{\% \text{ predominate anion}}{\sum \% \text{ remaining anions}} \quad (5)$$

6.1.7.5 The method given by Franko, et al (32) uses a water chemistry classification based on the principle of ion combinations that is attributed to the Gadza (33) and a modification of the Palmer system (20). The classification diagram of chemistry of mineral water (Fig. 6b) shown by Franko, et al (32) consists of two trilinear plots with a log-scaled, rectangular-shaped graph placed between the bases of the trilinear plots. The trilinear plots are for providing the percentages of the combined ion meq/L values. The rectangular-shaped graph is for providing the mg/L value of the dissolved solids for each analysis.

NOTE 10—Table 3 lists selected analyses from Franko, et al (32). Table 3 also gives the combined ion meq/L percentages in the order dictated by using the principle of ion combinations. Fig. 6b uses these meq/L percentages as plot positions. The dissolved solids value is positioned on the rectangular graph at right angles to the plotted point on the trilinear diagram.

NOTE 11—In Fig. 6b and Table 3, the symbol S1 is primary salinity, S2 is secondary salinity, S3 is tertiary salinity, A1 is primary alkalinity, A2 is secondary alkalinity, and A3 is tertiary alkalinity. In Fig. 6b and Table 3, the S1 (Cl) is combined with S1 (SO₄), and the S2 (Cl) is combined with S2 (SO₄) + S3 for plotting. The A2 and A3 (CaHCO₃ and MgHCO₃) are also combined.

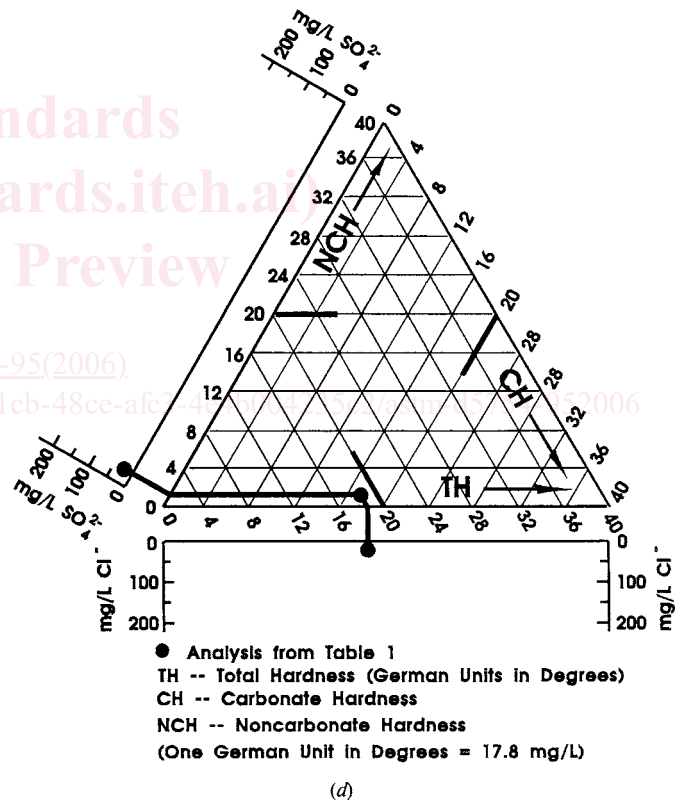
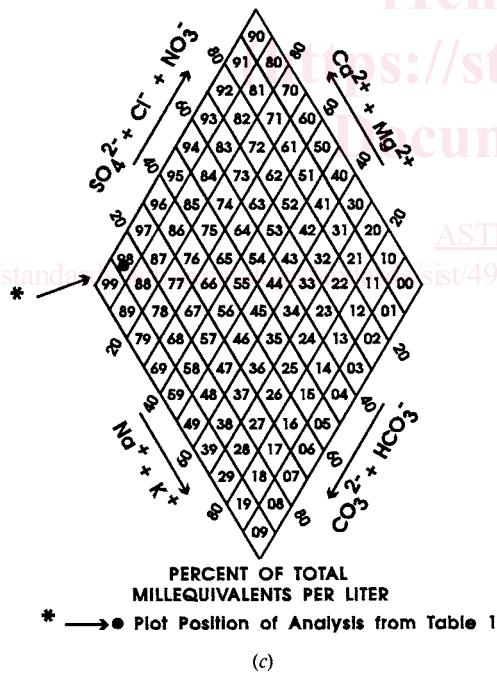
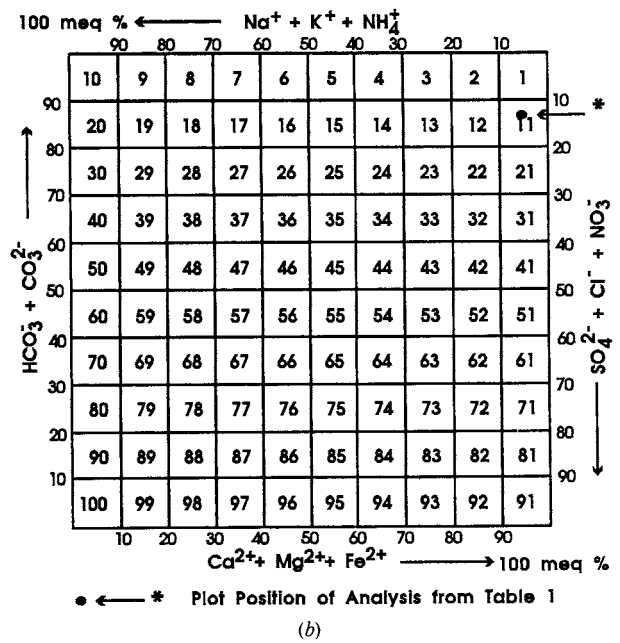
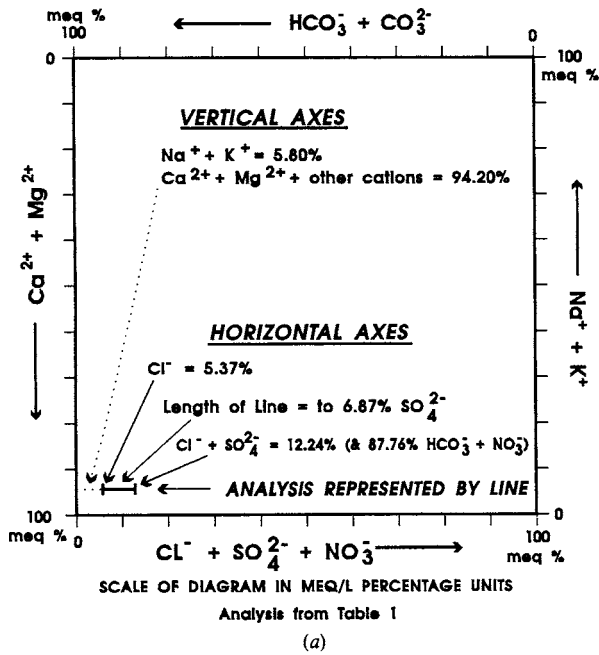


FIG. 5 Examples of Other Coordinate Diagrams: (a) Käss Four Coordinate Diagram, (b) Tolstichen Water-Type Diagram (See Ref (28)), (c) Furtak and Langguth Water-Type Diagram, and (d) Schwille Trilinear Hardness Diagram

6.1.7.6 D'Amore, et al (34) proposed a classification diagram that uses the diamond-shaped plot of Piper in conjunction with rectangular-shaped graphs (Fig. 7). The purpose of the combined graphs is to improve the definition of hydrochemical facies and to determine the percentages of parent waters in mixed waters better. The number of rectangular graphs included on a complete classification diagram depends on the

number of categories to be portrayed, with a category being one or more water analyses from an individual aquifer, lithologic unit, or distinct hydrologic source.

NOTE 12—The Piper plot is conventional, with the cations meq/L % plotted against anions meq/L %. As defined by D'Amore, et al, the rectangular graph uses six computations (Parameters A through F) to emphasize distinct water groups. Parameters other than those defined may

TABLE 1 Water Analysis^A

Cations	mg/L	meq/L	meq %
Na ⁺	8.26	0.3593	5.35
K ⁺	1.17	0.0299	0.45
NH ₄ ⁺	0.12	0.0080	0.10
Ca ²⁺	84.3	4.207	62.69
Mg ²⁺	25.5	2.098	31.26
Fe _{total}	0.24	0.0086	0.13
Mn ²⁺	0.03	0.0011	0.02
Totals		6.711	100.00
Anions	mg/L	meq/L	meq%
SO ₄ ²⁻	22.2	0.4622	6.87
Cl ⁻	12.8	0.3610	5.37
NO ₃ ⁻	2.61	0.0421	0.62
HCO ₃ ⁻	357.5	5.86	87.13
HPO ₄ ²⁻	0.02	0.0004	0.01
Totals		6.726	100.00
Total hardness		17.7° German units	
Carbonate hardness		16.4° German units	
Non-carbonate hardness		1.3° German units	
(one German unit in degrees = 17.8 mg/L)			
Dissolved solids, evaporated residue = 350.5 mg/L			

^AAnalysis selected from Ref (27).

be useful, depending on the geochemistry of the area studied. The anion and cation components are in meq/L units in the computations (see Table 4 for four analyses from four different sources). The minimum, maximum, and mean values can be plotted for each parameter when multiple analyses exist for a single source. Fig. 7 includes an example of the symbol used for multiple samples. Resultant parameters are normalized between -100 and +100 to widen the range of the plotted values. The computations as given by D'Amore are as follows:

$$\text{Parameter A: } \frac{100}{\sum (\text{anions})} (\text{HCO}_3 - \text{SO}_4) \quad (6)$$

Parameter A assists in distinguishing between water that circulates through calcareous terrains and those occurring in evaporitic rocks.

$$\text{Parameter B: } 100 \left(\frac{\text{SO}_4}{\sum (\text{anions})} - \frac{\text{Na}}{\sum (\text{cations})} \right) \quad (7)$$

Parameter B discriminates between sulfate-enriched waters circulating in evaporitic terrains and sodium-enriched waters that have encountered marly, clayey sedimentary terrains.

$$\text{Parameter C: } 100 \left(\frac{\text{Na}}{\sum (\text{cations})} - \frac{\text{Cl}}{\sum (\text{anions})} \right) \quad (8)$$

Parameter C tends to distinguish between waters deriving from volcanites and those coming from carbonate-evaporitic series or from a regional quartzitic schistose basement.

$$\text{Parameter D: } 100 \left(\frac{\text{Na} - \text{Mg}}{\sum (\text{cations})} \right) \quad (9)$$

Parameter D distinguishes between waters that have circulated in dolomitized limestones.

$$\text{Parameter E: } 100 \left(\frac{\text{Ca} + \text{Mg}}{\sum (\text{cations})} - \frac{\text{HCO}_3}{\sum (\text{anions})} \right) \quad (10)$$

Parameter E distinguishes between waters that have circulated in carbonate aquifers and those in sulfate-bearing aquifers.

$$\text{Parameter F: } 100 \left(\frac{\text{Ca} - \text{Na} - \text{K}}{\sum (\text{cations})} \right) \quad (11)$$

Parameter F reveals the increase of K concentration in water samples.

6.1.7.7 Carren~o (14, 35) described a system (he attributed to Hermion Larios) that consists of individual cation and anion trilinear diagrams (Fig. 8) that are divided into ten equal areas. These areas are numbered from zero through nine.

NOTE 13—The four small triangles shown within the larger triangles of Fig. 8 individually have the same area as each of the six irregular polygons. The plotted position (based on a 100 % meq/L scale) of the meq/L percentage cations or anions of an analysis falls within a numbered segment of each diagram. The cation number is combined with the anion number to signify a two-digit classification number, for example, Analysis 4 is classified 44, a sodium chloride water, such as from the ocean. Others shown in Fig. 8 and listed in Table 2 include Analyses 1 and 3 (99, calcium bicarbonate with a quantity of magnesium and sulfate) and Analysis 2 (38, sodium sulfate with a quantity of calcium and bicarbonate).

6.2 Minimum Data Requirements—The basic water analysis diagram requires water analyses that have a minimum number of major ions determined. The constituents used commonly on the diagrams are the cations calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K) and the anions bicarbonate (HCO₃), carbonate (CO₃), sulfate (SO₄), and chloride (Cl). If some other ions, such as dissolved iron (Fe²⁺) and ammonia (NH₄⁺), exceed the conventional group described above in special circumstances, and all water analyses for the study include these constituents, they can replace or be added to 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 (16, 18).

NOTE 14—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 (36) guidelines recommend a maximum of 1000 mg/L dissolved solids.

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 (the percentage is determined by multiplying the computed value times 100):

$$\% \text{ chemical balance } (\pm) \quad (12)$$

$$= \frac{\text{total cations} - \text{total anions (meq/L)}}{\text{total cations} + \text{total anions (meq/L)}} \times 100$$

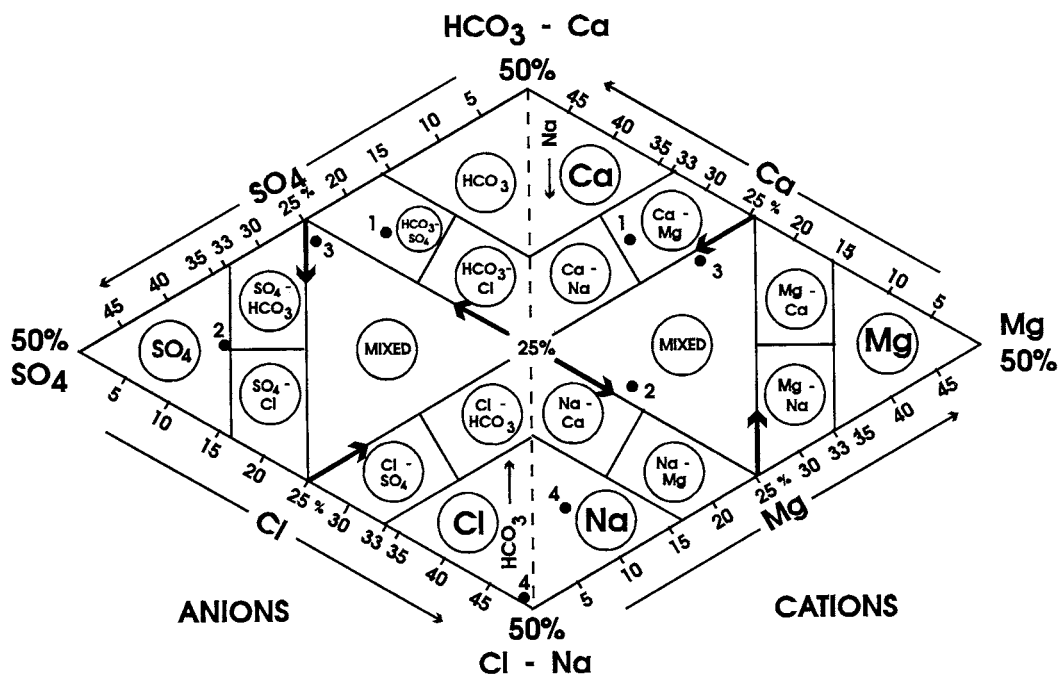
Recommended Chemical Balance for Use of Analyses on Water Analysis Diagrams

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 15—Minor amounts of ions such as fluoride (F), nitrate (NO₃), iron (Fe), and barium (Ba) may occur in natural groundwater, but normally they do not influence the chemical balance significantly. If any of these ions (for example, NO₃) occur in amounts that alter the chemical balance, they can be included in the computations for construction of water analysis diagrams (for example, include the NO₃ with Cl + SO₄ on the diamond-shaped diagram and SO₄ + NO₃ on the trilinear anion diagram). Other constituents may occur in minor amounts in a colloidal or suspended state, such as silica (SiO₂), iron hydroxide (Fe), and aluminum compounds (Al), and they are not considered in the chemical balance because they are not dissolved constituents.

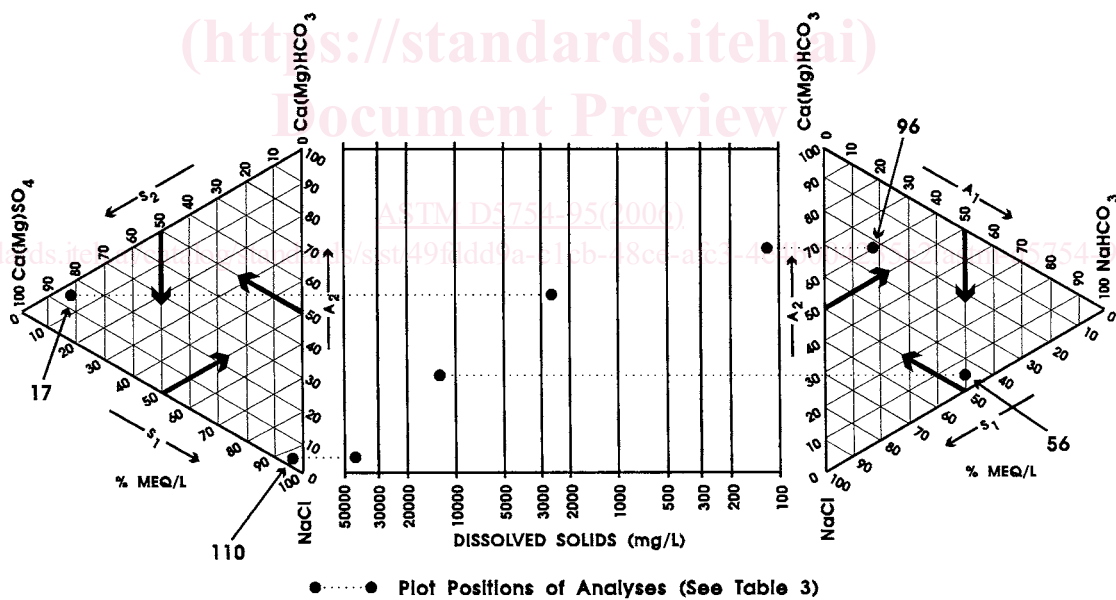
NOTE 16—In a study of the Delmarva Peninsula, Hamilton, et al (37) used 10 % as the error limit for the ionic charge balance of analyses with a complete set of major ions (nitrate was excluded as a major ion). In addition, there may be circumstances under which the ionic balance is greater than 10 % due to analytical error. If so, specify the circumstances.

6.4 Required Calculations for Diagram Construction:



SCALE OF DIAGRAM IN MEQ/L PERCENTAGE UNITS
 ● 1, 2, 3, 4 -- ANALYSES FROM TABLE 2

(a)



●.....● Plot Positions of Analyses (See Table 3)

(b)

FIG. 6 Filatov and Gazda Trilinear Diagrams: (a) Filatov Graphical Representation of Water Chemistry (Adapted from Ref (31)), and (b) Gazda Classification Diagram of Chemistry of Mineral Water (Adapted from Ref (32))

6.4.1 Equivalent Weight Factors—The factors (see 3.1.5) 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:

TABLE 2 Ion Percentages, Anion Coefficient, and Anion Classification^A

	Analysis 1	Analysis 2	Analysis 3	Analysis 4
Anions				
%Cl	5.9	7.25	2.5	48.26
%SO ₄	15.4	33.35	24.0	0.02
%HCO ₃	28.7	9.4	23.5	1.72
Cations				
%Ca	29.5	14.6	23.7	7.8
%Mg	11.3	11.2	18.6	3.5
%Na	9.2	24.2	7.7	38.7
Coefficient of predominate anion	1.3	2.0	0.92	27.8
Anion classification	HCO ₃ -SO ₄	SO ₄	SO ₄ -HCO ₃ -Cl	Cl

^AAnalyses selected from Ref (31) .

Cations
 calcium, 0.04990
 magnesium, 0.08229
 sodium, 0.04350
 potassium, 0.02558

Anions
 bicarbonate, 0.01639
 carbonate, 0.03333
 sulfate, 0.02082
 chloride, 0.02821

6.4.2 Individual Cation and Anion Diagram—The percentage values used for plotting on the water analysis diagram are determined by multiplying by 100 the number derived from dividing the total meq/L or epn value of either the cations or anions into the individual cation or anion value. For example, the number derived from dividing the total cation value (Ca + Mg + Na + K) into the meq/L or epn value of Ca is multiplied by 100 to yield the percentage of Ca in the total cations (by weight).

$$\% \text{ Ca} = \frac{\text{meq/L Ca}}{\text{meq/L (Ca + Mg + Na + K)}} \times 100 \quad (13)$$

This percentage is the plot value for Ca on the cation trilinear diagram. This procedure of computation is followed for each of the remaining cations (Mg and (Na + K)) (Fig. 9) and for each of the anions (Cl, SO₄, and (HCO₃ + CO₃)) for the anion trilinear diagram.

6.4.3 Combined Cation and Anion Diagram—The values used for plotting on the diamond-shaped, square, or rectangular diagram are determined by multiplying by 100 the number derived from dividing the total meq/L or epn value of either the cations or anions into the combined value of cations or anions. For example, the number derived by dividing the total cation value (Ca + Mg + Na + K) into the combined value of Ca + Mg is multiplied by 100 to yield the percentage of Ca + Mg of the total cations.

$$\% (\text{Ca} + \text{Mg}) = \frac{\text{meq/L (Ca + Mg)}}{\text{meq/L (Ca + Mg + Na + K)}} \times 100 \quad (14)$$

NOTE 17—The above percentage is the plot value for Ca + Mg on the cation axis of the diagram. The percentage of the cations (Na + K) is the remaining amount (percent of (Ca + Mg) + percent of (Na + K), equals 100 %); only one plotted position is therefore required along the cation axis (oriented from the lower right to upper left) (Fig. 10). The position on the anion axis (oriented from the lower left to upper right) is determined using a similar procedure with the anion values. For example, the total anion value (SO₄ + Cl + CO₃ + HCO₃) divided in the combined value of SO₄ + Cl yields the percentage SO₄ + Cl of the total anions. This percentage is the plot position for SO₄ + Cl on the anion axis of the diamond-shaped diagram. The plot position of the cation value on the cation axis is therefore placed at the cross point for the plot position of the anion value on the anion axis.

6.4.4 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 in Table 5.

6.4.4.1 Chemical Analysis—The following is the chemical analysis that is used as an example for demonstrating the steps needed for to plot constituent values.

(1) *Example of meq/L Computation:*

$$1.15 \text{ meq/L Ca} = 23 \text{ mg/L Ca} \times 0.04990 \text{ (conversion factor)} \quad (15)$$

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

$$97\% \text{ (balance)} = \frac{3.09 \text{ (anions)}}{3.18 \text{ (cations)}} \quad (16)$$

$$= \frac{2.80 + 0 + 0.02 + 0.27 \text{ (anions)}}{1.15 + 0.39 + 1.52 + 0.12 \text{ (cations)}} \times 100$$

6.4.4.3 Cation Trilinear Diagram—Plot positions (the percentage of each cation constituent) for the cation trilinear diagram are determined by dividing the total cation amount in meq/L into the meq/L amount for each cation (Fig. 11).

NOTE 18—Plot values are rounded to a whole number for illustration in Fig. 11.

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

$$36.2\% \text{ Ca} = \frac{1.15 \text{ meq/L Ca}}{3.18 \text{ meq/L cations}} \times 100 \quad (17)$$

$$12.2\% \text{ Mg} = \frac{0.39 \text{ meq/L Mg}}{3.18 \text{ meq/L cations}} \times 100 \quad (18)$$

$$51.6\% \text{ Na + K} = \frac{1.52 \text{ meq/L Na} + 0.12 \text{ meq/L K}}{3.18 \text{ meq/L cations}} \times 100 \quad (19)$$

6.4.4.4 Anion Trilinear Diagram—Plot positions (the percentage of each anion constituent) for the anion trilinear diagram are determined by dividing the total anion amount in meq/L into the meq/L amount for each anion.

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

$$90.6\% \text{ HCO}_3 + \text{CO}_3 = \frac{2.80 \text{ meq/L HCO}_3 + 0 \text{ meq/L CO}_3}{3.09 \text{ meq/L anions}} \times 100 \quad (20)$$

6.4.4.5 Cation/Anion Diamond or Square Diagram:

$$0.7\% \text{ SO}_4 = \frac{0.02 \text{ meq/L SO}_4}{3.09 \text{ meq/L anions}} \times 100 \quad (21)$$

$$8.7\% \text{ Cl} = \frac{0.27 \text{ meq/L Cl}}{3.09 \text{ meq/L anions}} \times 100 \quad (22)$$

Plot positions for the cation/anion diamond diagram are determined by dividing the Ca + Mg meq/L value and the Na + K meq/L value by the total cation meq/L value. The anion portion is determined by dividing the HCO₃ + CO₃ meq/L value and the SO₄ + Cl meq/L value by the total anion meq/L value.

(1) *Example of Plot Value (Cation/Anion Percentage) Computation:*

$$48.4\% \text{ Ca + Mg} = \frac{1.15 \text{ meq/L Ca} + 0.39 \text{ meq/L Mg}}{3.18 \text{ meq/L cations}} \times 100 \quad (23)$$

TABLE 3 Water Chemical Data and Gazda Classification

Chemical Parameters	Analysis 17 ^A	Analysis 56 ^A	Analysis 96 ^A	Analysis 110 ^A
Cations—meq/L (%) Ca	26.2 (35.62)	7.44 (1.97)	0.60 (20.03)	24.6 (1.75)
Sr + Ba + Mn + Fe + Al	0.35 (0.48)	0.53 (0.15)	0.08 (2.51)	4.87 (0.34)
Mg	8.80 (11.96)	2.84 (0.75)	0.25 (8.34)	12.8 (0.91)
Na + K	1.27 (1.74)	170.0 (45.14)	0.57 (19.02)	659.0 (46.82)
Li + NH ₄	0.15 (0.20)	7.49 (1.99)	0.01 (0.10)	2.49 (0.18)
Anions—meq/L (%) Cl	0.08 (0.10)	84.0 (22.02)	0.19 (6.01)	697.0 (49.13)
Br + B + F + NO ₂ + NO ₃	0.04 (0.05)	0.31 (0.09)	0.05 (1.67)	1.84 (0.13)
SO ₄	30.9 (42.30)	0.09 (0.02)	0.11 (3.57)	0.09 (0.01)
HCO ₃	5.50 (7.53)	106.0 (27.83)	1.20 (38.56)	10.4 (0.73)
CO ₃ + HPO ₄ + OH	0.02 (0.02)	0.15 (0.04)	0.01 (0.19)	0.01 (0.00)
Total mg/L	2504	13 754	121	41 646
Classification	17	56	96	110
S1(Cl) NaCl ^B	0.30 %	44.22 %	15.36 %	94.00 %
Remaining Na	1.79 %	25.02 %	11.44 %	0 %
Remaining Cl	0 %	0 %	0 %	2.26 %
S2(Cl) Ca(Mg)Cl ^C	0 %	0 %	0 %	4.52 %
Remaining Ca	48.06 %	2.86 %	30.88 %	0.74 %
Remaining Cl	0 %	0 %	0 %	0 %
S1(SO ₄) NaSO ₄ ^D	3.58 %	0.04 %	7.14 %	0.00 %
Remaining Na	0 %	25.00 %	7.87 %	0 %
Remaining SO ₄	40.51 %	0 %	0 %	0.01 %
S2(SO ₄) + S3 Ca(Mg)SO ₄ ^E	81.02 %	0 %	0 %	0.02 %
Remaining Ca	7.55 %	2.86 %	30.88 %	0.73 %
Remaining SO ₄	0 %	0 %	0 %	0 %
A2 + A3 Ca(Mg)HCO ₃ ^F	15.20 %	5.74 %	61.76 %	1.46 %
Remaining Ca	0 %	0 %	0 %	0 %
Remaining HCO ₃	0 %	25.00 %	7.87 %	0 %
A1 NaHCO ₃ ^G	0 %	50.00 %	15.74 %	0.00 %
Remaining Na	0 %	0 %	0 %	0 %
Remaining HCO ₃	0 %	0 %	0 %	0 %

^AAnalyses from Ref (32).

^BNa includes Na + K + Li + NH₄, and Cl includes Cl + Br + B + F + NO₂ + NO₃.

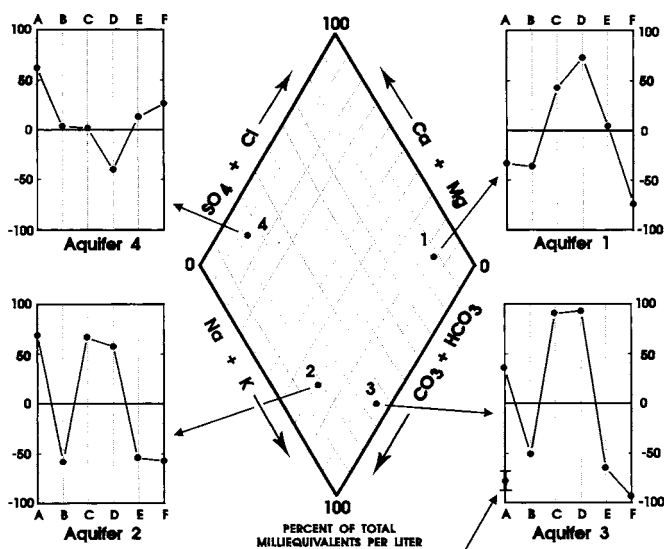
^CCa includes Ca + Mg + Sr + Ba + Mn + Fe + Al and Cl (see Footnote B).

^DNa (see Footnote B) and SO₄ includes SO₄.

^ECa (see Footnote C), and SO₄ (see Footnote D).

^FCa (see Footnote C) and HCO₃ includes HCO₃ + CO₃ + HPO₄ + OH.

^GNa (see Footnote B) and HCO₃.



NOTE: Multiple Analyses From A Source Are Shown By The Following Symbol -- \uparrow Maximum, \circ Mean, \downarrow Minimum

FIG. 7 D'Amore, et al Classification Diagram (see Table 4 for Plotted Parameters)

TABLE 4 Water Chemistry and D'Amore Classification Parameters^A

	Aquifer 1	Aquifer 2	Aquifer 3	Aquifer 4
Cations—meq/L (%)				
Ca	4.04 (6.7)	1.00 (13.7)	0.15 (1.5)	3.14 (38.7)
Mg	5.92 (9.7)	1.15 (15.8)	0.33 (3.3)	4.11 (50.6)
Na	50.90 (83.6)	5.13 (70.5)	9.44 (95.2)	0.87 (10.7)
Total	60.86	7.28	9.92	8.12
Anions—meq/L (%)				
Cl	25.39 (41.6)	0.31 (4.2)	0.54 (5.3)	0.65 (7.9)
SO ₄	27.90 (45.7)	0.96 (13.2)	2.96 (29.0)	1.31 (15.9)
HCO ₃	7.74 (12.7)	6.03 (82.6)	6.70 (65.7)	6.28 (76.2)
Total	61.03	7.30	10.20	8.24
Parameter A	-33.03	69.45	36.67	60.32
B	-37.91	-57.32	-50.98	5.18
C	42.03	66.22	89.87	2.83
D	73.91	54.67	91.83	-39.90
E	3.68	-53.07	-60.85	13.07
F	-72.00	-56.73	-93.65	27.96

^AAnalyses selected from Ref (60).

$$51.6\% \text{ Na+K} = \frac{1.52 \text{ meq/L Na} + 0.12 \text{ meq/L K}}{3.18 \text{ meq/L cations}} \times 100 \quad (24)$$