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Graphical Methods for Indicating the Mineral Character of Natural Waters

By Wilfred F. Langelier and Harvey F. Ludwig

IN THE solution of problems involving mineral analyses of natural waters, particularly in the fields of geology, agriculture and engineering, it is often desirable to classify waters on the basis of their major chemical constituents. These constituents fall into four groups, each with chemically similar components: c_1—the alkali cations, sodium and potassium; c_2—the hardness cations, calcium and magnesium; a_1—the strong acid anions, nitrate, chloride, and sulfate; and a_2—the weak acid anions, carbonate and bicarbonate. If the concentrations are expressed in terms of normality (equivalent hydrogen) or some convenient fraction thereof, e.g., milligram equivalents per liter (mE/l.),* the mineral character of the water is indicated by the total equivalent concentration, i.e., the total concentration of alkali and hardness constituents (Σ), and by the relative

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* The unit "equivalents per million grams" (epm.), tentatively approved by the American Society for Testing Materials in 1940 (1), appears to be more consistent when used together with the firmly established "parts per million" (ppm.), because each is a "weight per weight" unit. The abbreviation (epm.), however, introduces a serious inconsistency in that the letter m stands for "million grams" rather than for "million equivalents" as might be inferred from its significance in the term (ppm.). Because of this, and also because, in the use of weight per weight units, it is not always clear whether weights of *solution* or weights of *solvent* is meant, the authors prefer to use the weight per volume units, i.e. milligrams per liter (mg./l.) and milligram equivalents per liter (mE/l.). Each of these is consistent with the other; and in the case of saline waters, there can be no uncertainty as to whether or not a specific gravity correction has been applied.

magnitude of each constituent expressed as a percentage of Σ. In this method of grouping, based upon the work of Palmer (2), the slightly dissociated silicic and carbonic acids, trace elements, etc., are omitted from consideration. Since the electrical neutrality of solutions of salts requires that $c_1 + c_2 = a_1 + a_2$, it is necessary to determine only three of the groups in the laboratory, the value of the fourth being obtainable by calculation.

Asserting that, for purposes of geological classification, greater importance attaches to relative proportions of constituents than to absolute concentrations, Palmer bases his classifications upon "percentage of total" values for the cation and anion groups respectively. By expressing
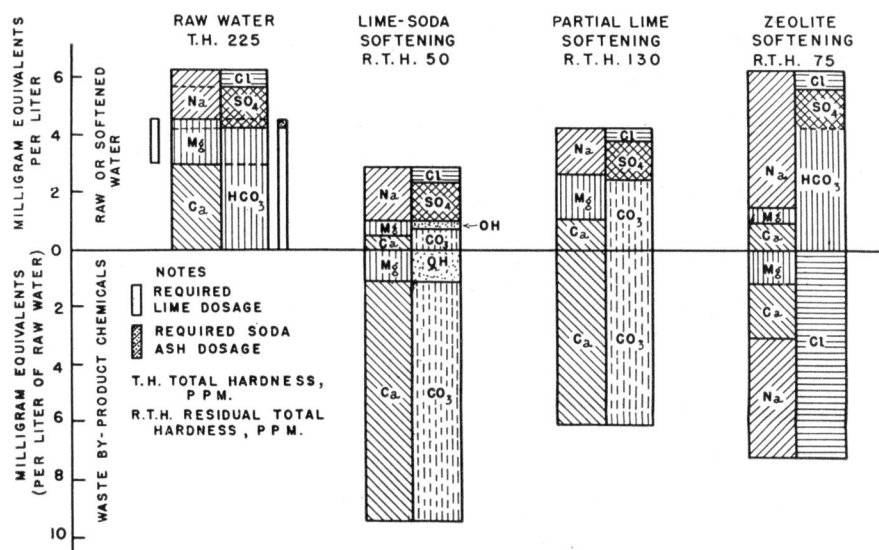
FIG. 1. Double-Bar Graphs, for visualizing chemical arithmetic of three proposed treatments for softening water from Corralitos Creek, Watsonville, Calif.

the results of an analysis in this form and by assuming balances between cations and anions in accordance with a prescribed order, a "character formula" of the water is obtained. In the Palmer system, the alkali and hardness cations are termed primary and secondary respectively. The non-carbonate and carbonate anions are termed salinity and alkalinity respectively. The property of primary salinity results from the presence of the c_1 and a_1 groups. If the former group is in excess, the property of primary alkalinity is also indicated. If, however, the latter group is in excess, the property of primary alkalinity is absent, and, instead, the property of secondary salinity is indicated. The property of secondary alkalinity results from the presence of the c_2 and a_2 groups. Thus, there

are four properties, but not more than three are represented in a given water. Palmer includes those waters which possess primary alkalinity in Class 1, and those which possess the property of secondary salinity in Class 3. Class 2 is reserved for those rare waters in which the c_1 group is exactly equal to a_1, and Class 4 for those equally rare waters in which c_2 is exactly equal to a_2.

By thus reducing the number of items of a water analysis into a smaller number of similarly reacting groups, the use of graphs and diagrams to indicate mineral character becomes practicable. Various types of graphs are possible; and these are especially useful when it is desired to compare the results of a number of analyses, or to ascertain the changes in character which a body of water undergoes as a result either of mixture with other waters under conditions of natural flow or of chemical treatment as in water softening. For these purposes, tabulated data are difficult to visualize, and the possibilities of classification are not so readily apparent. It is the purpose of the present paper to review this subject and to explore new possibilities.

Double-Bar Graphs

Perhaps the most widely used graphs designed to depict the mineral character of water are the double-bar graphs similar to those shown in Fig. 1. Graphs of this general type are believed to have been described first by Collins (3). The several graphs in Fig. 1 were prepared to illustrate the changes in character which a water would undergo as a result of softening by three indicated treatments. It will be noted that in these graphs much of the chemical arithmetic* of the three processes is visualized. The by-

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* The dosages of lime and soda ash indicated assume the absence of free carbon dioxide. In this process the magnesium is precipitated as insoluble hydroxide and the calcium as insoluble carbonate. Since the precipitation of magnesium as hydroxide requires the presence of OH ions in excess of the concentration that can exist in the presence of the weakly acid HCO_3 ions present in the water, the latter must be first neutralized to CO_3 ions. Since in this neutralization, each equivalent of HCO_3 produces two equivalents of CO_3, these latter become available to precipitate not only the calcium added in the form of lime but a portion or all of the calcium present in the water. Additional CO_3 ions in the form of Na_2CO_3 will be necessary only in the amount that Ca + Mg is greater than HCO_3, or that Cl + SO_4 is greater than Na.

In the example used for illustration, or in the softening of any water in which the chloride plus sulfate exceeds sodium, the use of NaOH to supply the deficiency of sodium will not only replace the Na_2CO_3 commonly used but will also reduce the lime requirement by the same amount. Normally, however, there would be no saving in cost resulting from this substitution because an equivalent weight of caustic soda would cost more than one equivalent weight each of soda ash and lime (see Arbatsky Method, p. 339).

products of the chemical reactions, those substances for which adequate
disposal facilities must be available, are shown in the graphs.   To convert
the indicated milligram equivalent weights into pounds per million gallons
of water treated it is necessary merely to multiply the scale differences for
any constituent by its equivalent weight and by 8.34, the weight of a
gallon of water.   A conversion chart (Fig. 2) can be used to facilitate
these computations.
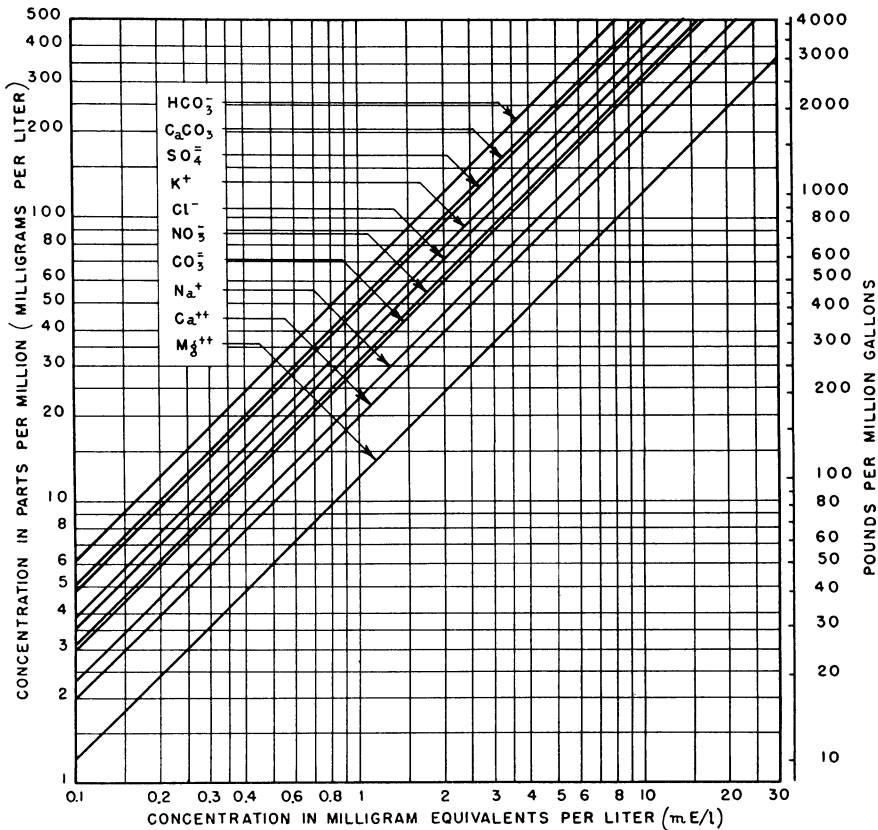
F<small>IG</small>. 2. Logarithmic Chart, for converting milligrams per liter (ppm.), or lb. per mil.
gal., into milligram equivalents per liter (mE/l.), or the reverse

   If desired, the double-bar type of graph can be used to indicate directly
both the relative and absolute concentrations.   In this modification the
percentage equivalent concentration of each constituent is plotted verti-
cally, and the total equivalent concentration is indicated by the width of
the double bars.   This modification has been described by Stabler (5).

Point Diagrams

In recent years, graphing techniques by means of which the character of one or more waters is indicated by the location of points upon suitably constructed diagrams have been described in the literature.   The more

FIG. 3. Two Examples of Use of Arbatsky Vector Diagram, in graphical computation of lime and soda requirements in water softening

important of these will be reviewed together with two new forms proposed by the authors.

Arbatsky Method

This method (4) was developed and is primarily useful in connection with the lime-soda or other precipitation methods of water softening.   It

makes use of a vector diagram in which incompatible substances, whether present in the water or used in the process of treatment, are plotted on opposite axes in such manner as to indicate directly the quantities of chemicals necessary for softening or, in the case of a softened water, the correctness of the dosages applied.

The method will be understood by reference to an example shown in Fig. 3. Here the hardness characteristics of a raw water are indicated by the location of point D in sector II, obtained by scaling the equivalent con-centrations of Ca, Mg, HCO_3 and H_2CO_3 each in a direction parallel to its vector axis, i.e., along lines OA-AB-BC-CD. It will be seen that this water can be softened by treatment with additions of Na_2CO_3 and CaO indicated by lines DE and EO respectively or by NaOH and CaO indicated by lines DF and FO respectively. In a similar manner the components CO_3, OH, Ca, and Mg of a softened water are scaled along lines OR-RS-ST-TU locating point U in sector I. Since maximum softening by this process requires the presence of a slight excess of CO_3 and OH ions, this point should fall slightly to the upper right of the origin, O, in sector V, and the indications are that the water in this example has been undertreated. Corrective treatment would require both Na_2CO_3 and CaO in amounts not less than indicated by UW and WO respectively, or Na_2CO_3 and NaOH in amounts not less than UV and VO respectively.

It will be noted that the plotted point of an untreated water falling directly upon the Mg axis must satisfy the conditions $Ca = CO_2 + 2HCO_3$ and that it will fall in sectors I or II depending upon whether Ca is greater or less than $CO_2 + 2HCO_3$. If the point falls in sector I, the soda ash requirement will be greater than the lime requirement. In sector II the reverse will be true. If, however, the end-point falls in sector III the water contains only carbonate or temporary hardness, and its lime require-ment will be equal to the vertical distance to the CO_3 axis, that is, D in the figure.

Especially in the field of boiler feed water conditioning this method of graphing the day-to-day treatment operations should prove to be of con-siderable value. Arbatsky's original papers should be consulted for additional uses of the method.

Hill Trilinear Method

Recently Hill (5) described a method of graphing the mineral character of waters encountered in irrigation practice. In this method, waters are classified into several primary types based upon arbitrary balances between certain cation and anion groups, somewhat as suggested by Palmer, and into subtypes dependent upon the proportionate concentrations of specific ions within the cation and anion totals. For this purpose a special form of

plotting chart, consisting of four equilateral triangles suitably lettered and arranged about a common apex, is used.   By plotting trilinearly the percentage equivalent concentrations of the three cation groups and the three anion groups in the two outer triangles respectively, it becomes possible by projection to locate the position of a third point within the two inner triangles which completes the classification.

In the Hill method, illustrated in Fig. 4, the character properties introduced by Palmer—primary salinity, primary alkalinity, secondary salinity and secondary alkalinity—are retained and designated as Groups Z_1, Z_2, Z_3, and Z_4 respectively, with the exception that, in the Z-group formulations, the sulfate is removed from the chloride ion group and included, instead, in the carbonate ion group.   Hill terms the four Z groups, in order, as common salt, alkali, bittern, and hardness groups respectively.

In Fig. 4, point A in the cation triangle at the left represents a water in the plotting of which the perpendicular distance to any side is proportional to the equivalent concentration of the cation indicated.   Similarly, in the anion triangle to the right, the anion groups are plotted to locate the anion point A.   From the two points thus obtained, parallels to the top or bottom sides of the figure are drawn to a point of intersection, which in the example falls in the upper right of the Z_3 triangle.   A study of the figure will show that each of the perpendiculars from this third point, as drawn, is proportional to the percentage of the particular Z group indicated.   This is explained by the fact that the value of Z_1 must equal either $(Na + K)$ or $(Cl + NO_3)$ and must fall, therefore, on the line of projection from the cation triangle.   Similarly, the value of Z_4 must equal either $100 - (Cl + NO_3)$ or $100 - (Na + K)$ and must fall on the line of projection from the anion triangle.   The point of intersection of the projected parallels, therefore, determines the values of Z_1 and Z_4, and these, in turn, determine the value of Z_3.

It should be noted that in obtaining the Z-group values by this method, independent values of Ca and Mg as well as of SO_4 and HCO_3 are used. This would be unnecessary if the object of the method were to determine merely the Z-group values, because the Z groups, as defined, involve only the relative magnitudes of certain ion-group totals.   One object of the Hill trilinear method, however, is to obtain a more comprehensive classification, i.e., one in which subtypes are indicated.   This is accomplished by adding to the Z-group classification terms to indicate the dominance of individual cations and anions.   For this purpose each of the four triangles is subdivided into four smaller triangles, and, by lettering or numbering each of these smaller triangles in accordance with a prescribed pattern, the location of the three points which define a given water can be formulated. Thus, in the example shown, water A is classed as bIIId.   The primary
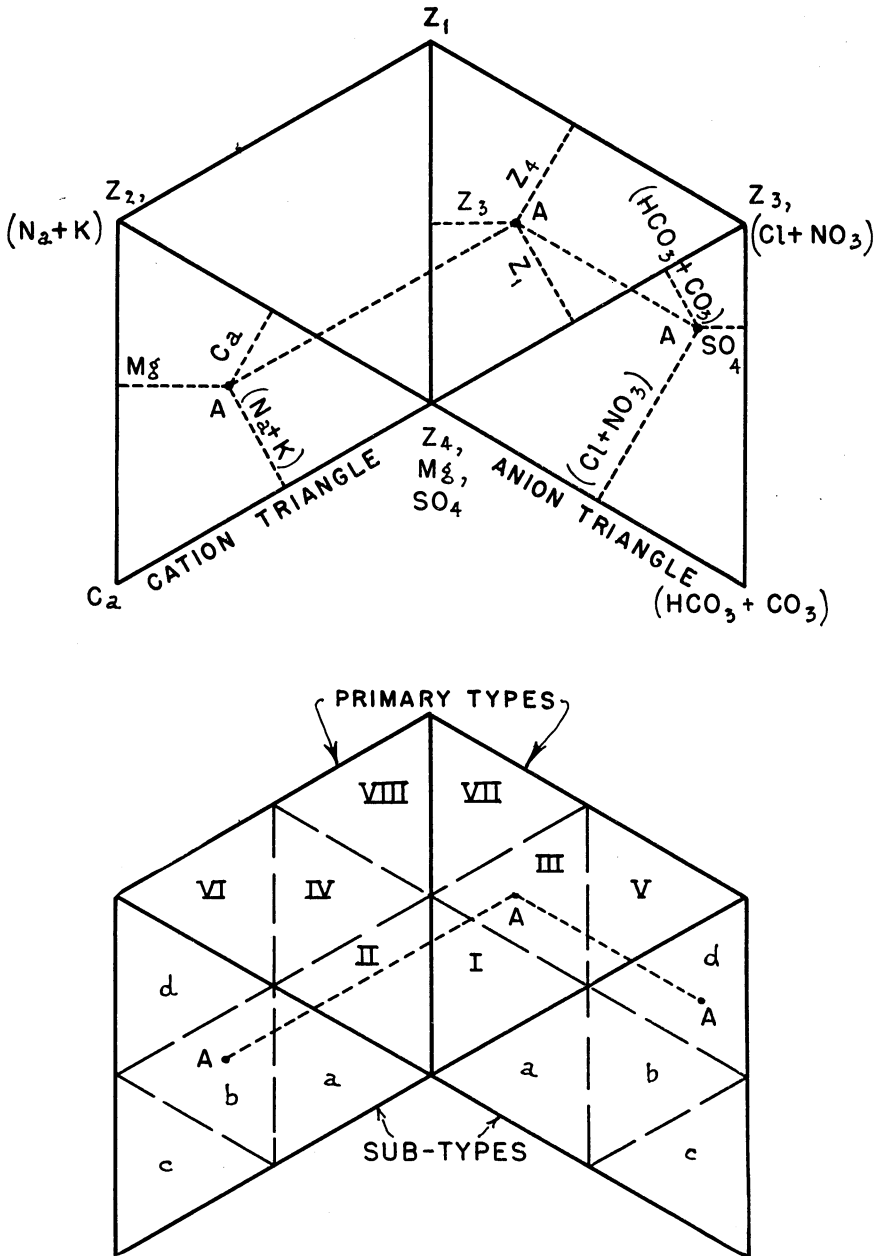
FIG. 4. (Top) Hill Trilinear Method of Plotting an Irrigation Water, to obtain percentage of each Z group present (each triangle has three percentage scales—not shown—, each perpendicular to a side); (Bottom) Same Diagram, with classification areas included (water A would be classed as bIIId)

classification is indicated by the Roman numeral. An odd numeral indicates the presence of salts of the Z_3 group. The particular numeral, III, representing the inner smaller triangle of the Z_3 triangle, indicates that none of the individual Z groups exceeds 50 per cent of the total. The prefix, b, representing the center subdivision of the cation triangle, indicates that none of the three cations exceeds 50 per cent of the total cation concentration. The suffix, d, representing the upper division of the anion triangle, indicates that the $(Cl + NO_3)$ group is in excess of 50 per cent of the total anion concentration. The complete classification $bIIId$ would therefore indicate a water of the bittern type (but not dominantly so) in which, of the ion groups, only the chloride is dominant.

It should be noted that in this method, as in the modifications to be described, the point locations indicate water types or classes based upon ratios of constituent parts. If total mineralization or absolute concentrations are desired they must be indicated by additional means. For this purpose Hill uses circles of varying diameter centered over the indicated points, making the circle areas proportional to total concentrations.

Hill's paper gives interesting applications of the method. One in particular shows the changes in the mineral character of Rio Grande River water at several stations along its course, and another describes the application of the method in proving that a water which is believed to be a mixture of two or more waters is in fact such a mixture.

A criticism by Scofield (5) carries the implication that graphical methods such as these may be of restricted application in irrigation practice because they omit from consideration certain trace constituents—as, for example, boron in irrigation waters—which may impart to them their most important characteristics. To the authors, however, it seems that, even in these waters, the mineral classification is desirable. It is always possible to indicate the amounts of trace elements or other minor constituents by the use of additional symbols.

Adaptation of Hill Method to Palmer Groupings

In attempting to adapt the Hill method to the Palmer groupings (wherein the sulfate ion is grouped with the chloride and nitrate rather than with the carbonates), it was found necessary to alter the outward shape of the diagram. This new form, illustrated in Fig. 5, permits the use of standard triangular co-ordinate graph paper as, for example, K. and E. No. 358-32. The essential features of the Hill method of plotting and of classification into types and subtypes is retained. It differs, necessarily, only in the arrangement of scales and in terminology. In this modification there are two primary classifications: Palmer Class 1, (middle triangle) and Palmer Class 3 (top triangle). Each of the larger primary triangles is subdivided

into smaller secondary triangular fields (*a, b, c, d*) for the purpose of indicating the dominance of a particular constituent or property. The pattern employed in lettering these fields has been selected to conform in alphabetical sequence with the order commonly used in reporting the constituents of a water analysis: *a* for sodium, chloride and primary salinity; *b* for magnesium, sulfate and either primary alkalinity or secondary salinity;
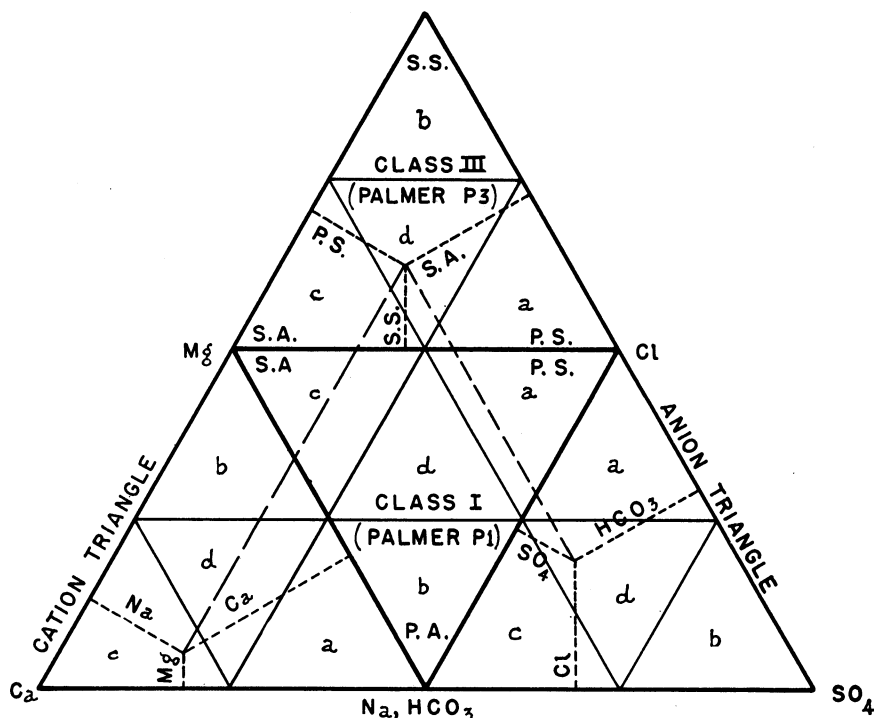
NOTES P.S. PRIMARY SALINITY   S.S. SECONDARY SALINITY
       P.A. PRIMARY ALKALINITY S.A. SECONDARY ALKALINITY

FIG. 5. Authors' Adaptation of Hill Trilinear Method to Palmer Geochemical Groupings—plotted water would be classed as *P3cdd* (*percentage scales not shown*)

c for calcium, carbonates, and secondary alkalinity. The smaller central triangular fields are each lettered *d* to indicate that, within these areas, none of the three variables is dominant, i.e. greater than 50 per cent of the total.

The example plotted in Fig. 5 shows a water of Class *P3*, type *d*, subtype *cd*. The complete classification would be written *P3dcd*, indicating a water which possesses the property of secondary salinity but in which none of the

geochemical properties exceeds 50 per cent, and in which, among the ions, only calcium is dominant.   In the complete classification, the sequence and the significance of each symbol should be easily remembered for the reasons which have been noted.

Authors' Single-Point Method

Figures 6 and 7 illustrate a method of graphing and water-typing which, though less comprehensive than the "three-point" trilinear methods already described, appears to offer compensating advantages in simplicity and practicability.   The method employs the simpler Cartesian co-ordinates and is based upon the original Palmer ion groupings in which there are only two independent variables, i.e. percentage of alkali cations plotted as ordinate and percentage of non-carbonate anions plotted as abscissa. The location of a plotted point within one of eight triangular areas charac- · terizes the water as belonging to one of two primary types each with four subtypes.

The plotting diagram, shown in Fig. 6, is a square, ruled with one hundred percentage units per side.   The square is divided into two primary triangular areas by a diagonal connecting the lower left and the upper right corners. Each of these primary areas is subdivided into four secondary triangular areas of equal size by lines connecting the midpoints of their three sides. The secondary areas of the upper primary field above the diagonal are lettered *A1*, *A2*, *A3*, and *AA* in accordance with a definite pattern; similarly, the secondary areas of the lower primary field are lettered *B1*, *B2*, *B3* and *BB*.
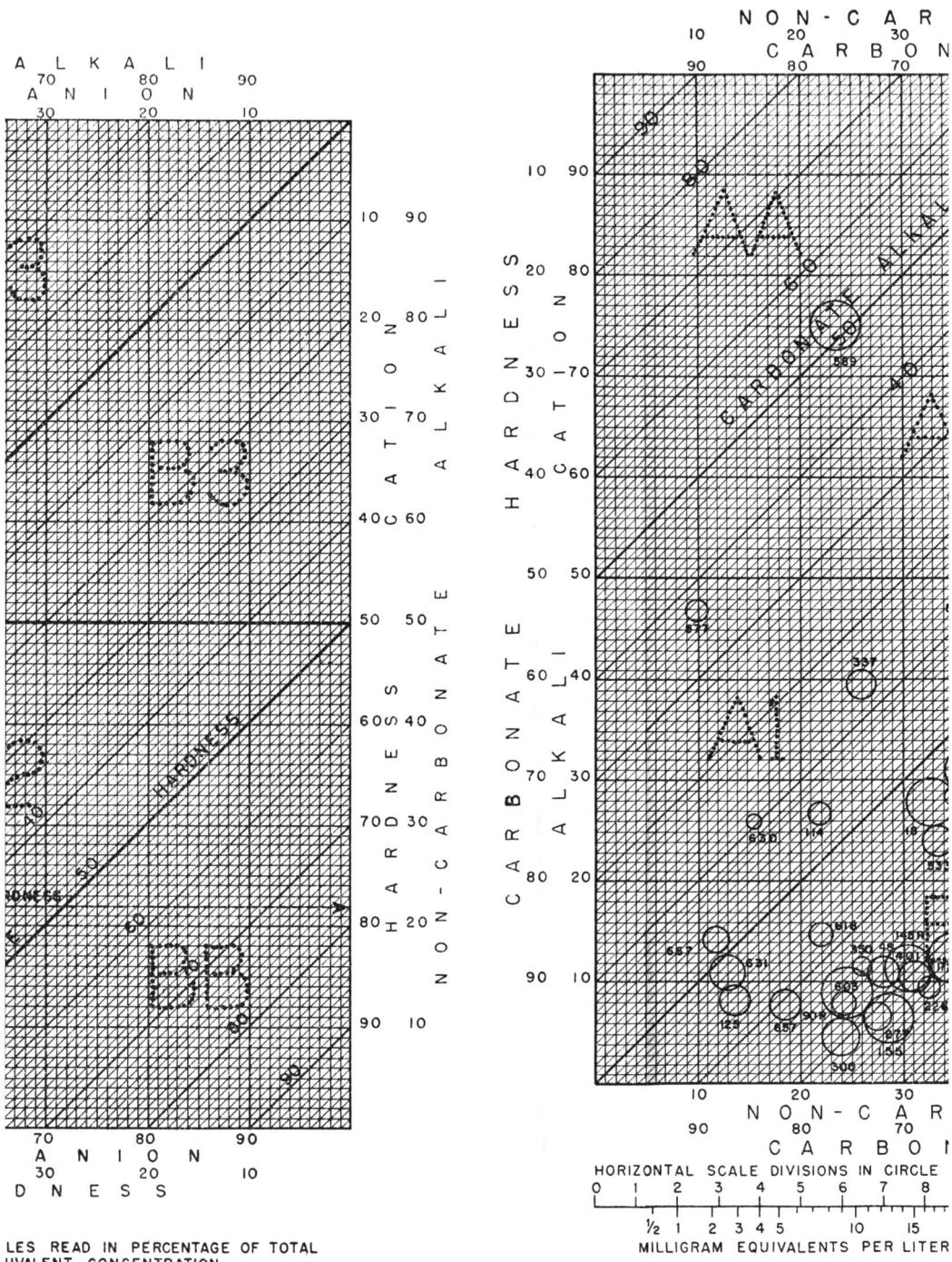
In the use of the diagram, if the percentage of alkali is greater than the percentage of non-carbonate anion, the plotted point will fall in the upper primary field; if the reverse is true, it will fall in the lower primary field. Since these percentage relationships are the basis of the Palmer classifications into Class 1 and Class 3 respectively; point locations in the two primary fields serve to identify waters of these two classes.   Also, since, by definition, two of the three percentage values, which express the character formula of the water, are equal to the perpendicular distances from the plotted point to the two sides of the primary right triangle, it follows that the third value will be proportional to the perpendicular distance to the hypotenuse.   Thus, with the incorporation of suitable scales, the character formula can be read directly from the diagram.   For this purpose the inner scales have been provided.

The use of the terms "primary" and "secondary" as proposed by Palmer in designating the mineral properties of water has not found wide acceptance among water technologists.   In the method of classification proposed by the authors a somewhat more self-indicating terminology has been

TABLE 1

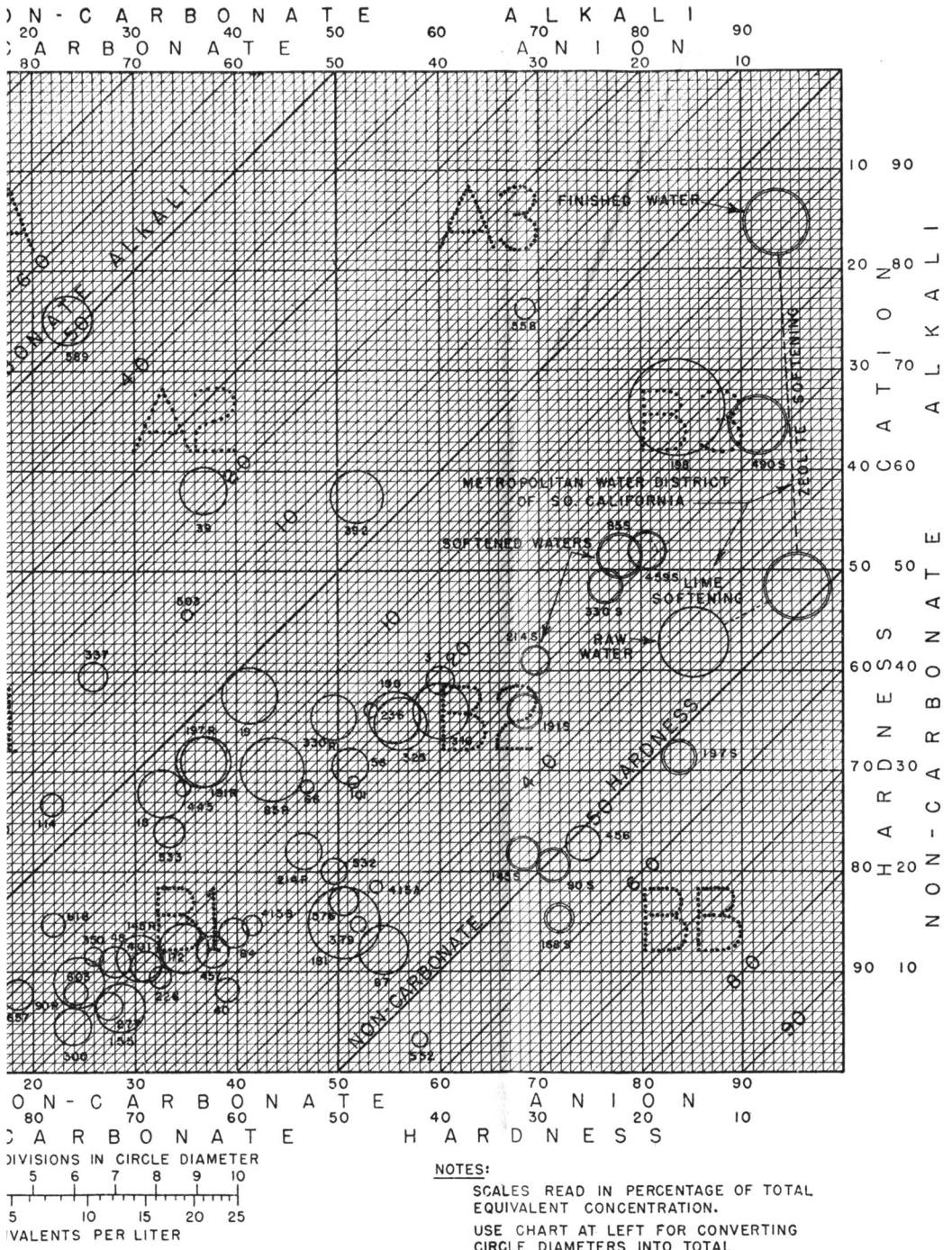*Classification of 68 Large U.S. Water Supplies Shown Graphically in Figure 7*

NO.	SUPPLY	CLASSIFICATION	NO.	SUPPLY	CLASSIFICATION
3	Birmingham, Ala.	B2-2.2	330r	St. Louis, Mo.	B1-5.0
18	Phoenix, Ariz.	B1-5.8	330s	St. Louis, Mo.	B2-3.3
19	Tucson, Ariz.	B1-7.7	337	Butte, Mont.	A1-2.3
39	Los Angeles, Calif.	A2-5.6	346	Omaha, Neb.	B2-7.9
40	Oakland, Calif.	B1-1.2	350	Reno, Nev.	B1-1.1
48	San Francisco, Calif.	B1-2.3	379	Newark, N.J.	B2-0.7
56	Denver, Colo.	B2-3.5	392	Albuquerque, N.M.	A3-7.3
66	Hartford, Conn.	B1-0.5	401	Buffalo, N.Y.	B1-2.6
84	Washington, D.C.	B1-2.2	415a	New York, N.Y. (Catskill)	B2-0.5
85r	Daytona Beach, Fla.	B1-10			
85s	Daytona Beach, Fla.	B3-5.4	415b	New York, N.Y. (Croton)	B1-1.2
87	Jacksonville, Fla.	B2-6.3			
90r	Miami, Fla.	B1-6.3	445	Winston-Salem, N.C.	B1-0.7
90s	Miami, Fla.	BB-2.7	456	Cincinnati, Ohio	BB-2.9
101	Atlanta, Ga.	B2-0.4	457	Cleveland, Ohio	B1-2.7
114	Boise, Idaho	A1-1.6	459s	Columbus, Ohio	B3-3.7
125	Chicago, Ill.	B1-2.8	490s	Oklahoma City, Okla.	B3-9.0
145r	Springfield, Ill.	B1-5.7	503	Portland, Ore.	A1-0.3
145s	Springfield, Ill.	B2-2.8	532	Philadelphia, Pa.	B1-1.8
155	Indianapolis, Ind.	B1-6.0	533	Pittsburgh, Pa.	B1-2.4
168s	Cedar Rapids, Iowa	BB-2.1	552	Providence, R.I.	BB-0.6
172	Des Moines, Iowa	B1-7.0	558	Charleston, S.C.	A3-1.1
181	Sioux City, Iowa	B2-13	576	Knoxville, Tenn.	B2-2.5
190	Kansas City, Kan.	B2-6.5	577	Memphis, Tenn.	A1-1.5
191r	Lawrence, Kan.	B1-7.2	589	Houston, Tex.	AA-6.5
191s	Lawrence, Kan.	B2-3.4	603	Salt Lake City, Utah	B1-1.6
197r	Topeka, Kan.	B1-7.2	618	Richmond, Va.	B1-1.3
197s	Topeka, Kan.	BB-3.5	630	Seattle, Wash.	A1-0.6
198	Wichita, Kan.	B3-24	631	Spokane, Wash.	B1-3.3
214r	New Orleans, La.	B1-3.6	657	Milwaukee, Wis.	B1-2.8
214s	New Orleans, La.	B2-2.4	667	Cheyenne, Wyo.	A1-1.8
226	Baltimore, Md.	B1-1.2	—	Metropolitan Water Dist. (S. Calif.):	
236	Boston, Mass.	B2-0.6			
277	Detroit, Mich.	B1-2.1		Raw	B2-13.0
300	Minneapolis, Minn.	B1-3.6		Lime Treated	B2-12.0
325	Kansas City, Mo.	B2-7.0		Zeolite Softened	B3-12.0

Fig. 6. Authors' Single-Point Method of Graphing and Classifying Waters for Miner

A L K A L I
ANION
70   80   90
30   20   10

10   90

20   80

C A T I O N   A L K A L I

30   70

40   60

50   50

60   40

H A R D N E S S   N O N - C A R B O N A T E

70   30

HARDNESS

80   20

90   10

70   80   90
ANION
30   20   10
D N E S S

LES READ IN PERCENTAGE OF TOTAL
IIVALENT CONCENTRATION.
: CHART AT LEFT FOR CONVERTING
CLE DIAMETERS INTO TOTAL
IIVALENT CONCENTRATION.

g Waters for Mineral Content

N O N - C A R
10   20   30
C A R B O N
90   80   70

10   90

C A R B O N A T E   H A R D N E S S

20   80

30 −70

40   60

50   50

C A R B O N A T E   A L K A L I

60   40

70   30

80   20

90   10

10   20   30
N O N - C A R
90   80   70
C A R B O I

HORIZONTAL SCALE DIVISIONS IN CIRCLE
0 1 2 3 4 5 6 7 8

½ 1   2 3 4 5   10   15
MILLIGRAM EQUIVALENTS PER LITER

FIG. 7. Example of Use of the Single-Point Di
mineral analyses of 68 municipal water sup
Suppl

The Single-Point Diagram, intended to show its value in plotting large number of analyses; showing municipal water supplies from throughout U.S.—analytical data are from U.S. Geological Water Supply Paper 658 unless otherwise indicated

adopted.   The four properties are named non-carbonate alkali, carbonate alkali, non-carbonate hardness, and carbonate hardness.

Since, for most purposes, it is desirable to know both relative and absolute concentrations, the scheme of representing each water by a circle, the area of which is proportional to total concentration of salts—as used by Hill in the trilinear method—is retained, and a convenient scale for making conversions of circle diameters into milliequivalents per liter, or the reverse, has been included as a part of the diagram.

As in the trilinear method, the subdivision of the primary areas into secondary areas serves the purpose of subclassification.   Point locations within a particular secondary area indicate that the value of a certain group property or a group constituent is either greater or less than 50 per cent. Reference to the diagram will show that classifications *A1* and *B1* indicate waters in which the property of carbonate hardness is dominant; that is, this property exceeds 50 per cent in the character formula.   These classifications differ, as do all *A* and *B* waters, in that the former are alkali carbonate and the latter non-carbonate hardness waters.   Waters in which these distinguishing properties are dominant will fall within the *AA* or *BB* sectors respectively.   The *A3* and *B3* classifications indicate waters of relatively high salinity, that is, waters in which the property of non-carbonate alkali is dominant.   The classifications *A2* and *B2* indicate waters in which none of the three properties is dominant.   The ionic group relationships, characteristic of each sector, are readily apparent.   Thus, the entire upper half of the diagram, sectors *AA*, *A2*, *A3* and *B3* represent types of waters in which the alkali ion group is dominant.   In the lower half, the hardness ion group is dominant.

In addition to simplicity and practicability, an advantage of the single-point method, as described, is that, by its use, a large number of analyses can be plotted upon a single diagram.   An example is shown in Fig. 7. On this diagram there are plotted analyses of 68 of the larger and more important municipal water supplies throughout the country.   An examination of this diagram will reveal interesting facts pertaining to these supplies which, were the data presented in the usual tabular form, might readily pass unnoticed.

A breakdown of the 56 *raw* waters plotted in Fig. 7 shows that 82 per cent fall into the *B* sectors and are therefore classed as non-carbonate hardness waters.   Of the 56 waters nearly two-thirds, 63 per cent, fall within the *A1-B1* quadrant indicating carbonate hardness as the dominant property; an additional 25 per cent fall within the *A2* and *B2* sectors, indicating no dominant properties; and the remaining 12 per cent are about equally distributed among the *A3-B3* quadrant and the *AA-BB* sectors.

The center of gravity of the plotted points, together with the median circle area, establishes what might be called a typical raw water. It is interesting to note that the largest body of fresh water in the world, the Great Lakes, furnishes the supplies most resembling this typical water.

The effect of water-softening by the lime-soda process is a shifting from the raw-water position to the right and slightly upward. Softening by the zeolite process causes a shifting from the raw-water position directly upward.

Problem of Mixtures

Frequently in hydrological studies, mineral water analyses are utilized in tracing the movements of ground waters, sometimes with a view to the confirmation of apparent mixtures. For this purpose, samples of water from selected locations are analyzed chemically, and consideration is given to the relative concentrations of certain ionic constituents. Since both the three-point and single-point methods of graphing are based upon the plotting of ratios, these diagrams can be used to advantage in the solution of problems of this character. Their value arises from the fact that the plotted point of any mixture of two waters must fall along a line which connects the plotted positions of the two waters composing the mixture. From this it must follow that the plotted position of a mixture of three waters must fall within the triangle formed by the plotted positions of the three waters composing the mixture. Also, since the total concentration Z of a true mixture can be neither lower than the lowest nor higher than the highest concentrations of the individual samples composing the mixture, the circle area of a true mixture must conform therewith. Accordingly, a mere examination of the plotted values of an apparent mixture and of its component parts will furnish a fair indication as to whether or not such mixture is a true, or quantitative, mixture.

Further confirmation of the presence of a quantitative mixture is readily obtained by two methods, each of which is applicable to the simpler single-point diagram. One of these is a completely graphical method adapted from the trilinear plotting method of Hill (5), and the other, a semi-graphical method involving a simple computation with readings taken from the graph. The following descriptions of these two methods refer to the respective plotted diagrams in Fig. 8, in which, for the purpose of clarity, the scale divisions have been omitted. In the upper left, K is an apparent mixture of waters A, B and C, each plotted in the usual manner. Directly below, the points K', A', B' and C' are plotted in the same manner, except that, in this series, the percentage values of either calcium or magnesium are plotted as ordinates against the a_1 values. The two triangles are

completed by drawing the lines connecting the outer points of each series of values. Intercepts a, b, c, and a', b', c' are obtained by projecting lines from each apex through K and K' respectively. If K is a quantitative mixture as presumed, the corresponding intercepts must fall on the same
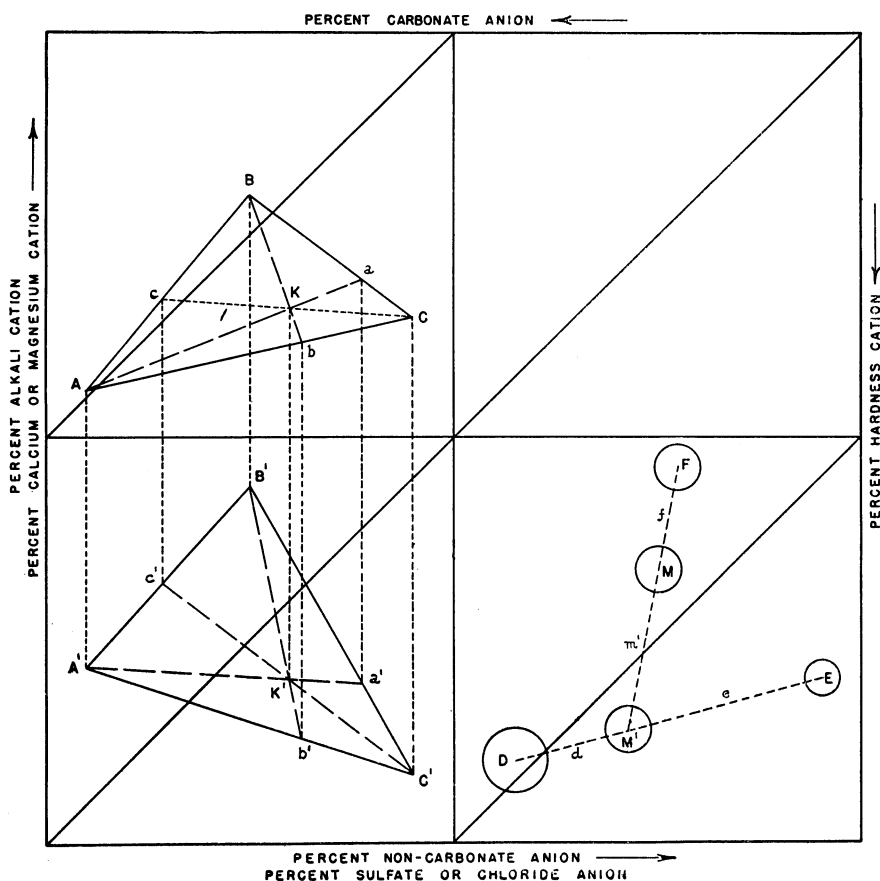

FIG. 8. Use of Single-Point Diagram (*scale divisions omitted*), to confirm an apparent mixture of three component waters—*Left*, Graphical Method; *Right*, Graphical-Algebraic Method

vertical lines. In the absence of independent values of calcium and magnesium, or if additional confirmation is desired, the same method of plotting can be used, substituting the value of either chloride or sulfate for the value of a_1 and plotting each against c_1. In this case the intercepts should fall on the same horizontal lines.

In the foregoing method the total concentration of the mixture Σ_m is not established; that is, neither dilution of the mixture by rain water nor concentration by evaporation would be indicated. The alternate method, illustrated on the right of Fig. 8, appears to offer a simpler solution to the problem of mixtures. In this method, M is an apparent mixture of waters D, E, and F. The intercept M', obtained by projecting the line FM to DE, represents a hypothetical mixture of D and E, in which the proportions of each are the same as are present in M. Letting the symbol Σ represent concentrations and V, volumes, by taking moments about the points D and E, two equations are obtained:

$$\Sigma_E \cdot V_E (e + d) = \Sigma_{M'} \cdot V_{M'} \cdot d$$

$$\Sigma_D \cdot V_D (e + d) = \Sigma_{M'} \cdot V_{M'} \cdot e$$

or
$$V_E = \frac{\Sigma_D \cdot V_D \cdot d}{\Sigma_E \cdot e}$$

If the volume of water D entering into the mixture M' be taken as unity, the volume of E becomes $\dfrac{\Sigma_D}{\Sigma} \cdot \dfrac{d}{e}$. The weight of salt contributed by D equals Σ_D and the weight contributed by E equals $\left[\dfrac{\Sigma_D}{\Sigma_E} \cdot \dfrac{d}{e}\right] \Sigma_E = \dfrac{\Sigma_D \cdot d}{e}$. Thus, the concentration of the mixture is

$$\Sigma_{M'} = \frac{\Sigma_D + \Sigma_D \cdot \dfrac{d}{e}}{1 + \dfrac{\Sigma_D}{\Sigma_E} \cdot \dfrac{d}{e}} \quad \text{or} \quad \frac{\Sigma_D \left(1 + \dfrac{d}{e}\right)}{1 + \dfrac{\Sigma_D}{\Sigma_E} \cdot \dfrac{d}{e}}$$

In the use of this equation to solve for the concentration value of M', the values of d and e are obtained by scaling the graph. The concentration value of M can then be obtained by the same procedure. In the example plotted the solution is as follows:

From chemical analysis:

Water	D	E	F	M
Σ (mE/l.)	10.0	3.00	5.00	5.15
c_1	10.0	20.00	47.50	30.00
a_1	57.5	95.00	77.50	74.50

By scaling $d = 37$, $e = 62$, $f = 33$, $m' = 50.5$.

$$\Sigma_{M'} = \frac{10 \left(1 + \dfrac{37}{6.2}\right)}{1 + \dfrac{10}{3} \cdot \dfrac{37}{62}} = 5.35 \text{mE/l.}$$

and

$$\Sigma_M = \frac{5.35\left(1 + \dfrac{50.5}{33.}\right)}{1 + \dfrac{5.35}{5.}\cdot\dfrac{50.5}{33.}} = 5.15\text{mE/l.}$$

The calculated value of Σ_M agrees with the analytical value and therefore affirms the presence of a true mixture.

Either of the methods described can be used to confirm apparent mixtures of two or more components, provided an analysis of each is available. Under the conditions of natural flow either underground or in surface streams, however, water mixtures in most instances must be regarded as extremely complex and probably not subject to a strictly quantitative treatment. The authors are inclined to agree with Collins (5) that "an actual irrigated plot of 15,000 acres does not act like a glass vessel or like a bed of pure silica sand." It is believed, however, that the methods described can be used to advantage in the solution of many problems involving the movements of subterranean waters.

Summary and Conclusions

It is believed that in the preparation and publication of results of water supply surveys and other hydrological investigations, the methods of graphing and water-typing which have been described should find an enlarging field of usefulness. With the exception of the double-bar method, the methods described are of recent origin, and it is too early to predict which method will prove to be of most value. The authors believe that there are uses for each method and that selection of a method for a particular purpose will depend upon the nature of the problem.

The double-bar graphs are more tedious to prepare but are very useful where it is desired to present a visualization of the data for the benefit of the general reader. In the fields of boiler feed water conditioning and water softening, uses may be found for vector diagrams as developed by Arbatsky. The trilinear and rectilinear methods of co-ordinate plotting should be found most useful in irrigation and water survey investigations, particularly where it is necessary to compare the results of large numbers of analyses. If future experience should indicate that it is desirable to classify waters into types that can be readily identified by symbols, the point method of graphing would seem to offer the most suitable basis for such classification.

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