times as great as it should have been. And in this case α was quite certainly practically one at entrance, and somewhat more at points downstream. It would seem, therefore, that a small systematic error must have resulted from taking α as 1.05 throughout.

A GRAPHIC PROCEDURE IN THE GEOCHEMICAL INTERPRETATION OF WATER-ANALYSES

Arthur M. Piper

General considerations--This paper outlines certain fundamental principles in a graphic procedure which appears to be 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. The procedure is based on a multiple-trilinear diagram (Fig. 1) whose form has been evolved gradually and independently by the writer during the past several years through trial and modification of less comprehensive antecedent forms. Neither the diagram nor the procedure here described is a panacea for the easy solution of all geochemical problems. Many problems of interpretation can be answered only by intensive study of critical analytical data by other methods.

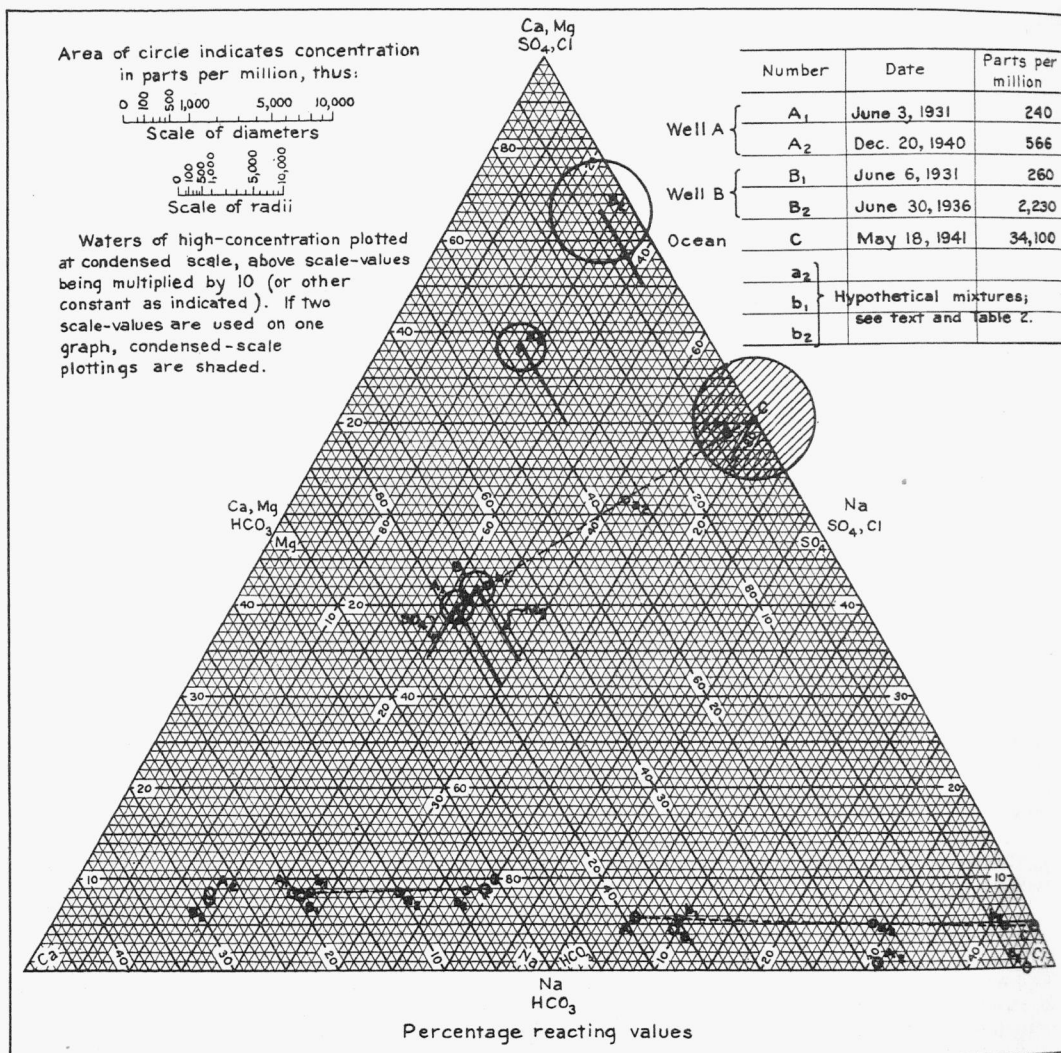| Number		Date	Parts per million
Well A {	A₁	June 3, 1931	240
	A₂	Dec. 20, 1940	566
Well B {	B₁	June 6, 1931	260
	B₂	June 30, 1936	2,230
Ocean	C	May 18, 1941	34,100
	a₂]		
	b₁ }	Hypothetical mixtures; see text and Table 2.	
	b₂]		

Fig. 1--Water-analysis diagram

In certain respects the diagram is analogous to, but in other respects differs fundamentally from, the "geochemical chart" described recently by HILL [see 1 of "References" at end of paper] and from the "water classification diagram" described by LANGELIER and LUDWIG [2]. As presented in Figure 1, the diagram is the mirror image of a prototype which in 1942 was circulated among colleagues in the United States Geological Survey and other coworkers in hydrology; thus, it conforms substantially to LANGELIER'S adaptation [3] of HILL'S diagram and to the conventional practice of arranging diagrams of water-analyses with cations shown to the left of the anions. Some details in Figure 1 embody adaptations which serve constructive criticisms of the prototype by colleagues and coworkers; for these criticisms the writer is grateful.

Most natural waters contain relatively few dissolved constituents, with cations (metals or bases) and anions (acid radicles) in chemical equilibrium with one another; commonly the waters contain some silicon, iron, and aluminum but these constituents are usually assumed to occur in the colloid state as oxides and not to be in chemical equilibrium with the ionized constituents. Ordinarily the most abundant cation constituents are two "alkaline earths", calcium (Ca) and magnesium (Mg), and also one "alkali", sodium (Na). Potassium (K) also occurs commonly, but ordinarily is much less abundant than sodium. Still other cation-constituents occur in appreciable quantities in highly concentrated natural waters and in some waters of unusual composition. For the graphic methods treated in this paper all these less abundant constituents are summed with the major three constituents to which they are respectively related in chemical properties, as indicated by the two ranks of entry in Table 1. The most common anion-constituents are one "weak acid", bicarbonate (HCO_3); also two "strong acids", sulphate (SO_4) and chloride (Cl). Less common anion-constituents are listed in Table 1; for plotting, these are summed with the major three anions to which they are respectively related. Thus, for much of the graphic methods here described, a natural water is treated substantially as though it contained only three cation-constituents and three anion-constituents.

Table 1--Common and minor constituents of natural waters

Cations	Reciprocal of combining weight	Anions	Reciprocal of combining weight
Alkaline earths		Weak acids	
Calcium (Ca^{++})	0.04990	Bicarbonate (HCO_3^-)	0.01639
Barium (Ba^{++})	0.01456	Carbonate ($CO_3^=$)	0.03333
Strontium (Sr^{++})	0.02282	Tetraborate ($B_4O_7^=$)	0.01288
Magnesium (Mg^{++})	0.08224	Orthophosphate ($PO_4^{\equiv}$)	0.03157
Alkalies		Strong acids	
Sodium (Na^+)	0.04348	Sulphate ($SO_4^=$)	0.02082
Potassium (K^+)	0.02558	Chloride (Cl^-)	0.02820
Caesium (Cs^+)	0.00752	Iodide (I^-)	0.00788
Rubidium (Rb^+)	0.01170	Bromide (Br^-)	0.01251
Lithium (Li^+)	0.14409	Fluoride (F^-)	0.05263
Ammonium (NH_4^+)	0.05543	Nitrate (NO_3^-)	0.01613
		Nitrite (NO_2^-)	0.02174

Notes: Of the second-rank constituents only potassium, carbonate, fluoride, and nitrate are commonly determined in a "complete" analysis. Reciprocals of combining weights are based on the international atomic weights of 1938.

In substantially all natural waters the cations are in chemical equilibrium with the anions. Accordingly, if the concentrations of the several dissolved constituents are measured in terms of percentage of reacting value--that is, according to their "equivalents per million" expressed as a percentage of the sum of the equivalents for all the constituents [the concentration of any constituent in equivalents per million (milligram equivalents per kilogram) is computed by multiplying its concentration in parts per million by the reciprocal of its combining weight]--the subtotals of the cations and anions are necessarily each 50 per cent of the whole.

Thus, to the extent that a natural water can be treated in terms of three cation-variables and three anion-variables, as has been outlined, and because the subtotals of its cations and anions are
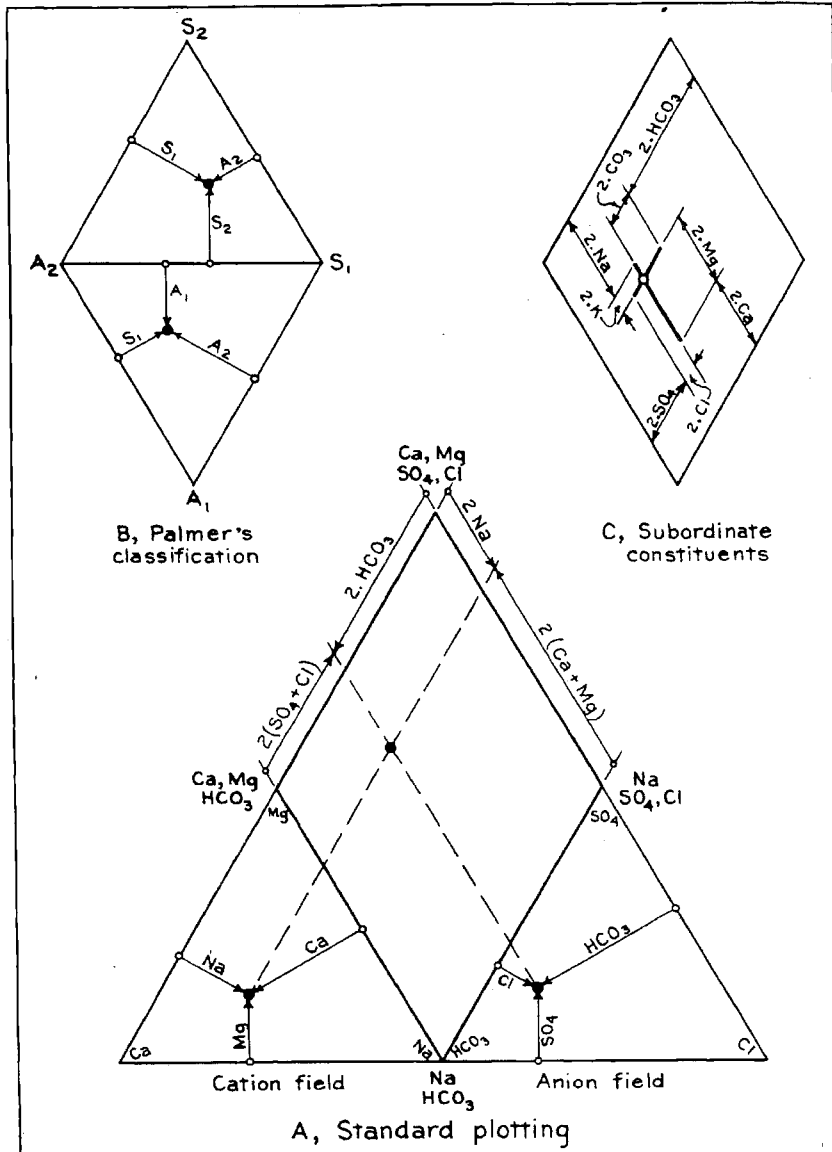
Fig. 2--Plotting key for water-analysis diagram (In diagram B, A_1 indicates primary alkalinity or "carbonate alkali", A_2, secondary alkalinity or "carbonate hardness", S_1, primary salinity or "noncarbonate alkali", S_2, secondary salinity or "non-carbonate hardness")

each 50 per cent of the total reacting value, the essential chemical character of the water can be indicated graphically by single-point plotting on trilinear coordinates. This is the basis of the diagram herein described.

Methods of plotting

The diagram herein described combines three distinct fields for plotting--two triangular fields at the lower left and lower right, respectively, with percentage scales reading in 50 parts; also an intervening diamond-shaped field with scales reading in 100 parts (see Figs. 1 and 2-A). In the triangular field at the lower left, the percentage reacting values of the three cation-groups (Ca, Mg. Na) are plotted as a single point according to conventional trilinear coordinates. The three anion-

groups (HCO3, SO4, Cl) are plotted likewise in the triangular field at the lower right. Thus, two points on the diagram--one in each of the two triangular fields--indicate the relative concentrations of the several dissolved constituents of a natural water.

The central diamond-shaped field is used to show the over-all chemical character of the water by a third single-point plotting, which is at the intersection of rays projected from the plottings of cations and anions as indicated on Figure 2-A. Using the scales of Figure 1, the position of this plotting indicates the relative composition of a water in terms of the cation-anion pairs that correspond to the four vertices of the field. This central-field plotting can also be taken directly from the analytical data according to the vectors shown along the outer margins of the field on Figure 2-A. For such plotting only one cation-variable and one anion-variable need be used--either alkaline earths or alkalies with either weak acids or strong acids; the two percentage reacting values selected from the analytical data are doubled to suit the numerical scales of Figure 1.

The three trilinear plottings just described will show the essential chemical character of a water according to the relative concentration of its constituents, but not according to the absolute concentrations. Because the absolute concentrations commonly are decisive in many problems of interpretation, it is convenient to indicate the plotting in the central field by a circle whose area is proportional to the absolute concentration of the water. Figure 1 shows such plottings for several dissimilar waters.

The diamond-shaped field of the writer's diagram is essentially a mirror image of LANGELIER'S diagram, sheared 30° to transform the latter from Cartesian to trilinear coordinates. Also, plottings in that field can be made or interpreted according to PALMER'S classification [4], as explained in the following paragraphs. This scheme of classification has many advantages but has not found universal favor, possibly because it implies certain specific combinations of dissolved constituents, which are hypothetical rather than real.

The classification by PALMER designates the alkaline cations (Na, K) as the "primary" constituents, the alkaline-earth cations (Ca, Mg) as the "secondary" constituents, the strong-acid anions (SO4, Cl, NO3) as the "saline" constituents, and the weak-acid anions (CO3, HCO3) as the "alkaline" constituents. It ascribes "primary salinity" to a water to the extent that the alkalies of that water are balanced by strong acids and "secondary alkalinity" to the extent that the alkaline earths are balanced by weak acids. Further, it ascribes "primary alkalinity" to the water to the extent that alkalies exceed strong acids and are balanced by weak acids, or "secondary salinity" to the extent that alkaline earths exceed weak acids and are balanced by strong acids. Because the latter two properties are mutually exclusive, a water can not possess both. Thus, the chemical character of most natural waters can be expressed by PALMER'S classification in terms of three hypothetical properties; in terms of percentage reacting value, the three must sum up to unity (analytical errors adjusted), of course. Accordingly, chemical character can be plotted as a single point with respect to trilinear coordinates.

A very few natural waters contain free acid in substantial quantity--that is, hydrogen is present as a cation; this cation PALMER designates as "tertiary". The chemical character of such waters can not be fully represented on the diagram.

If on the water-analysis diagram the two rays projected from the plottings of cations and anions intersect in the lower triangular half of the diamond-shaped field, the water has primary alkalinity (A_1), secondary alkalinity (A_2), and primary salinity (S_1) (see Fig. 2-B). Conversely, if the rays intersect in the upper triangular half of the field, the water has secondary salinity (S_2) rather than primary alkalinity.

Obviously, the plottings in the diamond-shaped field do not bring out critical ratios between certain constituents, such as the ratios between sodium and potassium, calcium and magnesium, carbonate and bicarbonate, or sulphate and chloride. When pertinent, these ratios can be indicated graphically by vectors that indicate four of the common eight constituents, as shown by Figure 2-C. In scaling these vectors, the percentage reacting values of the analytical data are doubled to suit the numerical scales of Figure 1.

With respect to the sources of dissolved constituents, or to progressive changes in chemical character within a particular area, many problems involve waters which differ only slightly in character or in which significant differences are masked by some common but preponderant constituent. Under such circumstances, the small differences in character can be emphasized by using the full diagram to represent proportionate subdivisions of the standard three plotting fields,
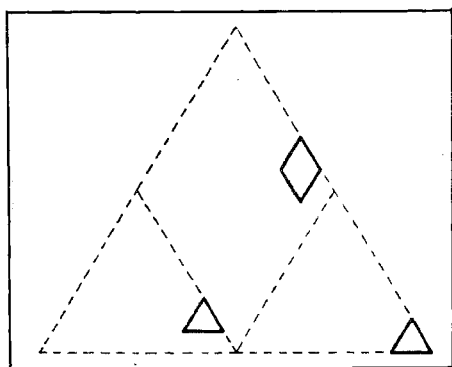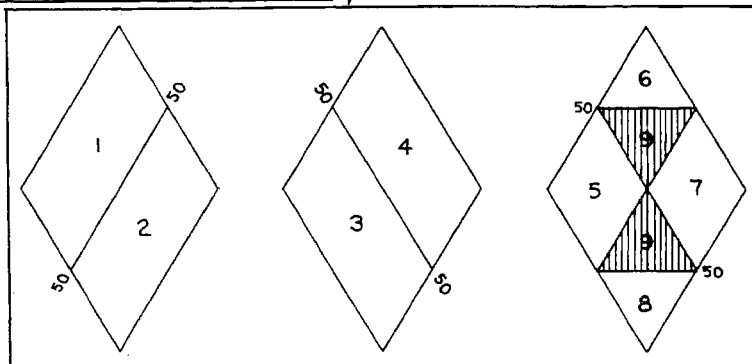
Fig. 3--Scheme of plotting by extended scales

Fig. 4--Subdivisions of the diamond-shaped field

and plotting the constituents with extended scales. For example, among brines similar to ocean water the minor constituents can be differentiated by plotting at five times the standard scale and using the full diagram to represent the small areas outlined in Figure 3. If desired, minor or accessory constituents can be so emphasized by vectors in the diamond-shaped field, as described in the preceding paragraph.

Differentiation of water-types

Certain distinct types can be quickly discriminated by their plottings in certain subareas of the diamond-shaped field, as indicated by Figure 4 and the following explanation: Area 1, alkaline earths exceed alkalies; Area 2, alkalies exceed alkaline earths; Area 3, weak acids exceed strong acids; Area 4, strong acids exceed weak acids; Area 5, secondary alkalinity ("carbonate hardness") exceeds 50 per cent--that is, chemical properties of the water are dominated by alkaline earths and weak acids; Area 6, secondary salinity ("non-carbonate hardness") exceeds 50 per cent; Area 7, primary salinity ("non-carbonate alkali") exceeds 50 per cent--that is, chemical properties are dominated by alkalies and strong acids--ocean water and many brines plot in this area, near its right-hand vertex; Area 8, primary alkalinity ("carbonate alkali") exceeds 50 per cent--here plot the waters which are inordinately soft in proportion to their content of dissolved solids; Area 9, no one of the cation-anion pairs in PALMER'S classification exceeds 50 per cent.

These subareas might serve as a basis for numerical or other symbols to designate specific classes, types, and subtypes of water. Symbols for this purpose have been introduced by PALMER [4] and HILL [1]; however the writer feels that inflexible classifications of this sort tend to confuse by over-emphasizing differences in composition that may not be significant to the problem under consideration.

To serve most needs for classifying waters by types the writer proposes--in lieu of symbols such as those introduced by PALMER, HILL, and others--to designate a water by a binomial symbol written in the form of a decimal fraction, whose two terms are (1) the percentage of hardness-causing constituents among the bases and (2) the percentage of bicarbonate (and carbonate, if present) among the acids. For example, the symbol 64.80 would indicate a water in which the hardness-causing constituents (Ca + Mg) amount to 64 per cent of all the bases, in terms of reacting values

(equivalents); also in which the weak acids (CO_3 + HCO_3) amount to 80 per cent of all the acids, in like terms. Numerically, the first term is twice the percentage reacting value of calcium and magnesium irom analytical data in which the percentage base is the sum of all dissolved constituents, both bases and acids. The first term can be read directly from the numerical scales on the diamond-shaped field of the diagram, in accord with Figure 2-A. Likewise, the second term of the symbol is twice the percentage reacting value of carbonate and bicarbonate, or is scaled directly from the diagram. This form of symbol has the distinct advantage of indicating the general character of a water specifically, without the disadvantage of implying that two waters have distinctly different characters merely because their analyses plot on either side of a boundary between arbitrary subdivisions of any water-analysis diagram. For treatment in a text, waters can be grouped according to limiting values for the two terms of the symbol here proposed, and those limits can be varied at will to suit the discussion of the problem at hand.

This decimal-fraction symbol indicates numerous characteristics of a water simply but specifically. Thus, the more common type of natural water contains chiefly calcium, magnesium, and bicarbonate; its symbol approaches 100.100 as a limit. For its fairly common opposite, the alkali-carbonate water, the symbol approaches 0.100 as a limit. The first term of the symbol indicates relative hardness in percentage of total equivalents. If the second term exceeds the first, all the

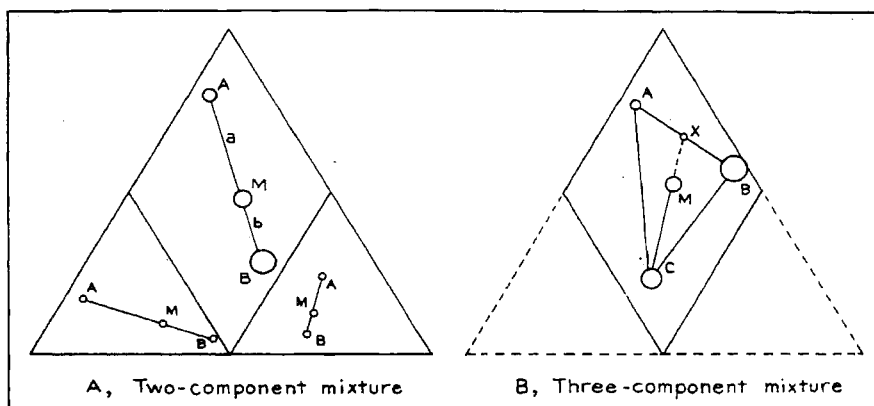A, Two-component mixture   B, Three-component mixture

Fig. 5--Preliminary confirmation of mixtures

hardness is carbonate or "temporary" hardness. However, if the second term is smaller, some of the hardness is non-carbonate or "permanent" and the relative amount of non-carbonate hardness is indicated by the numerical difference between the two terms. The first term of the symbol is the percentage complement of the "per cent sodium" introduced by SCOFIELD [5] to measure the effect of a water on the physical properties of a soil when applied for irrigation. Thus, if this term is greater than about 50 the physical condition of the soil is not likely to be impaired seriously, but if the term is less than about 40 such impairment may result.

Mixtures of waters

Many hydrologic problems involve apparent mixtures of natural waters, which the investigator seeks to confirm or disprove. The solution of such problems is facilitated by use of the diagram as described beyond; this use has been anticipated in the initial paper by HILL and in the paper by LANGELIER and LUDWIG, which have been cited.

Mixtures of two waters in all proportions, if all products remain in solution, plot in the three fields on the respective straight lines that join the points representing the respective chemical characters of the two waters mixed. Thus, in Figure 5-A the straight lines AB will include the plottings of every possible mixture of two waters whose chemical characters are represented by points A and B, respectively. Point M represents a possible mixture in one particular proportion.

There is an obvious application of this procedure in demonstrating a cause for deterioration of water quality in a coastal area--whether or not due to simple invasion by ocean water. If so, chemical analyses of the progressively deteriorated water must, within reasonable limits of error, plot on a set of three vectors directed toward the composition of ocean water. If the analyses do

not so plot, simple admixture of sea-water is not a valid and adequate explanation of the deteriora-
tions. For example, on Figure 1 there are plotted the chemical characters of five natural waters
from a long shore-area in whose ground-waters, at certain places, the content of chloride and
certain other constituents has changed very substantially in recent years. The five waters include:
Two from well A, in 1931 and 1940, respectively; two from adjacent well B, in 1931 and 1936, re-
spectively; and one from the ocean a few miles away. From the plottings on Figure 1 it is obvious
that this deterioration in ground-water quality could not have been caused by a simple intermingling
of the fresh ground-water with ocean water.

   To demonstrate conclusively that a certain water is a quantitative mixture of two other waters--
neither diluted, concentrated, nor chemically modified after the mixing--one graphic criterion and
one graphic-algebraic criterion must be satisfied. First, by the graphic criterion, in all three
fields of the diagram the apparent mixture must plot on straight lines between the plottings of its
two inferred components. Also, the area-concentration plottings in the central field must conform
to the principle that the concentration of a mixture is necessarily greater than the least, but less
than the greatest, of the several concentrations of its components. This graphic criterion alone is
not decisive because it involves only percentage reacting values and does not involve absolute con-
centrations. Neither is any other simple graphic construction on the diagram decisive. The second
and decisive criterion requires satisfaction of the following equations:

   With reference to Figure 5-A let: V_a = proportionate volume in mixture M of water having com-
position A; V_b = proportionate volume of water having composition B; E_a = concentration of water
A, in equivalents; E_b = concentration of water B, in equivalents; E_m = concentration of the mixture,
in equivalents; a = intercept between the plottings of A and M, measured in any of the three fields of
the diagram and at any convenient scale; and b = intercept between the plottings of B and M. Then it
follows and can be shown that

$$(a/b) = (V_b \cdot E_b / V_a \cdot E_a) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots .(1)$$

$$(V_a/V_b) = (b \cdot E_b / a \cdot E_a) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots .(2)$$

$$E_m = [E_a \cdot E_b (a + b)]/(a \cdot E_a + b \cdot E_b) \dots\dots\dots\dots\dots\dots\dots\dots .(3)$$

$$V_a = b \cdot E_b / (a \cdot E_a + b \cdot E_b) \text{ and } V_b = a \cdot E_a / (a \cdot E_a + b \cdot E_b) \dots\dots\dots\dots .(4)$$

   Further, with respect to any particular chemical constituent, let: C_a = concentration in com-
ponent water A, in equivalents or parts per million as desired; C_b = concentration in component B;
and C_m = concentration in the mixture. Then

$$C_m = (C_a \cdot V_a) + (C_b \cdot V_b) \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots .(5)$$

   Decisive proof of a quantitative mixture is accomplished when, for the water of intermediate
composition, agreement is shown between analytical data and corresponding values computed from
equation (3) for total concentration and from equations (4) and (5) for concentration of individual
chemical constituents. Equation (3) is numerically equivalent to a corresponding equation derived
by LANGELIER and LUDWIG [2, pp. 350-351], but is expressed in a form that facilitates the neces-
sary computations.

   As has been pointed out by HILL [1 (1940), pp. 48-49], the chemical character of a mixture of
waters will plot at the center of gravity of the plottings of the respective components, each having
been weighted according to its concentration and its proportionate volume in the mixture. Based on
this principle, graphic-algebraic criteria for decisive proof of quantitative mixtures are perhaps
feasible for a three-component system but become involved for systems with more than three com-
ponents. Problems involving three or more components are likely to be infrequent; accordingly, it
seems most practicable to solve them by an adaptation of the two-component criteria given above.
Thus, on Figure 5-B let M represent a water presumed to be a mixture of waters A, B, and C. To
prove or disprove a quantitative mixture project a straight line on the diagram through C and M to
intersect AB at point X, which represents the chemical composition of a hypothetical mixture of
waters A and B in the same proportions that these waters would enter a mixture of composition M.
From preceding equations (3), (4), and (5) determine the composition and concentration of water X.
Then, treat water M as a presumed mixture of waters X and C. As desired, this procedure is
readily adaptable to mixtures of more than three components.

Application to geochemical problems

The greatest utility of the diagram herein described probably is in "screening" a large number of water-analyses for critical study with respect to sources of the dissolved constituents, modifications in chemical character as a water passes through an area, and related geochemical problems.

Changes in the chemical character of a natural water by solution of progressively increasing amounts of some particular mineral must plot on a set of straight-line vectors directed in each of the three fields toward the point representing the chemical composition of the mineral. This case is analogous to mixing one water with another whose concentration is infinitely great.

A natural water may be concentrated progressively by evaporation until it becomes saturated with respect to certain constituents, which then separate out in the solid phase. Until a saturation-point is reached, the chemical character of the concentrating water is represented by a single fixed point in each of the three fields of the diagram. If the material separating in the solid phase is of constant composition then, as evaporation continues, the character of the water will be traced on the respective fields by straight-line vectors directed away from the points that represent the composition of the separating solid. If the solid phase is a simple compound of one cation and one anion, the vector in the central field will be directed away from one of the apexes of that field, each of which represents a particular simple salt or group of salts. In the two triangular fields, the vector will be directed away from the respective apexes that represent the cation and anion composing the solid phase. For example, on Figure 6-A point A represents the composition of a hypothetical water that is saturated with respect to calcium sulphate ($CaSO_4$). As evaporation then

A, Separation of calcium
sulphate in solid phase

B, Reduction of sulphate

C, Base-exchange softening

D, Chemical reaction and
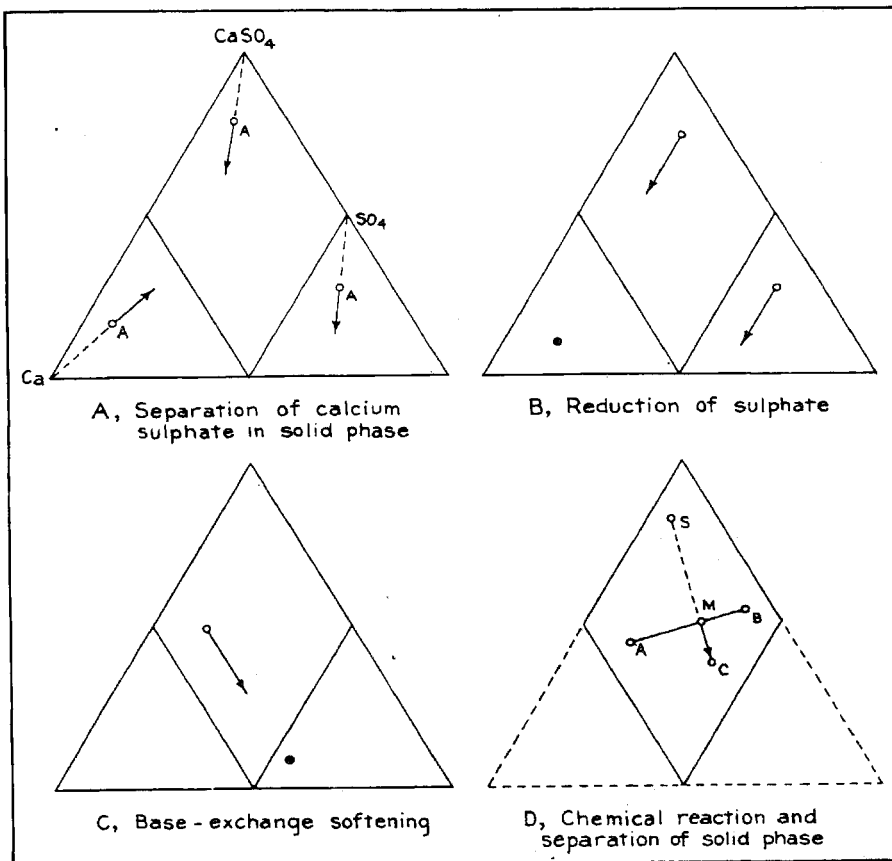separation of solid phase

Fig. 6--Vectors characteristic of certain geochemical processes

continues and calcium sulphate forms in solid phase, the changing composition of the liquid phase will trace the three vectors shown. If a separating solid phase is a mixture of salts in a constant proportion, a straight line will be traced in the central field trending away from the point that corresponds to the constant composition of the mixture; straight lines may or may not be traced .in the two triangular fields.

Certain changes in the chemical character of a water are caused by chemical reactions which in effect substitute one cation or one anion for another, molecule for molecule. Thus, reduction of sulphate [6] is equivalent to substitution of bicarbonate (HCO_3) for an equivalent amount of sulphate (SO_4); natural softening by reacting with base-exchange minerals [7], to substitution of sodium and potassium (Na, K) for calcium and magnesium (Ca, Mg). These two chemical changes are traced on the diagram by straight-line vectors parallel to the bases of the central field as shown by Figures 6-B and 6-C, respectively.

If two waters (or a water and a mineral) react chemically when brought together and some product or products of the reaction form in solid phase, the chemical character of the products remaining in solution will not plot on the straight line joining the points that represent the two reacting waters. Rather, it will plot on the extension of the straight line drawn from (1) the point that represents the composition of the solid phase to (2) the point that indicates the proportionate volumes and compositions of the two reacting waters. Thus, in Figure 6-D suppose that waters A and B are brought together in a proportion indicated by point M on the straight line AB, and that a solid phase of composition S results; then, the soluble products will plot on the extension of the straight line SM, as at point C. If the precipitate is a compound of one base and one acid, this relation between points A, B, M, S, and C will apply likewise in the two triangular fields (not shown and point S will fall on one apex of each field. If the two waters are brought together in various proportions and the product S is appreciably soluble, the composition of the liquid phase will traverse line AB up to the point of saturation with respect to product S and then, beyond the point of saturation, will deflect away from point S.

The chemical composition of a natural water may undergo complex changes by an interplay of several or numerous processes. The causes are commonly obscure. However, when comprehensive chemical data are available the diagram herein described can assist greatly in a preliminary discrimination of causes, by application of the principles just described. Doubtless other useful principles will be developed as this diagram and similar diagrams are more widely used.

Preliminary analysis of a typical problem

The plottings on Figure 1, to which reference has been made, are typical of a problem in the saline contamination of fresh ground-water in a longshore area. Table 2 gives the corresponding numerical data.

From their analytical data one could infer that waters B_1, A_2, and B_2 represent progressive stages in the contamination of water A_1 by some unknown high-chloride source. Because these are longshore ground-waters from wells only about 200 feet deep, the ocean is an obvious potential source of a high-chloride contaminant. However, Figure 1 shows conclusively that the contaminated ground-waters are not simply a mixture of ocean water with uncontaminated water A_1, because their plottings do not conform to the graphic criterion for a simple mixture as already developed. Specifically: (1) In the cation-triangle, waters A_2 and B_2 do not fall between the plottings of A_1 and C, although all the plottings are in substantial alignment; (2) in the anion-triangle, B_1, A_2, and B_2 all plot below the line A_1C; and (3) in the central diamond-shaped field B_1 plots very slightly above, but A_2 and B_2 plot far above the line A_1C. If the analysis of water B_2 had not been available these discordances would not have been obvious in the analytical data. Neither would the analysis of water B_1 have shown clearly that it represented the incipient stage of contamination.

With reference to the corresponding two hypothetical mixtures, waters A_2 and B_2 contrast sharply in two respects: (1) Their content of calcium is much greater and that of sodium is much less; in percentage reacting value the excess of calcium is substantially equal to the deficiency of sodium, as though the hypothetical mixtures had been hardened by an ion-for-ion exchange of base with the water-bearing material (see Fig. 6-C). (2) Their content of sulphate is substantially deficient, as would be expected if sulphate had been reduced to bicarbonate (see Fig. 6-B). These two contrasts also appear to apply in a small measure to water B_1, thus tending to confirm the inference that this water represents an incipient stage in a common process of contamination.

Table 2--Principal chemical constituents of certain longshore ground-waters and of ocean water

Constituent	A_1	B_1	b_1	A_2	a_2	B_2	b_2	C
Parts per million								
Calcium (Ca)	39	40	39	102	42	466	65	393
Magnesium (Mg)	10	10	11	19	22	77	98	1,228
Sodium (Na) Potassium (K)	47	52	56	{54 3.6}	152	255	808	{10,220[a] 353}
Carbonate (CO$_3$)	....	....	....	0	....	....	....	0
Bicarbonate (HCO$_3$)	204	207	204	203	203	166	199	139
Sulphate (SO$_4$)	24	21	26	6.7	49	0	207	2,560
Chloride (Cl)	16	32	32	199	199	1,346	1,346	18,360
percentage reacting values (adjusted)								
Calcium (Ca)	20.2	19.6	18.4	28.0	10.0	28.6	3.5	1.7
Magnesium (Mg)	8.5	8.1	8.6	8.6	8.6	7.8	8.7	8.8
Sodium and potassium (Na + K)	21.3	22.3	23.0	13.4	31.4	13.6	37.8	39.5
Totals	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Bicarbonate (HCO$_3$)	38.9	35.9	34.9	18.3	16.7	3.3	3.6	0.2
Sulphate (SO$_4$)	5.8	4.6	5.7	0.8	5.1	0	4.7	4.6
Chloride (Cl)	5.3	9.5	9.4	30.9	28.2	46.7	41.7	45.2
Totals	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0

[a]Calculated.
Notes: A_1 and A_2 indicate water from Well A on June 3, 1931, and December 20, 1940, respectively. B_1 and B_2 indicate water from Well B on June 6, 1931, and June 30, 1936, respectively. C indicates water from the ocean a few miles from wells A and B. a_2, b_1, and b_2 indicate hypothetical mixtures of waters A_1 and C in such proportions that their chloride contents are equal to those of A_2, B_1, and B_2, respectively.

Obviously the data here presented are not adequate fully to define this water-quality problem, in part because the analyses of waters A_1, B_1, and B_2 are approximate only. However, as an elementary example of procedure they are especially effective because they afford a striking comparison but involve only water-quality and time as principal variables. A complete solution of the problem here suggested involves data so voluminous that it is not feasible to introduce them.

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[1] R. A. HILL, Geochemical patterns in Coachella Valley, Trans. Amer. Geophys. Union, Part I, pp. 46-49, 1940; also Salts in irrigation waters, Trans. Amer. Soc. Civ. Eng., v. 107, pp. 1,478-1,493, 1942.
[2] W. F. LANGELIER and H. F. LUDWIG, Graphical methods for indicating the mineral character of natural waters, J. Amer. W. W. Assn., v. 34, pp. 335-352, 1942.
[3] Op. cit., Fig. 5.
[4] CHASE PALMER, The geochemical interpretation of water analyses, U. S. Geol. Surv., Bull. 479, 31 pp., 1911.
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DISCUSSION

RAYMOND A. HILL (Consulting Engineer, Los Angeles, California)--When the use of trilinear diagrams in the interpretation of water-analyses was suggested by the writer (R. A. HILL) at a meeting of the Section of Hydrology, American Geophysical Union, it was not expected that so many variations in the form of the diagram would be developed by others. In fact, as stated by the writer in his paper on Salts in irrigation water [Trans. Amer. Soc. Civ. Eng., v. 107, 1942], it has been a matter of regret that so much effort has been directed toward modification of the diagram rather than toward its application as a tool in solving hydrological problems. However, such being the case, it is probable that the most desirable form of diagram has not yet been developed.

The form of diagram used by the author (PIPER) is essentially the same as that suggested by the writer in Figure 12 of his closing discussion of the above mentioned paper. This form tends to be somewhat confusing in actual application because there is no marked differentiation between the three component parts of the diagram, that is, the cation-triangle, the anion-triangle, and the geochemical diamond. Since all graphical projections from either of the triangles to the diamond are along diagonal lines, the triangles can be separated from the diamond as shown in Figure 1, on which, for illustration, have been plotted the points corresponding to the analysis of sample A_1 in Table 2 of Mr. PIPER'S paper as follows:

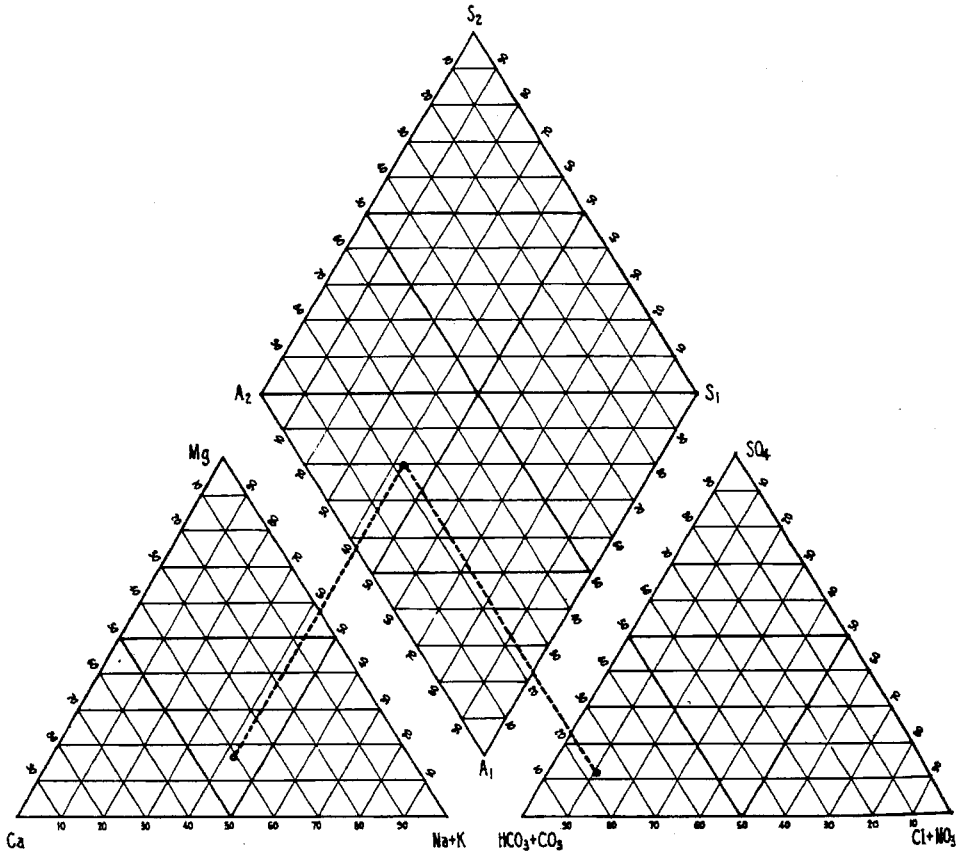|	pct		pct		pct
Ca	40.4	HCO_3	77.8	Primary alkalinity	20.4
Mg	17.0	SO_4	11.6	Primary salinity	22.2
Na + K	42.6	Cl	10.6	Secondary alkalinity	57.4
	100.0		100.0		100.0

Fig. 1--Illustrative plotting of Sample A, Table 2

While the use of circles of different areas to indicate relative concentrations was suggested by the writer in his paper (Op. cit.) it is doubtful whether this is of value in many cases. Better visual representations of differences in concentration can be had by the use of bar-diagrams.

The reversion by the author to the practice of computing percentage reacting values so that the sub-total of the cations and of the anions each equals 50 per cent seems to introduce unnecessary confusion. Furthermore, as the cations are positive and the anions are negative their sum is properly equal to zero. If the equivalent weight of each cation be recorded as a percentage of the equivalent weight of all cations, and the same be done for the anions, then it would be unnecessary to double the percentage reacting values as described by the author throughout his paper.

The use of the reciprocal of the combining weight of each ion also tends to be confusing. Almost everyone conversant with such matters remembers the combining weights of the more common ions, while it is not to be expected that the reciprocals can be remembered. The only advantage in using reciprocals would be ease of multiplication as compared to division. The data, however, are subject to far greater error than are ordinary slide-rule computations and division on a slide-rule is as simple as multiplication.

In his discussions of mixtures of waters the author resorts to algebraic computations which become involved in actual use. It was for this reason that the writer in his paper (Op. cit., pp. 1,484) suggested the use of tons-equivalent, abbreviated to "T_e", being the equivalent tons of hydrogen in the quantity of water under consideration. When this quantity is given in acre-feet the total equivalent weight of any ion is equal to the quantity of water times the concentration in milligram-equivalents of hydrogen per liter divided by 735, or algebraically, $T_e = (CQ/735)$, in which C is the concentration of salts in equivalents per million and Q is the quantity of water in acre-feet. The factor 735 comes directly from the use of acre-feet and tons as units. Any corresponding factor would likewise come directly from any other system of measurements.

None of the systems of classification of different waters dependent on reference to the plotted position of a point on a diagram can be remembered readily and hence all such fail of being descriptive. It was for that reason that the writer suggested in his closing discussion of his paper on Salts in irrigation water that the most satisfactory classification would be one that merely defined the predominate cation and the predominate anion.

In closing, attention is invited to the fact that any trilinear diagram adapted to the interpretation of water-analyses is only a tool; hence the form of the tool should be subordinated to the use which is made of it.

W. F. LANGELIER (Professor of Sanitary Engineering, University of California, Berkeley, California)--In a recent paper to which the author has made reference [his reference 1], LANGELIER and LUDWIG described several methods of graphing water-analyses and suggested possible applications thereof. Among the methods described is one to which we referred as our own adaptation of the trilinear method of R. A. HILL [Salts in irrigation water, Proc. Amer. Soc. Civ. Eng., v. 67, p. 975, 1941]. This method, it appears, is substantially the same as that proposed in the paper under discussion. Our adaptation of the HILL method consisted merely in changing the outward form of the diagram so as to permit the use of standard triangular graph-paper. We wish to disclaim any originality in developing the basic trilinear method. To us, this three-point method seems to be unnecessarily cumbersome in execution and, in the graphs, difficult of visual interpretation; moreover, we believe that the multiple graph is not well suited to the study of any considerable number of dissimilar analyses upon a single diagram.

In the multiple trilinear form of graph as proposed, each analysis is regarded as comprising six component-ions, or ion-groups, which require three points upon the diagram for complete identification and interpretation. For most uses, it would appear that a more practicable method is one in which the general character of the sample is indicated by the position of a single point, and wherein more specific or critical data are indicated by special characters or symbols. We have described such a method and, in order to distinguish it from the one at present under consideration, have referred to it as the "single-point" method. In the single-point method, the cations and anions are divided into chemically similar groups, essentially as proposed by PALMER, that is, the cations are divided into alkali-groups and non-alkali groups, and the anions are divided into carbonate and non-carbonate groups. Since the total equivalent concentrations of the cations and anions are equal, and since there are only two groups in each category, it follows that there will be only two independent variables and that therefore the analysis can be represented by a single point upon a rectangular graph. The significance of the plotted point in this diagram is identical to that of the third point
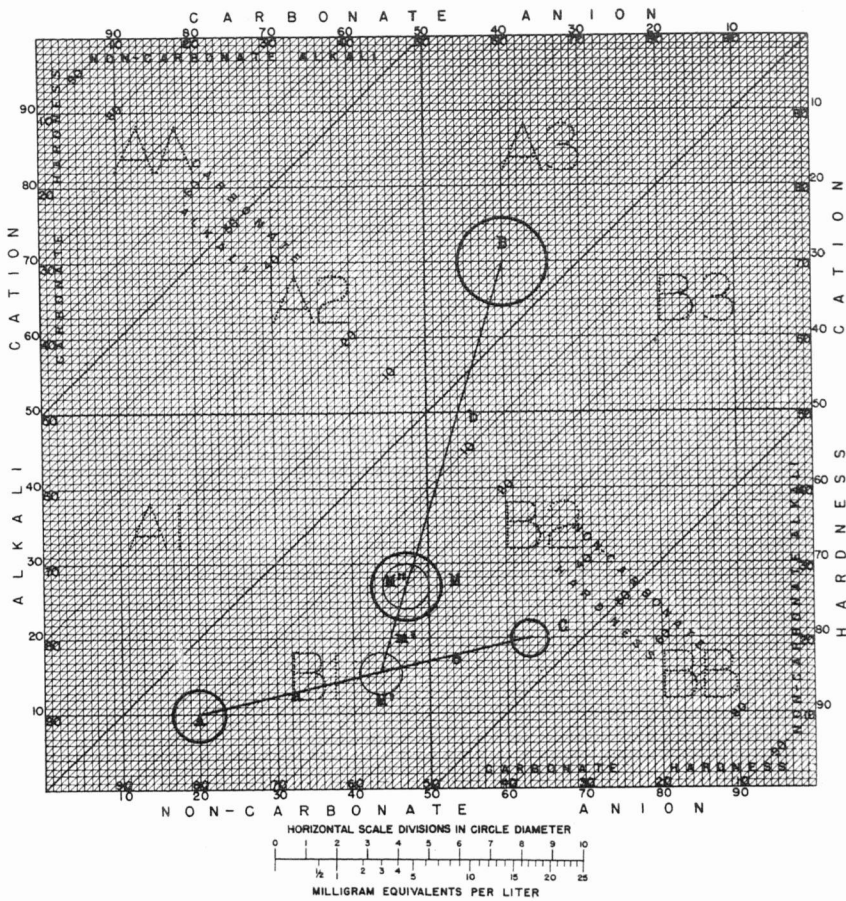
Fig. 1--Use of water-classification diagram in confirming a presumptive
mixture of three component waters [After Langelier and Ludwig (J. Amer.
Water-Works Ass'n., v. 34, pp. 335-352, 1942)]

(obtained by projection) in the multiple trilinear graph. It should be noted that in either diagram
the position of the identifying point--which actually classifies the sample--is not altered by changes
in the ratio of either Ca to Mg or Cl to SO_4.

As an illustration of the use of the rectangular graph as applied to the problem of mixtures,
reference is made to Figure 1, in which circle A in the triangle B1 represents a water of which
the total cation-concentration is 12.0 milligram equivalents per liter (mE/ℓ). Its plotted location
indicates that it contains 1.2 mE/ℓ of alkali cation and 2.4 mE/ℓ of chloride plus sulphate anions.
The fact that its position lies below the SW-NE diagonal indicates that the non-carbonate anion-con-
tent of this water is greater than its alkali content and, in accordance with PALMER, the water may
be said to be characterized by the property of secondary salinity or non-carbonate hardness. The
three properties--non-carbonate alkali, non-carbonate hardness, and carbonate hardness--can be
read directly from the inside scales as 10, 10, and 80 per cent of the total salt-concentration, equal
to 1.2, 1.2, and 9.6 mE/ℓ, respectively. Similarly, the properties of water samples B, C, and M are
apparent from their plotted positions.

The significance of the six outer lettered triangles of the diagram is that each delimits a prop-
erty which, measured in percent, is greater than the other two combined. Within the inner triangles
A2 and B2, the three properties are more evenly balanced, and none exceeds 50 per cent of the total.

Sample M falls within the triangle formed by the plotted positions of A, B, and C, and its total
concentration of dissolved salts is greater than the lowest and less than the highest of the three

waters. This is presumptive evidence that the sample might possibly constitute a mixture of the three samples, A, B, and C. That it is not an exclusive mixture of any two of the three samples is readily proved by mere inspection of the diagram. It has been repeatedly pointed out that a basic principle of these graphic methods is that the plotted location of a mixture of any two waters must lie on the line which connects the plotted positions of the two component parts and that the proportion of each component in the mixture is related to the exact position of the point upon the connecting line. Thus in Figure 1, sample M cannot be an exclusive mixture of any two of the three samples represented, because its plotted position does not coincide with the lines interconnecting any two of the samples. However, it might possibly be a mixture of all three samples. The proof that M is not a quantitative mixture of all three samples takes into further consideration the total concentration of the sample as indicated by the diameter of the circle. If M were an exclusive mixture of A, B, and C, it could be considered to be a two component mixture of B and a hypothetical mixture M', the latter composed of waters A and C. As indicated by the author, we demonstrated in our earlier contribution, the relationship which must be satisfied between ΣM, the total concentration of M', and the analytical values of Σ_A, Σ_C, and the scaled distances of a and c. The formulation is

$$\Sigma_{M'} = \Sigma_A [\, 1 + (a/c)]/[\, 1 + (\, \Sigma_A/\Sigma_C)(a/c)]$$

In the example under consideration the computed value of $\Sigma_{M'}$ will be found to equal 7.8 mE/ℓ. Applying the same formulation, Σ_M, if it were a mixture of B and M', would equal 9.3 mE/ℓ. Since this computed value differs from its actual or analytical value of 20.0 mE/ℓ, sample M cannot be an exclusive mixture of A, B, and C.

In addition to the above method of confirming mixtures, we have described a completely graphical method which, however, requires that the analytical data be rearranged into six groups rather than four. For this purpose and for other uses wherein a considerable number of analyses are represented we recommend large graph sheets approximately 18 inches square.

We concur in the author's opinion that there exists a wide and practically untried field of usefulness in the application of graphical methods to geochemical water-supply investigations.

ARTHUR M. PIPER (author's reply and closure)--In his lead paper on the general topic of graphic methods in geochemical studies the writer sought to define his own procedure in order that its elements might be compared with those of procedures outlined by HILL and by LANGELIER in their respective antecedent papers, and thereby possibly to stimulate the evolution of some technique even more effective. He had no thought of claiming originality for all elements in his procedure as outlined. That procedure is founded on a multiple-trilinear diagram which was developed by the writer independently, but which fortuitously had evolved to essentially its present form about contemporaneously with the papers by HILL and by LANGELIER in 1942. However, the writer here acknowledges with embarrassment that he had been confused by the dual publication under the title of "Salts in irrigation water" [R. A. HILL, Proc. Amer. Soc. Civ. Eng., v. 67, pp. 975-990, 1941; also idem, v. 68, pp. 1,478-1,493, 1942] and heretofore has overlooked not only the discussions by SCOFIELD and others but also HILL'S "alternate form of geochemical chart" [op. cit. pp. 1,494-1,518, Fig. 12, 1942], which is essentially identical with the water-analysis diagram of the lead paper.

The diagram of the lead paper is conceived by the writer as a technician's tool which--for the particular purpose of segregating related chemical analyses from a mass of such data in the study of a geochemical problem--has substantial advantages over either a set of bar-diagrams or a rectilinear graph, and which seems not to sacrifice any great advantage. Its over-all utility is afforded by the use of trilinear coordinates to indicate the chemical character of a water by single-point plotting for preliminary segregation of data and by three-point plotting for more critical segregation. It is conceded that such coordinates may seem awkward to the novice but that awkwardness passes quickly as familiarity with the diagram is acquired.

The central or diamond-shaped field in the diagram of the lead paper is essentially a counterpart of the LANGELIER "water-classification diagram", except that its coordinates are triangular rather than rectilinear. On that central field, single-point plottings for preliminary segregation of data are made and the characters of waters are disclosed precisely as on the LANGELIER diagram. With either diagram, this single-point plotting treats the sum of calcium and magnesium as a single variable, and the sum of sulphate and chloride as another single variable. Within this restrictive treatment the rectilinear LANGELIER diagram is entirely adequate and probably simpler than the central field in the diagram of the lead paper; however, for a more critical segregation of data this restrictive treatment is not adequate because it does not treat all six "first-rank" constituents as

independent variables. On the diagram of the lead paper all six are treated independently by means of the three-point plotting, which is feasible only with triangular coordinates.

Fundamentally, the HILL "geochemical chart" differs from the diagram of the lead paper only in that it treats chloride and sulphate-plus-bicarbonate as complementary anion-constituents, rather than chloride-plus-sulphate and bicarbonate. In the writer's judgment the grouping of sulphate with bicarbonate on the HILL chart would confuse rather than clarify many geochemical problems and does not seem peculiarly adapted to problems of irrigation-waters.

With respect to the demonstration of a quantitative mixture of two waters, one fundamental point seems not to have been made sufficiently clear--that is, not only must the three-point plottings on the diagram of the lead paper or on the HILL "geochemical chart" define three straight lines in the several plotting fields but also the analytical data must conform to equation (3) of the lead paper, or to the equivalent of that equation. This two-element demonstration is adequate only with respect to the six "first-rank" constituents. With respect to any one "second-rank" constituent, a quantitative mixture is demonstrated only when equations (4) and (5) of the lead paper also are satisfied. With only one-point plottings on either of these two diagrams or on the LANGE-LIER diagram, a quantitative mixture is demonstrated only when a straight line is defined on the diagram and equations (3), (4), and (5) of the lead paper (or equivalents of those three equations) are satisfied with respect to both first-rank and second-rank constituents. The three-point plottings are much more quickly made than the additional computations required with single-point plottings.

In his discussion of the lead paper HILL implies that equations (3), (4), and (5) are needlessly involved. In this connection it seems unnecessary to point out that these equations express the inescapable basic principles in simple form, also that the concept of "tons-equivalent" merely introduces an additional conversion-factor.

Although graphic methods are very useful in discriminating two-component mixtures, it is felt that their primary utility lies in tracing chemical reactions between a natural water and materials with which that water comes in contact. The lead paper describes several principles that are applicable in such studies and perhaps creates a background for delineating other useful principles and for evolving an ultimate comprehensive technique.

CORRELATION OF GROUND-WATER LEVELS AND PRECIPITATION ON LONG ISLAND, NEW YORK

C. E. Jacob

(Published with the approval of the Director, U. S. Geological Survey)

PART II--CORRELATION OF DATA

A brief though concise statement of the history of ground-water studies on Long Island, beginning with the early water-level observations in Brooklyn by STODDARD in 1854, was given by THOMPSON [see 7 of "References" at end of paper]. These and other early data were considered later by LEGGETTE [8]. He evaluated them by means of a graph of the cumulative departure of precipitation. More recent studies by LEGGETTE [9] and by the writer have lead to the procedure outlined in Part I of this paper [10], which was founded upon an empirical approach suggested by LEGGETTE and was later justified by analysis based on the theory of BOUSSINESQ [11].

Figure 1 is a map of the central part of Long Island showing contours on the water-table as of May, 1943, and also the locations of 14 New York City test-wells upon whose records the present study is based. The contours are based upon data from many more wells than are actually shown on the map. The 14 wells whose water-levels are analyzed in this study were first measured by the Department of Water Supply, Gas, and Electricity of the City of New York. They were chosen because of the length and continuity of their records and because together they adequately cover the range of water-table elevations in the area with more or less uniform distribution. Other wells with records of equal or greater length were eliminated because of less favorable situation with respect to centers of pumpage, points of natural discharge, etc., or because they duplicated records of one of the 14 wells.