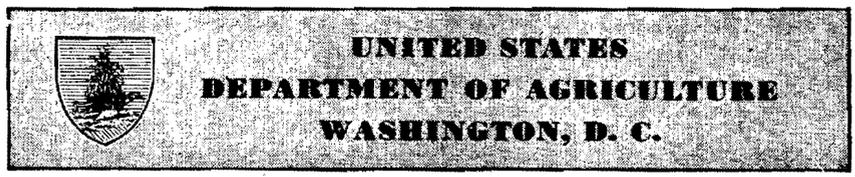


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# The Quality of Water for Irrigation Use <sup>1</sup>

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**T**HE rapid development in irrigation farming that followed the passage of the Reclamation Act in 1902 continued in many areas until essentially all available irrigation water was utilized. Less attention was then paid to the quality of the water than to the quantity. As a result, in some areas waters of very poor quality have been used for irrigation, but more recently much greater importance has been attached to their quality. This interest may be due, in part at least, to the fact that significant changes have taken place in the quality of certain irrigation waters as a result of upstream diversions and drainage returns. These changes, by increasing the salt content, have been making the waters less desirable for agricultural use.

In districts irrigated from wells, changes in quality often take place when the withdrawal of water from the underground reservoir exceeds the replenishment. In some wells the quality has been improved; in others it has become poorer.

It is not always possible to anticipate the direction or rate of change of quality in ground waters. Changes in both surface and ground waters are still in progress and can be expected to continue as long as

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there is active development in irrigation or drainage. They should be determined from time to time and the facts made use of in the management of irrigation systems. Methods of determining the changes in water and of interpreting analyses as given in this bulletin may be summarized as follows.

### SUMMARY

Natural waters vary greatly in the concentration and composition of dissolved constituents and correspondingly in their suitability for irrigation use. Limits for several constituents have been proposed by different workers and in general the values are in good agreement.

An estimate of the quality of an irrigation water is usually based on a chemical analysis, and the estimate can be no better than the analysis. This bulletin discusses methods of analysis, their accuracy, and the significance of the several constituents in respect to the soil and to plants.

Analyses of typical surface and ground waters are given in a series of tables. Other tables show the effect of repeated diversions along a river channel and the variation in composition with rate of flow.

The interpretation of an analysis is considered and a procedure outlined.

### COMPOSITION OF IRRIGATION WATERS

Irrigation waters vary greatly both in concentration and composition of the dissolved salts. Some of the constituents are beneficial to plants, others in moderate concentration appear to have little effect on plants or soils, while still others impair plant growth or are harmful to soils. The major constituents include the cations—calcium, magnesium, and sodium—and the anions—bicarbonate, sulfate, and chloride. Potassium, carbonate, nitrate, silica, and boron may be present but usually only in low concentrations. Small quantities of other substances may be found in some waters, but their influence on the quality of the water for irrigation use is not important and they are usually neglected. The total concentration of dissolved salts varies from a few parts per million (p. p. m.) to several thousand. Most irrigation waters fall within the range of 100 to 1,500 p. p. m., with a few as high as 5,000 p. p. m., the higher concentrations being used on the more tolerant crops. Accurate analytical methods for most of the constituents have been available for many years, so that the older published analyses that represent careful work on representative samples are fully trustworthy and are of great value as a frame of reference.

The interpretation of the analysis of an irrigation water is largely empirical, being based on field observation, experience, and plant-tolerance research. Significantly, however, there is good agreement on this subject among the workers in this field. An interpretation of an analysis should take into consideration the effect of the dissolved salts on both the plants and the soil. These two reactions can be studied separately in the laboratory, and a considerable body of valuable information is available. In the field, however, any plant response, whether favorable or unfavorable, must be recognized as the result of these two reactions operating simultaneously. Present standards of quality of irrigation water are presented below, to-

gether with a new procedure that takes into account the effect of the water on the soil as well as on the plants.

The objectives of this bulletin are: (1) To discuss the significance of the several dissolved constituents; (2) to show the analyses of certain typical waters and the variation in composition of natural waters; (3) to discuss the interpretation of analyses and propose a new procedure that takes into account the effect of the water on the soil; and (4) to present analytical methods of acceptable accuracy.

## REVIEW OF LITERATURE

Several important articles on the composition of natural waters have been published. Collins and Howard (9, 10)<sup>2</sup> have indexed the analyses of natural waters of the United States. An investigation, participated in by the United States Geological Survey and the then United States Reclamation Service, was begun in 1905 to study the waters likely to be used on the reclamation projects. This was reported by Stabler (38) in 1911, and the data are important as a frame of reference for more recent analyses. The surface waters of California were studied in 1905-08 by Van Winkle and Eaton (46). Forbes (19) investigated the quality of the water of the Colorado River at Yuma in 1900-01. More recent studies include the Rio Grande Joint Investigation (44) and the Pecos River Joint Investigation (45). Current work on the Rio Grande, carried on cooperatively by the United States Section of the International Boundary and Water Commission, the United States Bureau of Reclamation, and the United States Bureau of Plant Industry, is reported in the Water Bulletins (22) of the International Boundary Commission. The United States Geological Survey has been active in quality-of-water investigations in the West. The findings are published in the Water-Supply Papers of that agency.

Ground waters are extensively used as irrigation sources in certain parts of California and have been the subject of a number of quality-of-water investigations. The California Division of Water Resources, cooperating with the United States Bureau of Plant Industry, made a detailed survey of the irrigation waters of the South Coastal basin, which comprises parts of San Bernardino, Riverside, Orange, and Los Angeles Counties (31). In connection with the study of the occurrence of boron in natural waters, the United States Bureau of Plant Industry has published several papers (12, 15, 35) that contain a large number of analyses. In addition to the above, a great many unpublished analyses that are available for reference are on file at State agricultural experiment stations and United States Department of Agriculture laboratories.

Methods suitable for the analysis of irrigation waters have been assembled and published by the Association of Official Agricultural Chemists (4) and jointly by the American Public Health Association and the American Water Works Association (1). The methods used by the United States Geological Survey are described by Collins (8), and those in use at the Rubidoux Laboratory of the United States Bureau of Plant Industry, Soils, and Agricultural Engineering are described by Wilcox and Hatcher (49). In addition, there are several

<sup>2</sup> Italic numbers in parentheses refer to Literature Cited, p. 29.

procedures that are useful. Scofield (30) described the electrical conductivity method. The Barber and Kolthoff (5) method for sodium is used with only slight modification. Potassium (48) and boron (47) are determined by the procedures worked out by Wilcox. Methods of reporting and accuracy are discussed by the above (1, 4, 8, 49) and in addition by Magistad, Reitemeier, and Wilcox (27). The interpretation of an analysis in terms of plant response or soil reaction is discussed by Scofield (32), Eaton (12), Wilcox and Magistad (50), and Magistad and Christiansen (25).

## METHODS AND ACCURACY

### COLLECTION OF SAMPLES

Samples of water for analysis are collected in clean containers, preferably glass bottles, of one-half gallon capacity. Each container should be rinsed with the water to be sampled just before taking the sample and filled nearly full. It is a wise precaution to tie the stopper in securely, store in a cool place, and transfer to the laboratory promptly. Samples from surface streams should be taken from running water and if possible at a gaging station. Samples of ground water should be collected after the well has been operating for some time, in order to avoid stagnant water. Each sample should be marked by a name or number sufficient to identify it and should be accompanied by a detailed description that should include (1) the date of collection; (2) collector's sample number, name, and address; (3) the name of the stream, or, if a well, the name of the owner; (4) the location; (5) the discharge; (6) for a well, the depth, casing diameter, depth to upper perforations, static level, draw-down, temperature, odor, and color; (7) the approximate acreage served by the water; (8) the condition of the crops and the reason for collecting the sample.

### METHODS OF ANALYSIS

The methods used for the analysis of an irrigation water should be as expeditious as possible and yet yield results of the desired accuracy. The appendix gives a set of procedures that have been in use for many years and have proved satisfactory. Neither the semiquantitative field methods nor the highly precise techniques used in research work are included, as these have little place in quality-of-water work.

### METHODS OF REPORTING

The results of an analysis of a water can be reported in any one of several units. Parts per million is the unit in which most of the older analyses are reported, while milligram equivalents per liter (me./l.) or equivalents per million (e. p. m.) have come into use more recently. This latter unit (e. p. m.) is preferred for the cations and anions, because the data, being in terms of the chemical equivalent weights of the ions, are more easily checked for accuracy and are more readily compared or classified. The unit, equivalents per million, was suggested by Committee D-19 of the American Society for Testing Materials and was adopted by that society at its meeting in 1941 (2). It is defined as a unit chemical equivalent weight of a constituent per million unit weights of solution. Equivalents per

million and milligram equivalents per liter are numerically identical where the specific gravity of the solution is 1.0. The percentage difference between the true specific gravity and 1.0 is less than the analytical error in most cases involving irrigation waters. Boron is reported as p. p. m.; dissolved solids (D. S.) as p. p. m. or as tons per acre-foot (t. a. f.).

#### ACCURACY

An estimate of the precision or reproducibility that may be expected for each determination from the above methods under ordinary conditions is shown in table 1. This table is based on studies made independently by two workers and represents the experience of several years and many thousands of water analyses.

TABLE 1.—*Maximum deviations from the mean that may be expected in the course of analyses of successive portions of the same sample; the deviations may be either negative or positive*

Ion or substance determined	Low total salinity		High total salinity	
	Concentration	Deviation	Concentration	Deviation
Electrical conductivity ( $EC \times 10^6$ at 25° C.)	500	10	5,000	50
Dissolved solids (D. S.)	350	10	2,500	50
Boron (B)	.5	.02	4.0	.05
Calcium (Ca)	2.0	.05	20.0	.1
Magnesium (Mg)	2.0	.1	20.0	.2
Sodium (Na)	2.0	.02	20.0	.05
Bicarbonate ( $HCO_3$ )	2.0	.1	5.0	.15
Sulfate ( $SO_4$ )	2.0	.1	25.0	.2
Chloride (Cl)	2.0	.1	30.0	.2
Approximate maximum deviation		.5		1.0

At the lower concentration shown in table 1 the maximum deviation between anions and cations is 0.5 e. p. m., which is 8 percent of the mean, while at the higher concentration the deviation is 1.0 e. p. m., representing 2 percent. If deviations substantially greater than these are encountered, errors of analysis or calculation are indicated and the work should be repeated.

There are certain derived values that are helpful in judging the accuracy of an analysis or in locating an error. The numerical value of the ratio, electrical conductivity times  $10^6$  divided by anions ( $EC \times 10^6$ /anions), should be between 90 and 100 for most waters. In hard bicarbonate or sulfate waters the value may drop below 80, while in soft chloride waters the value may be above 110. This term is analogous to equivalent conductance of single-salt solutions. The numerical value for the ratio, dissolved solids in tons per acre-foot divided by electrical conductivity (D. S. in t. a. f./ $EC \times 10^6$ ), should be between 0.0008 and 0.001 in most cases. A third ratio, dissolved solids in tons per acre-foot divided by anions (D. S. in t. a. f./anions),

has a value of about 0.09. These values are based on experience, as there is very little published information on mixed-salt solutions such as natural waters.

## DISSOLVED CONSTITUENTS AND THEIR SIGNIFICANCE

This section lists the more important constituents that occur in natural waters and outlines the significant facts in respect to their chemistry, their effect upon the soil, and their relation to plant growth. It should be recognized that many of these effects are complicated and interrelated, and often the effects of several constituents are additive, so that it is not always possible to segregate the reaction of each constituent. The constituents are considered in three groups: (1) Minor constituents; (2) anions and cations; and (3) total concentration of constituents.

### MINOR CONSTITUENTS

In this group are included boron, silica, fluoride, nitrite, sulfide, phosphate, iron, aluminum, ammonia, hydrogen ion as measured by pH, and organic matter. These constituents usually occur in low concentrations and, with the exception of boron, are not of great importance in their relation to the soil or plants. They serve to characterize the water and often are useful in tracing the source of replenishment of ground waters.

#### BORON

Boron (chemical symbol B; atomic weight, 10.82; valence 3) occurs in nature in many forms but principally as borax (tincal), calcium borate (colemanite), or as boric acid in hot mineral springs or geysers. It has been found in all irrigation waters thus far examined, although the concentrations may vary from mere traces to several hundred p. p. m. In acid waters, boron would appear as un-ionized boric acid ( $H_3BO_3$ ), while in alkaline waters of pH below 9.2 both boric acid and tetraborate ion ( $B_4O_7$ ) would be present, and at pH 9.2 only tetraborate could occur. Metaborate ( $BO_2$ ) forms in solutions more alkaline than pH 9.2. Most ordinary compounds of boron are soluble in water to the extent that they are toxic to plants (16, p. 45), so that there is no known method that is economically feasible for precipitating or removing boron from an irrigation water.

Boric acid in neutral or acid solution reacts quantitatively with such polyhydric alcohols as mannitol or glycerol to liberate 1 hydrogen ion for each molecule of boric acid present. This reaction is made use of in the determination of boron. Boron, in the concentrations found in irrigation waters, has no noticeable effect on soil. It is fixed to some extent by soil, especially upon drying, but most of it is released upon successive washings with water (16). Boron is an essential element for normal plant growth, but at concentrations only slightly above optimum it is exceedingly toxic to many plants. Eaton (14) reported that many plants made normal growth in sand cultures with a trace (0.03 to 0.04 p. p. m. B), and that injury occurred in a number of cases in cultures of 1 p. p. m. boron. The role of boron in the plant is not thoroughly understood, although there is a large body of literature on the subject. Irrigation water containing more than 1 p. p. m. of boron is likely to cause injury to the more sensitive plants (35).

## SILICA

Silica ( $\text{SiO}_2$ ; molecular weight, 60.06) occurs abundantly in nature, uncombined in crystalline and amorphous forms and combined with bases as the silicate minerals. It is sparingly soluble in hot water and more soluble in carbonate alkali. Natural waters contain from 10 to 50 p. p. m. silica. It is a major constituent of all soils, but the small quantity carried by the irrigation water appears to have very little effect, either physical or chemical, on the soil. Silicon, probably in the form of silicate ion, is absorbed by all plants and in large quantities by the grasses in which it is deposited in the epidermis, forming a dense, protective coating.

## FLUORIDE

Fluoride (F; atomic weight, 19.00; valence 1) occurs chiefly as fluor spar ( $\text{CaF}_2$ ) and cryolite ( $3\text{NaF}\cdot\text{AlF}_3$ ), but it often is present in significant quantities in natural waters, particularly hot springs. In the low concentrations found in irrigation waters it has little or no effect on soils or growth of plants. It is important in human nutrition in that small quantities are necessary for the normal development of the teeth, while higher concentrations produce a serious dental disorder known as mottled enamel. The injury occurs on the permanent teeth at the time they are forming but before they erupt. As little as 1 to 2 p. p. m. fluoride in the domestic water used by children will cause a mild to moderate mottling of the teeth, according to Smith (37).

## NITRITE

Nitrite ( $\text{NO}_2$ ; molecular weight, 46.008; valence 1) is not present in a normal irrigation water. Its presence in a water signifies anaerobic conditions, such as sometimes prevail in a stagnant well. Nitrite is assumed to be an intermediate step in the oxidation of organic nitrogen to nitrate, thus protein nitrogen to ammonia to nitrite to nitrate. The nitrites are readily soluble and if present in an irrigation water in low concentration would not affect the soil chemically, although a disturbance of the microbiological equilibrium might result. Poorly aerated soils often contain measurable quantities of nitrite, which has been shown by Klotz and Sokoloff (23) to be associated with conditions toxic to citrus and avocado trees.

## SULFIDE

Sulfide sulfur (S; atomic weight, 32.06; valence 2) is a constituent of a large number of important minerals, as pyrite, sulfide of iron; galena, sulfide of lead; cinnabar, sulfide of mercury, and others. In natural waters it usually appears as hydrogen sulfide and is easily detected by the odor, even in very low concentration. Waters from many deep wells along the trough of the San Joaquin Valley in California contain substantial quantities of this constituent. These waters are low in sulfate, lower in fact than the replenishing waters, and low in calcium and magnesium.

Eaton (12, 13) called attention to these facts and suggested that the sulfide was derived from sulfate by anaerobic reduction and that the corresponding oxidation involved the conversion of carbon in re-

duced forms, possibly petroleum gas, to carbonate, which precipitated the calcium and magnesium. Sulfide as such is not usually determined in the analysis of an irrigation water, but satisfactory methods are available if it is desired.

Hydrogen sulfide, in the concentrations found in natural waters, has no apparent effect on soils, probably due to the fact that it is rapidly oxidized to sulfate in a well-aerated soil. A definite prejudice by water users against sulfide waters may be due to the presence of other constituents, such as sodium and boron, that are usually found in such waters. The effect on plants is not harmful under conditions where oxidation can take place rapidly and may be beneficial as a source of sulfur.

#### PHOSPHATE

Phosphate ( $\text{PO}_4$ , (orthophosphate); molecular weight, 94.98; valence 3) is a constituent of nearly all igneous rocks and occurs in small quantities in all soils. Vast deposits of calcium phosphate are found in this country, in Canada, and elsewhere, and are the principal source of phosphate for fertilizer use. The solubility of calcium phosphate is very low in neutral or slightly alkaline solutions, and as a result only traces are found in most natural waters of the West. The small quantity of phosphate brought to the soil by the irrigation water has no noticeable effect, either physical or chemical, on the soil. It is probably precipitated as tricalcium phosphate. Phosphate is one of the most important substances in plant nutrition, and its presence in a water is therefore desirable. Many areas in the irrigated West are either deficient in phosphate or the phosphate is not available, and in these areas large quantities of the superphosphate type of fertilizer are used. Orthophosphoric acid is being used to a limited extent as a source of phosphate in southern California and Arizona. The acid is allowed to drip into the irrigation water at a weir box just before distribution on the land.

#### IRON

Iron (Fe; atomic weight, 55.85; valence 2 (ferrous) and 3 (ferric)), next to aluminum, is the most abundant metal. There are hundreds of mineral species of which iron is a normal constituent, and during the process of weathering many of these become incorporated into the soil. Iron, either ferrous or ferric, is relatively insoluble in mild alkali such as that found in most western waters. The concentration of iron in solution seldom exceeds a few tenths of a part per million, but some waters carry sufficient iron in colloidal suspension to be troublesome if used for domestic or industrial purposes, due to the formation of scale deposits. In soil, the action of the colloidal iron is to cement finer particles into larger aggregates. Iron is an essential element in plant nutrition and is present in sufficient quantity in practically all soils. Iron chlorosis, that is recognized in many areas and on many species, does not appear to be caused by a deficiency of iron in the soil but rather to the inability of the plant to utilize the iron.

#### ALUMINUM

Aluminum (Al; atomic weight, 26.97; valence 3) is the most abundant metal in nature and is an important constituent of clays. It

is relatively insoluble in mildly alkaline waters but quite soluble in dilute acid or strong alkali. In the low concentrations ordinarily present in irrigation waters it has no noticeable effect on soils or plants. In higher concentrations, such as are encountered in acid soils, toxic reactions are recognized in many plants. In small quantities it is a normal constituent of most plants but is not thought to be essential to plant growth.

#### AMMONIUM ION

Ammonia ( $\text{NH}_3$ ; molecular weight, 18.04; valence 1) is found in some fumarolic and in stagnant waters, but is ordinarily not present in well-aerated waters. A large quantity of ammonia gas handled in pressure cylinders is used as a nitrogen fertilizer. It is introduced into the irrigation stream in low concentration, but at frequent intervals. It was shown by Fireman and coworkers (17) that ammonium salts produce some unfavorable reactions in the soil, tending toward deflocculation and impermeability, but these effects are probably not lasting, as the oxidation to nitrate is usually rapid. The small quantity that might be found in natural waters would have little effect on the soil, and any effect on plants would probably be beneficial.

#### HYDROGEN ION AS MEASURED BY pH

Hydrogen ion ( $\text{H}^+$ ; atomic weight, 1.008; valence 1) which is the cation part of all acids, is less widely distributed than the element, hydrogen, which forms about one-ninth part by weight of water, and is therefore found almost everywhere in nature. Some mineral springs contain free acid. Many soils in the humid regions are acid, as differing from the arid soils that are characteristically alkaline. An understanding of the acid-alkali equilibrium in an aqueous solution, such as a natural water, involves a clear visualization of three concepts: (1) The total acidic hydrogen present; (2) the fraction of the acidic hydrogen that is dissociated and appears as hydrogen ion; and (3) the equilibrium between hydrogen and hydroxyl ions that is represented by the pH scale.

Considering these three points in order, the total acidic hydrogen in a solution includes both the undissociated hydrogen and the hydrogen ion. It is determined by titration with standard alkali and is reported in units of quantity as equivalents or milligram equivalents.

When an acid is dissolved in water, a part of the acid molecules dissociates into positively and negatively charged ions; thus, for hydrochloric acid: Hydrogen chloride molecule=hydrogen-ion, positively charged + chloride ion, negatively charged. The strength of an acid is dependent upon the proportion of hydrogen ions to undissociated acid molecules. Such strong acids as hydrochloric, nitric, and sulfuric dissociate almost completely in dilute solution. Weak acids are only partially dissociated; for instance, acetic acid in normal solution contains less than 1 percent hydrogen ion and boric acid less than 0.01 percent. A measure of the hydrogen ion concentration indicates the acidic intensity of the solution and is reported as a pH value.

In water or in aqueous solutions of acid or alkali, the product obtained by multiplying the concentration of hydrogen ions by the concentration of hydroxyl ions is a constant, thus:  $(\text{H}^+) (\text{OH}^-) = K_w$ ,

where  $K_w$  has the rounded value  $10^{-14}$ . This means that in acid solutions the concentration of hydroxyl ions is extremely low, and, conversely, in alkaline solutions the concentration of hydrogen ions is extremely low. Also, from this relationship, it is possible to express concentrations from strong acid through neutral to strong alkali in terms of hydrogen ion concentration. These values are awkward to handle, so for purposes of simplification the negative logarithms are used. These negative logarithms of the hydrogen ion concentration are referred to as pH units, i. e.,  $pH = -\log_{10} (H^+)$ . The pH scale starts at 0 on the acid side and extends through neutral at pH 7 to pH 14 in strong alkali. To illustrate these relationships, consider a neutral solution such as pure water that has, by definition, equal quantities of hydrogen and hydroxyl ions, or from the above equation  $(10^{-7})H^+(10^{-7})OH^- = 10^{-14}$ . If the hydrogen ion concentration is taken as  $10^{-7}$  equivalents per liter, the  $pH = -\log_{10} (H^+) = -\log_{10} (10^{-7}) = 7$ .

#### ORGANIC MATTER

The color in the natural waters of the West is due almost wholly to organic matter. This color interferes to some extent with some of the analytical procedures but probably has no detrimental effect on either soils or plants.

#### ANIONS AND CATIONS

In this group are considered the cations—calcium, magnesium, sodium, and potassium—and the anions—carbonate, bicarbonate, sulfate, chloride, and nitrate. These are grouped together because of their rather general occurrence and the fact that most detailed water analyses include them. These constitute the bulk of the dissolved constituents and very largely determine the quality of the water.

#### CALCIUM

Calcium (Ca; atomic weight, 40.08; valence 2) is one of the most abundant metals, but it is never found in nature uncombined. It is an essential constituent of many minerals and rocks. Of agricultural importance are limestone (calcium carbonate), gypsum (calcium sulfate), and calcium phosphate. Calcium is found in nearly all natural waters, soils, plant tissue, and animal bones. The salts of calcium vary greatly in solubility, the carbonate and phosphate being relatively insoluble in water but readily soluble in acid. The sulfate, gypsum ( $CaSO_4 \cdot 2H_2O$ ), is soluble to the extent of about 30.6 e. p. m. (2,634 p. p. m.), and the chloride and nitrate are both readily soluble in water. Hard water, as the term is ordinarily used, is characterized by a high concentration of calcium or magnesium, or both. These two ions precipitate soap, forming scum that is objectionable. The term is used in a slightly different sense in connection with analyses of irrigation waters. If the proportion of calcium plus magnesium to total cations is high, the water is said to be hard, regardless of the total concentration. This will be discussed below under Sodium.

To a great extent, the cations present in the soil solution determine the physical as well as the chemical properties of the soil. A calcium soil is friable and easily worked, permits water to penetrate readily, and does not "run together," or puddle, when wet. These reactions

will be considered in more detail under Interpretation of a Water Analysis.

Calcium is essential to normal plant growth. It is abundantly supplied by most irrigation waters and soils of the West, although there is some evidence that calcium is not available in the presence of carbonate alkali (24, pp. 209-211). Calcium deficiency is recognized and is widespread in the humid regions of the eastern part of the United States.

#### MAGNESIUM

Magnesium (Mg; atomic weight, 24.32; valence 2) is abundant in nature, being a normal constituent of such igneous rocks as the amphiboles, pyroxenes, and micas. Talc and serpentine are silicates of magnesium, and dolomite is a carbonate of magnesium and calcium. Mineral springs and sea water contain relatively high concentrations, while most natural waters contain some magnesium. The carbonate, the hydroxide, the oxide, and the phosphate of magnesium are sparingly soluble in water but readily soluble in acid. Most of the other compounds are water-soluble. The reaction of magnesium ion with the soil is much like that of calcium. It is essential to plant nutrition and can replace calcium partially but not completely. It is an important constituent of the chlorophyll of green plants.

#### SODIUM

Sodium (Na; atomic weight, 22.997; valence 1) is widely distributed and is the most abundant of the alkali metals. It is a constituent of many igneous rocks and rock salt. Most fresh waters contain at least measurable concentrations of the element, while in sea water the concentration is high. All of the common salts of sodium are water-soluble. Sodium, like the other cations, when applied to the soil in the irrigation water reacts with certain clay minerals known as the base-exchange material of the soil. Unfavorable physical conditions result when sodium is the predominant cation. As long as the total concentration of the water in contact with the soil remains unchanged the adverse effects develop slowly.

If the total concentration is lowered substantially, as by a change in quality of water or by a good rain, the soil undergoes a very pronounced change, both physical and chemical. When wet, the soil deflocculates or "runs together" and becomes sticky and impervious. On drying, large cracks and hard clods form, making it difficult to work into a seedbed. Chemical changes take place that result in the formation of carbonate (black) alkali. The so-called "slick spots" sometimes found in irrigated fields and the playas of the desert are usually alkali areas. Reclamation of alkali soils involves, among other things, the replacement of the adsorbed sodium by calcium or magnesium and the removal of the sodium by leaching. This can often be accomplished if a high calcium (hard) water is available for the leaching, otherwise it may be necessary to apply gypsum or some other soluble calcium salt to the soil before leaching. In this connection, Scofield (34) summarized the results of a series of reclamation experiments in the frequently quoted statement: "Hard water makes soft land and soft water makes hard land."

The ordinary crop plants develop normally with little or no sodium available to them so that, if sodium is essential, the requirement is very low. It is taken up freely from saline soils by many plants, but it appears to serve no other function than to increase the osmotic concentration of the cell sap and thus retard desiccation. In higher concentrations sodium ion is toxic to plants.

The adverse effect on the soil is more closely related to the ratio of sodium in the irrigation water to total cations than to the absolute concentration of sodium. This ratio is called the "percent sodium" (percent Na) and is defined by the following equation, in which concentrations are in terms of equivalents, as e. p. m.:

$$\text{Percent Na} = \frac{\text{Na} \times 100}{\text{Ca} + \text{Mg} + \text{Na} + \text{K}}$$

#### POTASSIUM

Potassium (K; atomic weight, 39.096; valence 1) is found in many rocks, but is more abundant in igneous than sedimentary rocks. It is a constituent of many of the complex silicates that make up the soil. Great deposits of potassium minerals are found in the saline beds near Stassfurt, Germany, and Carlsbad, N. Mex., and the element is abundant in the brines of Searles Lake, Calif. The soils of the West are, in general, well supplied with potassium, and there are only a few areas that appear to be deficient. With the exception of the silicate minerals, most of the compounds of potassium are readily soluble, but the concentration seldom exceeds a few tenths of an equivalent per million in soil solutions or natural waters. The reaction with the soil is similar to that of sodium, but the effects are not so harmful. Potassium is essential to plant growth and is one of the three major plant-food elements.

#### CARBONATE

Carbonate ( $\text{CO}_3$ ; molecular weight, 60.01; valence 2) in the form of limestone (calcium carbonate), dolomite (calcium and magnesium carbonate), and iron carbonate is widely distributed. The first two are constituents of fertile soils and often used as soil amendments. Alkali carbonates are often present in mineral springs but only in traces in most natural waters. The carbonates of the alkali bases, sodium and potassium, are water-soluble, but the carbonates of the alkaline-earth bases, calcium and magnesium, and of the heavy metals are quite insoluble in water but soluble in acid. If soluble carbonate in the irrigation water is applied to the soil one of two reactions takes place. In the absence of calcium or magnesium the soil becomes alkaline and takes on the unfavorable characteristics described under sodium, above. If an excess of a soluble calcium salt such as gypsum is present, calcium carbonate is precipitated and little change in the soil is noted. Alkali carbonate, such as sodium carbonate, is undesirable in the irrigation water and soil solution and is extremely toxic to plants.

#### BICARBONATE

Bicarbonates ( $\text{HCO}_3$ ; molecular weight, 61.018; valence 1) are not found to any extent in nature except in solution in natural waters. Calcium bicarbonate is more soluble than the normal carbonate, but the

compound is unstable and is known chiefly in solution. A rise in temperature or evaporation results in the loss of carbon dioxide and the precipitation of calcium carbonate, thus:



Most irrigation waters carry some calcium bicarbonate in solution, so that from these waters calcium carbonate is deposited in the soil. This reaction is of great importance in irrigation agriculture, as it tends to keep an excess of calcium in the soil. Carbon dioxide that is given off by plant roots and micro-organisms adds to the bicarbonate content when dissolved in the soil water. The equilibrium involving carbonate, bicarbonate, carbon dioxide, and the cations not only determines the pH of the water but also holds the pH reasonably constant for long periods of time. This equilibrium pH value for most natural waters of the West falls between 7.5 and 8.5.

Plants use large quantities of carbon dioxide in the process of photosynthesis. In the case of land plants the carbon dioxide is taken from the air in gaseous form, while in aquatic plants the carbon dioxide is in solution, possibly entering the plant as bicarbonate ion. The bicarbonate in solution in irrigation waters is probably of little direct importance in plant nutrition.

#### SULFATE

The most abundant sulfate ( $\text{SO}_4$ ; molecular weight, 96.06; valence 2) compound in nature is the calcium salt, gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). It occurs in deposits of great extent and is also widespread in lower concentration in both soils and waters. Sodium and magnesium sulfates are readily soluble, while calcium sulfate is sparingly soluble. (See under Calcium, above.) Sulfate has no characteristic action on the soil other than to increase the salinity. Sulfur is an essential element in plant nutrition, and in the form of sulfate it is readily available to plants.

#### CHLORIDE

Chloride (Cl; atomic weight, 35.457; valence 1) as a constituent of sodium chloride (common salt) is found as rock salt and in solution in sea and natural waters. The common chlorides are all soluble, so that the concentration builds up in soil solutions or drainage waters. (See table 4, below.) Plants develop normally in solutions containing only traces of chloride, so that if chloride is essential the quantity required is small. It inhibits the growth of most crop plants and becomes definitely toxic at moderate concentrations. Formerly, the chloride concentration was used as the most important criterion in judging the quality of an irrigation water, i. e., the less chloride the better the water.

#### NITRATE

Nitrates ( $\text{NO}_3$ ; molecular weight, 62.008; valence 1) are not found in extensive deposits in the United States. The principal source of nitrate is Chile, where the material is recovered as an impure sodium nitrate. All the nitrate salts are soluble and easily lost by leaching. Fertile soils contain nitrate that is presumed to come from the oxidation of nitrogenous organic matter or from the fixation of atmospheric

nitrogen by soil organisms. Surface waters contain only traces of nitrate, while ground waters often contain measurable quantities but usually less than 1 e. p. m.  $\text{NO}_3$ . These concentrations have little effect on the soil, but the continued use of sodium nitrate fertilizer may impair its structure and permeability (17). Nitrate is one of the three major elements in plant nutrition and is usually the first to become limiting in the arid soils of the West. Nitrate promotes a succulent type of growth that is desirable in forage crops when adequately supplied with water, but less nitrate is needed when the crop consists of tubers or fruit.

#### TOTAL CONCENTRATION OF CONSTITUENTS

The usual water analysis affords three measures of total concentration: (1) Electrical conductivity; (2) total anions; and (3) dissolved solids. The significance of each is given below.

#### ELECTRICAL CONDUCTIVITY

In an aqueous solution such as a natural water, a large proportion of the inorganic salts dissolved in the water are ionized. Thus sodium chloride ( $\text{NaCl}$ ) ionizes to form positively charged sodium ions ( $\text{Na}^+$ ) and negatively charged chloride ions ( $\text{Cl}^-$ ). These charged ions can conduct an electric current, and use is made of this property in the determination of conductivity. The electrical resistance, between platinum electrodes, is measured with a Wheatstone bridge, using a previously calibrated conductivity cell. The electrical conductivity ( $\text{EC} \times 10^6$  at  $25^\circ \text{C}$ .),<sup>3</sup> which is calculated from the above measurement, is related to the total ions present and correlates well with plant response.

#### TOTAL ANIONS

In any solution, the number of equivalents of positive ions (cations) must equal the number of equivalents of negative ions (anions). Then, either total anions or total cations expressed in terms of equivalents can be used satisfactorily as a measure of total salinity. Anions have been used almost exclusively, because, until recent years, it was not possible to make a direct determination of sodium, one of the principal constituents of the cations.

<sup>3</sup>The expression "electrical conductivity" is synonymous with "specific electrical conductance." The standard unit for conductivity is the mho/cm. It is such a large unit that most natural waters have a value of much less than 1 unit. For instance, the Colorado River sample (No. 10642, table 2) has a conductivity of 0.00117 mho/cm. For purposes of convenience in recording or expressing such results, the value in mho/cm. is multiplied by  $10^6$  (decimal point moved 6 places to the right) and reported as  $\text{EC} \times 10^6$  at  $25^\circ \text{C}$ . Much of the earlier work on natural waters was reported as  $\text{K} \times 10^4$  at  $25^\circ \text{C}$ . This value multiplied by 10 gives  $\text{EC} \times 10^6$  at  $25^\circ \text{C}$ . The relation between the several methods of reporting conductivity is shown below, using as an example, the conductivity of the Colorado River, mentioned above:

$$\begin{aligned} \text{EC} &= 0.00117 \text{ mho/cm.} \\ \text{EC} \times 10^6 &= 1.17 \text{ millimhos/cm.} \\ \text{EC} \times 10^4 &= 117 (\text{K} \times 10^4) \\ \text{EC} \times 10^3 &= 1,170 \text{ micromhos/cm.} \end{aligned}$$

## DISSOLVED SOLIDS

The value for dissolved solids (D. S.) is obtained by evaporating to dryness an aliquot of the water and weighing the dry residue. The water must be freed from such suspended matter as silt. The weight of the dry residue is corrected for the aliquot portion taken and reported as dissolved solids in parts per million or in tons per acre-foot (t. a. f.). T. a. f. is obtained by multiplying p. p. m. by the constant 0.00136, and is used in estimates of salt balance in irrigated areas (33).

There is no simple relationship between the three methods of indicating total concentration. For natural waters, the following give approximate values:

$$\begin{aligned} EC \times 10^6 \times 0.7 &= \text{D. S. in p. p. m.} \\ EC \times 10^6 \div 100 &= \text{e. p. m. anions.} \end{aligned}$$

## SIGNIFICANCE OF CONSTITUENTS

Of the minor constituents, boron is the most important. In the concentrations found in certain irrigation waters it is toxic to many plants, but extremely small quantities are required by all plants. The concentration of boron is one of the three criteria by which the quality of a water is judged, the other two being total concentration and percent sodium.

The cations—calcium, magnesium, and sodium—react with the base-exchange material of the soil and determine very largely the physical character of the soil. Calcium and magnesium, in proper proportion, maintain the soil in a good condition of tilth and structure, while the opposite is true if sodium predominates. Under conditions of high salinity, chloride is often the principal anion, owing chiefly to the fact that the chloride salts are soluble.

Considering the three methods for expressing total concentration, electrical conductivity is most used in characterizing a water, total anions (or total cations) is used for checking the accuracy, and dissolved solids is used in salt-balance studies.

## TYPICAL WATERS AND VARIATION IN COMPOSITION

## SURFACE WATERS

There are presented, in the tables that follow, the analyses of a number of surface and ground waters. These are typical of the natural waters of the West, and all are being or have been used for irrigation. Surface waters vary considerably, depending on flow, so that the analyses shown should be recognized as representing the conditions at the time the sample was taken but not necessarily the high or low extremes. Except as noted, the analyses were made by the Rubidoux Laboratory, of this Bureau, using the methods herein described. Analyses of a series of 12 surface waters arranged in ascending order of conductivity are given in table 2.

The first five analyses of table 2 represent waters of low total salinity and are low in boron and percent sodium as well. These are excellent irrigation waters. Sample No. 16920 is from Cache Creek in northern California and is characterized by its high boron content. This water causes injury to boron-sensitive plants, but is satisfactory for such tolerant crops as sugar beets and alfalfa. The next three, the

TABLE 2.—Chemical analyses of surface waters of important streams from which water is diverted for irrigation

Items of comparison	River or creek											
	Ya-kima <sup>1</sup>	Sacramento <sup>2</sup>	Columbia <sup>3</sup>	Yellowstone <sup>4</sup>	North Platte <sup>5</sup>	Cache Creek <sup>6</sup>	San Joaquin <sup>7</sup>	Arkansas <sup>8</sup>	Rio Grande <sup>9</sup>	Colorado <sup>10</sup>	Gila <sup>11</sup>	Pecos <sup>12</sup>
Sample No.-----	17514	18409	10397	14043	18355	16920	7653	18042	18554	16642	7546	-----
Electrical conductivity (EC × 10 <sup>6</sup> at 25° C.)-----	117	150	151	191	280	508	764	933	1, 120	1, 170	1, 330	5, 420
Percent sodium-----	23	18	13	29	22	32	52	25	50	39	60	40
Boron (B)-----p. p. m.	.02	.05	.05	.06	.03	1. 78	.18	.08	.20	.16	.20	.37
Dissolved solids (D. S.)---t. a. f.	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	5. 44
pH-----	7. 6	7. 9	7. 0	7. 5	7. 5	-----	7. 0	8. 2	8. 3	7. 8	-----	-----
Silica (SiO <sub>2</sub> )-----p. p. m.	19	25	-----	-----	15	-----	19	22	41	-----	15	22
Cations:												
Calcium (Ca)-----e. p. m.	.56	.63	.90	.89	1. 61	1. 31	1. 79	5. 06	4. 14	5. 06	3. 39	25. 06
Magnesium (Mg)-----e. p. m.	.35	.51	.39	.59	.57	2. 40	1. 58	2. 66	1. 49	2. 30	1. 59	12. 66
Sodium (Na)-----e. p. m.	.28	.26	.19	.61	.63	1. 77	3. 84	2. 63	5. 77	4. 70	7. 75	25. 79
Potassium (K)-----e. p. m.	.04	.04	-----	0	.07	-----	.16	.21	.21	-----	.25	.61
Total-----e. p. m.	1. 23	1. 44	1. 48	2. 09	2. 88	5. 48	7. 37	10. 56	11. 61	12. 06	12. 98	64. 12
Anions:												
Carbonate (CO <sub>3</sub> )-----e. p. m.	0	0	0	0	0	.40	0	.05	.25	( <sup>13</sup> )	.30	-----
Bicarbonate (HCO <sub>3</sub> )-----e. p. m.	1. 00	1. 22	1. 26	1. 18	1. 59	3. 37	2. 50	2. 70	3. 33	2. 52	2. 75	1. 34
Sulfate (SO <sub>4</sub> )-----e. p. m.	.07	.13	.21	.52	1. 12	.61	3. 90	7. 39	4. 97	7. 16	2. 29	35. 64
Chloride (Cl)-----e. p. m.	.15	.12	.07	.10	.09	1. 05	1. 04	.47	3. 02	2. 30	7. 07	26. 79
Nitrate (NO <sub>3</sub> )-----e. p. m.	( <sup>13</sup> )	( <sup>13</sup> )	( <sup>13</sup> )	.03	.03	( <sup>13</sup> )	.04	( <sup>13</sup> )	.03	.03	.01	0
Total-----e. p. m.	1. 22	1. 47	1. 54	1. 83	2. 83	5. 43	7. 48	10. 60	11. 60	12. 01	12. 42	63. 77

<sup>1</sup> From main canal on Sunnyside Project, composite sample for August 1943.

<sup>2</sup> At Tisdale, a large capacity weir, approximately 35 miles above Sacramento, July 13, 1945.

<sup>3</sup> At Wenatchee, Wash., Nov. 25, 1935.

<sup>4</sup> From canal at Huntley, Mont., June 7, 1940.

<sup>5</sup> From canal near Scottsbluff, Nebr., May 23, 1945.

<sup>6</sup> At Capay Dam, Yolo County, Calif., composite sample for August 1941.

<sup>7</sup> Near Vernalis, Calif., Aug. 10, 1933.

<sup>8</sup> At point of diversion of Rocky Ford High Line Canal, Pueblo County, Colo., July 21, 1944.

<sup>9</sup> At El Paso, Tex., composite sample for August 1945.

<sup>10</sup> At Yuma, Ariz., composite sample for Aug. 1-10, 1942.

<sup>11</sup> At Ashurst-Hayden Dam, Ariz., Aug. 2, 1933.

<sup>12</sup> Near Orla, Tex., 19 miles downstream from Red Bluff Dam, composite sample for Aug. 1-10, 1943. Analysis by U. S. Geological Survey (21, p. 70).

<sup>13</sup> Trace.

San Joaquin, the Arkansas, and the Rio Grande, are waters of moderate salinity. These streams in the upper reaches are of low salinity, but these samples were collected at sites within or below the irrigated areas that are influenced by drainage return flow. Such waters are satisfactory on well-drained land, but are not so satisfactory if drainage is impaired.

The next sample (No. 16642) is a representative analysis of Colorado River water as delivered to the Imperial and Yuma Valleys since the completion of Hoover Dam. (See table 5 for analyses prior to the construction of the dam.) The concentration has not been subject to the fluctuation occurring before storage began. The boron and percent sodium are low, and it is a satisfactory water on permeable soils.

Gila River water (sample No. 7546) has a higher total salinity and sodium percentage and is, characteristically, a chloride water, as differing from the Colorado, which is a sulfate water. This water is used on well-drained soils without much difficulty, but on heavier soils deflocculation and impermeability often develop.

The last analysis is from the Pecos River and represents the water available for irrigation in the Pecos and Barstow areas. The choice of crops is limited to the more tolerant species, and farming is confined almost wholly to the light, well-drained soils. A study of the salinity problems of the area was made in connection with the Pecos River Joint Investigation (45).

#### GROUND WATERS

Analyses of a series of representative ground waters from areas where wells constitute the principal source of irrigation water are given in table 3.

The first two analyses of table 3 are typical ground waters from two fertile irrigated areas. They represent excellent supplies that, under normal conditions, cause no trouble either to plants or the soils. The next analysis (sample No. 18005) is of a water that might be expected to cause unfavorable reactions in the soil. Large quantities of early potatoes are produced in the area, and it has been found that waters of high sodium percentage, such as this one, tend to make the soil less permeable. This makes it necessary to hold the water on the fields much longer. To overcome this, it has become the practice to make a generous application of gypsum before planting.

The next two waters are from the Arvin area southeast of Bakersfield. The first (sample No. 18067) is of satisfactory quality and has produced good crops for many years. The other (sample No. 18071) is from a well not far away that is entirely unfit for irrigation because of the high boron and sodium percentage. Only the most boron-tolerant plants survived the use of this water, and it has since been discontinued.

Sample No. 15397 is from a well near the highway between El Centro, Calif., and Yuma, Ariz., and represents the ground water in the desert. It is interesting to note that the water is of relatively high chloride and low sulfate content, resembling more nearly the Gila than the Colorado River water.

The next two (samples Nos. 17969 and 8540) are representative waters of moderate salinity and are considered good wells in the areas. A sample (No. 14084) from Ventura County, Calif., is rather high in

both salinity and boron, but a good orange grove is being irrigated with this water.

Many years ago a large planting of deciduous trees was made in the western part of Fresno County. The trees did not do well, and the cause was assumed to be related to the irrigation water. Only in recent years has it been shown that the trouble was caused by a high boron content in the water. Sample No. 18646 is one of the better waters that is still in use on cotton and grain. The high sodium produces unfavorable reactions in the soil that are easily recognized.

Boron is not given for the artesian water used in the vicinity of Roswell, N. Mex., but from other samples it is known to be low. Good yields of the less sensitive crops are produced.

The last analysis (sample No. 18443) represents a highly saline water that under most conditions would not be suitable for irrigation. It is typical Gila River underflow and is being used fairly successfully on very permeable soil for the production of alfalfa and Bermuda grass seed.

#### VARIATION IN COMPOSITION

The effect of irrigation diversions and drainage returns on the composition and concentration of the water in the main channel of a river is shown in table 4. Data from eight stations on the Rio Grande are shown, the upstream station being at Otowi Bridge near Santa Fe, N. Mex., and the lower one at Fort Quitman, Tex., about 80 miles below El Paso. Irrigation developments are all along the river, except along the reservoir section from San Marcial to Caballo. The values are weighted means of monthly composite samples for the year 1945, weighted in each case in proportion to the total flow.

It is apparent that as the total flow decreases, owing to irrigation use, the total concentration as measured by electrical conductivity or dissolved solids increases (table 4). Likewise, both boron and percent sodium increase. This table emphasizes the difficulties that may befall water users in the lower reaches of a river, involving both quality as well as quantity of water resulting from upstream developments.

Usually, though not always, the quality of the water in a stream varies with the flow and is better during flood periods. The Colorado River exemplified this to a marked degree prior to the completion of Hoover Dam. To illustrate this, a number of analyses of the Colorado River, as sampled at Yuma, Ariz., are reported in table 5. The first 12 analyses cover the year 1932 at approximately monthly intervals. During this time the discharge varied from less than 3,000 c. f. s. to more than 80,000. The maximum conductivity was 1,900, and the minimum 446. The last analysis in table 5 represents the quality of water at Yuma 5 years after the Lake Mead Reservoir was put in operation. The composition has remained very constant since storage began.

Ground waters show variations in composition that are related in most cases to the strata from which the waters are pumped. Some of these differences are illustrated in the analyses reported in table 6.

The first two samples are from wells in the vicinity of Talent, Oreg. The first is characteristic of a shallow stratum, while the second represents deeper water. In this case, the shallow water is of excellent

TABLE 3.—*Chemical analyses of waters of representative irrigation wells*

Items of comparison	Irrigation well-No.											
	18203 <sup>1</sup>	18032 <sup>2</sup>	18005 <sup>3</sup>	18067 <sup>4</sup>	18071 <sup>4</sup>	15397 <sup>5</sup>	17969 <sup>6</sup>	8540 <sup>7</sup>	14084 <sup>8</sup>	18646 <sup>9</sup>	( <sup>10</sup> )	18443 <sup>11</sup>
Electrical conductivity (EC×10 <sup>6</sup> at 25° C.)	300	391	442	536	789	919	1,120	1,230	1,680	2,120	4,550	7,210
Percent sodium	43	38	87	48	96	69	20	36	26	93	59	64
Boron (B) p. p. m.	.02	.14	.13	.76	6.93	.20	.20	.84	.97	1.68		1.28
pH	7.7	7.7	8.3	8.1	8.3	7.8	7.9	7.7	7.7	7.9		7.9
Silica (SiO <sub>2</sub> ) p. p. m.			17	29	22					26		36
<b>Cations:</b>												
Calcium (Ca) e. p. m.	1.43	1.94	.52	2.21	.24	1.56	6.04	2.97	9.19	.85	12.78	14.91
Magnesium (Mg) e. p. m.	.28	.55	( <sup>12</sup> )	.40	.02	1.08	3.12	5.40	5.29	.47	6.33	11.84
Sodium (Na) e. p. m.	1.29	1.50	3.61	2.57	7.28	5.96	2.36	4.79	5.04	18.72	27.06	48.10
Potassium (K) e. p. m.			.03	.12	.01					.06		.32
Total e. p. m.	3.00	3.99	4.16	5.30	7.55	8.60	11.52	13.16	19.52	20.10	46.17	75.17
<b>Anions:</b>												
Carbonate (CO <sub>3</sub> ) e. p. m.	0	0	( <sup>13</sup> )	( <sup>14</sup> )	.41	( <sup>15</sup> )	0	0	0	( <sup>16</sup> )		( <sup>17</sup> )
Bicarbonate (HCO <sub>3</sub> ) e. p. m.	2.18	2.39	1.86	2.99	1.98	2.22	4.71	5.89	4.86	5.50	2.74	6.34
Sulfate (SO <sub>4</sub> ) e. p. m.	.06	.31	.52	.68	2.48	2.12	2.18	4.87	12.39	1.07	13.95	13.13
Chloride (Cl) e. p. m.	.20	.80	1.74	1.07	2.47	4.10	4.30	2.54	1.90	13.50	29.47	55.06
Nitrate (NO <sub>3</sub> ) e. p. m.	( <sup>18</sup> )	.51	( <sup>19</sup> )	.58	.04	.03	.18	.03	.29	.10	.02	.02
Total e. p. m.	2.98	4.01	4.12	5.32	7.38	8.47	11.37	13.33	19.44	20.17	46.18	74.55

<sup>1</sup> Irrigation well, 0.5 mile NW of Indio, Riverside County, Calif., Dec. 9, 1944.

<sup>2</sup> Irrigation well, 11 miles west of Lancaster, Los Angeles County, Calif., Sept. 12, 1944.

<sup>3</sup> Irrigation well, 10 miles north of Bakersfield, Kern County, Calif., Sept. 5, 1944.

<sup>4</sup> Irrigation well, southeast of Bakersfield, Kern County, Calif., Oct. 10, 1944.

<sup>5</sup> Gray's well, Imperial County, Calif., between El Centro, Calif., and Yuma, Ariz., Feb. 14, 1941.

<sup>6</sup> Irrigation well, 1.5 miles northwest of Carpinteria, Santa Barbara County, Calif., Aug. 11, 1944.

<sup>7</sup> Irrigation well, 2 miles south of Hollister, San Benito County, Calif., Apr. 19, 1934.

<sup>8</sup> Irrigation well, 2 miles southeast of Fillmore, Ventura County, Calif., June 24, 1940.

<sup>9</sup> Irrigation well, near Huron, Fresno County, Calif., Jan. 31, 1946.

<sup>10</sup> Well in sec. 15, T. 10 S., R. 24 E., near Roswell, N. Mex., July 24, 1940. Analysis by U. S. Geological Survey (45, p. 116, analysis No. 1).

<sup>11</sup> Irrigation well, 5 miles southwest of Roll, Yuma County, Ariz., Aug. 19, 1946.

<sup>12</sup> Trace.

TABLE 4.—*Weighted mean concentration of water samples from eight stations on the Rio Grande for 1945*

Items of comparison	Station							
	Otowi Bridge <sup>1</sup>	San Marcial <sup>2</sup>	Elephant Butte <sup>3</sup>	Caballo Dam <sup>4</sup>	Leasburg Dam <sup>4</sup>	El Paso <sup>5</sup>	County Line <sup>6</sup>	Fort Quitman <sup>7</sup>
Total discharge, acre-feet.....	1,131,550	813,750	839,690	882,920	814,170	568,900	280,620	207,710
Electrical conductivity (EC×10 <sup>3</sup> at 25° C.).....	280	567	662	740	778	1,210	2,880	3,200
Percent sodium.....	24	41	42	43	44	51	60	62
Boron (B)..... p. p. m.	.03	.10	.11	.11	.12	.18	.32	.33
Dissolved solids (D. S.)..... t. a. f.	.26	.51	.59	.65	.69	1.09	2.54	2.81
<b>Cations:</b>								
Calcium (Ca)..... e. p. m.	1.67	2.56	2.90	3.13	3.23	4.46	8.62	8.73
Magnesium (Mg)..... e. p. m.	.49	.80	.98	1.08	1.13	1.55	2.96	3.67
Sodium (Na)..... e. p. m.	.69	2.30	2.76	3.20	3.43	6.33	17.70	20.02
Total..... e. p. m.	2.85	5.66	6.64	7.41	7.79	12.34	29.28	32.42
<b>Anions:</b>								
Carbonate+bicarbonate (CO <sub>3</sub> +HCO <sub>3</sub> )..... e. p. m.	1.72	2.48	2.66	2.89	2.84	3.80	4.40	4.11
Sulfate (SO <sub>4</sub> )..... e. p. m.	.97	2.33	3.10	3.24	3.53	5.29	9.51	10.34
Chloride (Cl)..... e. p. m.	.14	.89	.99	1.40	1.53	3.43	15.60	18.17
Nitrate (NO <sub>3</sub> )..... e. p. m.	( <sup>8</sup> )	.02	( <sup>8</sup> )	.01	.01	.01	.02	.01
Total..... e. p. m.	2.83	5.72	6.75	7.54	7.91	12.53	29.53	32.63

<sup>1</sup> Near Santa Fe, N. Mex. Samples and discharge data by U. S. Geological Survey.

<sup>2</sup> At the upper end of Elephant Butte Reservoir. Samples and discharge data by International Boundary Commission.

<sup>3</sup> Reservoir outlet. Samples and discharge data by U. S. Bureau of Reclamation.

<sup>4</sup> Samples and discharge data by U. S. Bureau of Reclamation.

<sup>5</sup> About 2.4 miles above the International Dam. Samples and discharge data by International Boundary Commission.

<sup>6</sup> Hudspeth County, Tex. Samples and discharge data by U. S. Bureau of Reclamation.

<sup>7</sup> Approximately 80 miles below the International Dam at El Paso. Samples and discharge data by International Boundary Commission.

<sup>8</sup> Trace.

TABLE 5.—Chemical analyses of water samples from the Colorado River at Yuma, Ariz.

Items of comparison	Date collected												1942
	1932												
	Jan. 9	Feb. 6	Mar. 12	Apr. 10	May 9	June 3	July 7	Aug. 11	Sept. 10	Oct. 8	Nov. 7	Dec. 10	
Sample No.-----	5397	5601	5789	5900	6104	6229	6434	6570	6683	6804	6867	6963	6642
Discharge----- c.f.s. <sup>1</sup>	3,790	2,890	11,200	17,600	29,000	83,500	62,000	14,100	10,400	5,850	4,760	4,320	7,390
Electrical conductivity (EC × 10 <sup>3</sup> at 25° C.)-----	1,840	1,720	1,300	1,110	746	557	446	1,180	1,860	1,820	1,900	1,790	1,170
Percent sodium-----	45	45	48	41	37	33	30	38	30	44	43	43	39
Boron (B)----- p.p.m.	.21	.24	.12	.13	.18	.12	.07	.14	.14	.19	.24	.27	.16
Dissolved solids (D. S.)----- t.a.f.	1.73	1.65	1.19	1.03	.69	.48	.39	1.17	2.00	1.73	1.93	1.79	1.10
pH-----	7.9	8.4	8.0		8.0	8.1	8.1	7.9	7.8	8.2	7.8	7.9	7.8
<b>Cations:</b>													
Calcium (Ca)----- e.p.m.	6.36	6.02	4.53	4.23	3.10	2.37	2.05	5.23	11.02	7.28	7.27	6.78	5.06
Magnesium (Mg)----- e.p.m.	4.13	3.94	2.43	2.87	1.77	1.43	1.13	2.54	3.64	3.68	4.30	4.46	2.30
Sodium (Na)----- e.p.m.	8.48	8.07	6.35	4.99	2.89	1.86	1.36	4.78	6.34	8.62	9.02	8.59	4.70
Potassium (K)----- e.p.m.									.28	.21	.31	.35	
<b>Total</b> ----- e.p.m.	18.97	18.03	13.31	12.09	7.76	5.66	4.54	12.55	21.28	19.79	20.90	20.18	12.06
<b>Anions:</b>													
Carbonate (CO <sub>3</sub> )----- e.p.m.	0	.30	0	0	0	0	0	0	0	0	0	( <sup>2</sup> )	( <sup>2</sup> )
Bicarbonate (HCO <sub>3</sub> )----- e.p.m.	4.30	4.00	3.20	3.20	2.65	2.55	2.10	2.85	2.70	3.30	3.85	4.20	2.52
Sulfate (SO <sub>4</sub> )----- e.p.m.	9.31	8.82	6.34	6.19	3.81	1.93	1.75	7.56	16.26	11.45	12.24	10.95	7.16
Chloride (Cl)----- e.p.m.	5.45	5.65	3.40	2.50	1.30	1.15	.65	2.30	2.35	4.95	5.18	4.61	2.30
Nitrate (NO <sub>3</sub> )----- e.p.m.	.16	.16	.17	.09	.15	.04	.03	.13	.13	.11	.21	.16	.03
<b>Total</b> ----- e.p.m.	19.22	18.93	13.11	11.98	7.91	5.67	4.53	12.84	21.44	19.81	21.48	19.92	12.01

<sup>1</sup> (41, 42).

<sup>2</sup> Mean value derived from U. S. Geological Survey data (45, p. 30).

<sup>3</sup> Traces.

THE QUALITY OF WATER FOR IRRIGATION USE

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TABLE 6.—Chemical analyses of ground waters, showing variation in composition due to depth and to length of time of pumping

Items of comparison	Date collected										
	1936		1934	1945	1946						
	Oct. 15 <sup>1</sup>	Oct. 15 <sup>2</sup>	Apr. 25 <sup>3</sup>	Aug. 4 <sup>4</sup>	Apr. 17 <sup>5</sup>	Apr. 18 <sup>5</sup>	Apr. 18 <sup>5</sup>				
Sample No.....	11163	11164	8541	18427	18758	18759	18761	18763	18765	18766	18767
Well depth.....feet..	30	325	220	220	200	200	200	200	200	200	200
Pumping time.....hours..					0	.08	.5	2	12	24	36
Electrical conductivity (EC×10 <sup>6</sup> at 25° C.)..	390	702	503	389	624	827	894	963	1,040	1,080	1,100
Percent sodium.....	18	72	59	28	37						35
Boron (B).....p. p. m.	.15	2.14	4.06	.10							
Dissolved solids (D. S.).....t. a. f.					.55						1.00
pH.....	7.7	7.6	7.8	7.7	7.8						7.8
<b>Cation:</b>											
Calcium (Ca).....e. p. m.	2.82	1.24	1.10	1.28	3.17						5.55
Magnesium (Mg).....e. p. m.	.88	.98	1.24	1.50	.71						1.40
Sodium (Na).....e. p. m.	.84	5.58	3.36	1.07	2.32						3.89
Potassium (K).....e. p. m.					.13						.18
Total.....e. p. m.	4.54	7.80	5.70	3.85	6.33						11.02
<b>Anions:</b>											
Carbonate (CO <sub>3</sub> ).....e. p. m.	0	0	0	0	0	0	0	0	0	0	0
Bicarbonate (HCO <sub>3</sub> ).....e. p. m.	3.96	6.73	3.73	2.64	2.99	3.69	3.69	3.89	3.94	4.04	3.99
Sulfate (SO <sub>4</sub> ).....e. p. m.	.51	.28	.33	.50	1.87						3.90
Chloride (Cl).....e. p. m.	.25	.75	1.34	.68	.95	1.25	1.30	1.45	1.60	1.65	1.70
Nitrate (NO <sub>3</sub> ).....e. p. m.	( <sup>6</sup> )	.07	( <sup>6</sup> )	.04	.41	.80	1.00	1.26	1.48	1.63	1.75
Total.....e. p. m.	4.72	7.82	5.40	3.86	6.22						11.34

<sup>1</sup> Shallow well, ½ mile west of Talent, Oreg.<sup>2</sup> Irrigation well, 2 miles east of Talent, Oreg.<sup>3</sup> Irrigation well, San Benito County, Calif.<sup>4</sup> Same well as number 8541. Sample collected from an inflow of water into the casing at a depth of 38 feet, which was above the static water level.<sup>5</sup> Irrigation well in Coachella Valley, Riverside County, Calif. Samples collected at intervals from the start of pumping to 36 hours.<sup>6</sup> Trace.

quality and the deeper water is of poor quality. Samples 8541 and 18427 are from the same well. No. 8541 represents the well as pumped for irrigation use and is a mixture of water from several water-bearing strata. The well was subsequently abandoned because of the very poor quality of the water. In 1945, it was discovered that water was flowing into the well above the static water surface. This inflowing water was sampled (No. 18427) and found to be of excellent quality. Samples Nos. 18758 to 18767 are from the same well and were collected during the course of a 36-hour irrigation run. The total concentration increased as well as the concentration of each ion. This is the exception rather than the rule, as most wells remain remarkably constant in composition for long periods of pumping. Another interesting feature of this water is the relatively high nitrate concentration.

### INTERPRETATION OF ANALYSES OF IRRIGATION WATER

An interpretation of a chemical analysis of an irrigation water should take into consideration the effect of the dissolved salts on both plants and soil. These two reactions can be studied separately in the laboratory, and a considerable body of valuable information is available. In the field, however, plant response is the result of these and other reactions operating simultaneously, and the effect of each reaction cannot be distinguished readily. Attempts have been made to anticipate the effect of water on a soil by means of equations of the mass-law type (11, 26). Factors not included as variables in the equation, such as drainage, soil texture, and type of clay mineral present, profoundly affect the equilibrium, and the results obtained from such equations may be questionable. Accordingly, the scheme for interpretation, presented below, is largely empirical and is based on experience to a great extent. It is worthy of note, however, that earlier proposals (12, 25, 32, 50) agree very well, and agree exactly as to the upper limit of total concentration.

Three characteristics of a water must be known in order to make an estimate of the quality: (1) The total concentration, (2) the percent sodium, and (3) the concentration of boron. The total concentration can be expressed in terms of electrical conductivity, total equivalents per million of anions (or cations), or dissolved solids. If only dissolved solids is known, corresponding values for conductivity or equivalents per million, for use in table 7, can be approximated, as shown under Dissolved Solids (p. 15). Percent sodium is defined under Sodium (p. 11). The effect of boron concentration on the quality is discussed in a subsequent paragraph.

The permissible limits for electrical conductivity and percent sodium, as suggested by Scofield (32, p. 286), are shown in table 7. While it is possible to classify irrigation waters reasonably satisfactorily by reference to table 7, especially as regards electrical conductivity, it is thought that a better classification in respect to sodium percentage can be made by means of a diagram. Such a diagram is shown in figure 1. The limits for electrical conductivity in the diagram are similar to those in table 7 and cover the same range. The percent sodium is shown in an inverse curvilinear relationship to con-

ductivity. This relationship of high sodium percentage associated with low total concentration in each class seems reasonable and appears to fit the observed facts.

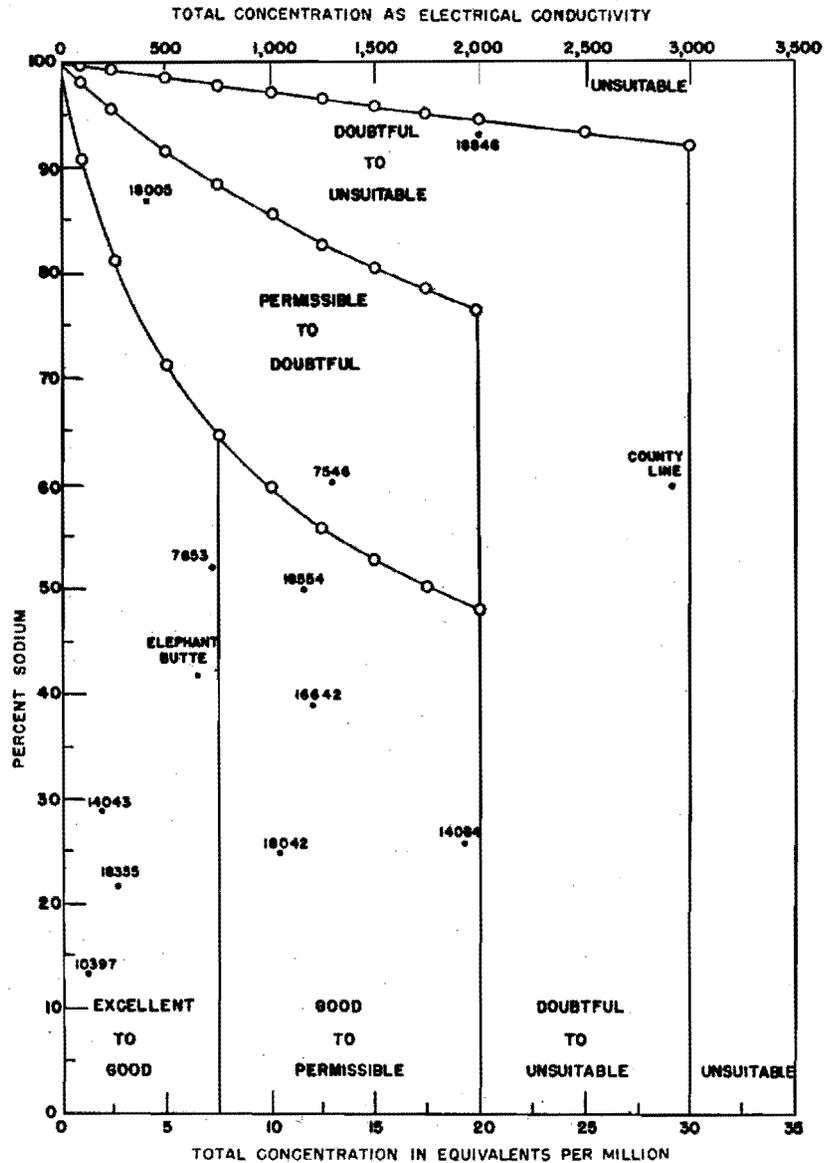


FIGURE 1.—Diagram for use in interpreting the analysis of an irrigation water.

The diagram in its present form has been in use for more than 2 years and has proved useful in the interpretation of water analyses. The horizontal axis of the diagram (fig. 1) represents total concentration in equivalents per million. The related values for electrical conductivity are shown on the upper margin. Three ordinates divide the

scale at 7.5, 20, and 30 e. p. m. into four classes of water, based on total concentration alone. The vertical axis represents the percent sodium in the irrigation water. Three curves complete the diagram and form the upper boundaries, in terms of percent sodium of the several classes of water.

TABLE 7.—Permissible limits for electrical conductivity and percent sodium of several classes of irrigation water

Classes of water		Electrical conductivity	Percent sodium
Rating	Grade		
		<i>EC</i> × 10 <sup>6</sup> at 25° C.	
1	Excellent.....	<250	<20
2	Good.....	250 to 750	20 to 40
3	Permissible.....	750 to 2,000	40 to 60
4	Doubtful.....	2,000 to 3,000	60 to 80
5	Unsuitable.....	>3,000	>80

Using the two characteristics of a water, the percent sodium and total concentration as coordinates, locate a point on the diagram. The position of the point determines the quality classification to which the water is assigned. For instance, sample No. 16642 of table 2 is from the Colorado River at Yuma and has a sodium percentage of 39 and total concentration of cations of 12.06 e. p. m. The corresponding point is located on the diagram in the area marked "good to permissible," and this designation, therefore, becomes the quality classification of the water. Points representing a number of the waters reported in the tables are shown on the diagram and are identified by the sample numbers. The points marked "Elephant Butte" and "County Line" represent annual weighted means (table 4) and are not identified by sample numbers.

#### EFFECT OF BORON CONCENTRATION ON QUALITY

The occurrence of boron in toxic concentrations in certain irrigation waters makes it necessary to consider this element in grading the quality. Scofield (32, p. 286) proposed limits for boron that have proved satisfactory and are recommended. They are shown in table 8. The crop groups suggested by Eaton (12, p. 9) are shown in table 9.

TABLE 8.—Permissible limits for boron of several classes of irrigation water

Classes of water		Sensitive crops	Semitolerant crops	Tolerant crops
Rating	Grade			
		<i>P. p. m.</i>	<i>P. p. m.</i>	<i>P. p. m.</i>
1	Excellent.....	<0.33	<0.67	<1.00
2	Good.....	0.33 to .67	0.67 to 1.33	1.00 to 2.00
3	Permissible.....	.67 to 1.00	1.33 to 2.00	2.00 to 3.00
4	Doubtful.....	1.00 to 1.25	2.00 to 2.50	3.00 to 3.75
5	Unsuitable.....	>1.25	>2.50	>3.75

TABLE 9.—*Relative tolerance of crop plants to boron*

[In each group the plants first named are considered as being more sensitive and the last named more tolerant]

Sensitive	Semitolerant	Tolerant
Lemon	Lima bean	Carrot
Grapefruit	Sweetpotato	Lettuce
Avocado	Bell pepper	Cabbage
Orange	Tomato	Turnip
Thornless blackberry	Pumpkin	Onion
Apricot	Zinnia	Broadbean
Peach	Oat	Gladliolus
Cherry	Milo	Alfalfa
Persimmon	Corn	Garden beet
Kadota fig	Wheat	Mangel
Grape (Sultanina and Malaga)	Barley	Sugar beet
Apple	Olive	Palm ( <i>Phoenix canariensis</i> )
Pear	Ragged Robin rose	Date palm ( <i>P. dactylifera</i> )
Plum	Field pea	Asparagus
American elm	Radish	Athel ( <i>Tamarix aphylla</i> )
Navy bean	Sweet pea	
Jerusalem-artichoke	Pima cotton	
Persian (English) walnut	Acala cotton	
Black walnut	Potato	
Pecan	Sunflower (native)	

## RELATIVE TOLERANCE OF CROP PLANTS TO SALT CONSTITUENTS

In most irrigated areas there are tracts of land that for one reason or another (usually poor drainage) contain excessive concentrations of salt in the soil. If such areas are farmed it is necessary to select and plant crops that are sufficiently tolerant to withstand the salt. Hayward and Magistad (20, p. 21) list the more important crop plants in the order of increasing tolerance to salt constituents in the soil solution. This list is not complete but represents the best information now available.

## DISCUSSION OF METHOD OF INTERPRETATION

Any method for the interpretation of analyses assumes that the water will be used under average conditions as related to soil, permeability, drainage, quantity of water used, climate, and crops, and is not directly applicable where unusual situations are found. The scheme here proposed is no exception, and it must be emphasized strongly that the conditions mentioned above should be considered in evaluating a water. To illustrate, water No. 18443 of table 3 is classed as unsuitable and would be so under most conditions. By copious use of the water on a very permeable, well-drained soil, a limited number of crops are grown. Conversely, water from the Colorado River, at Yuma (sample 16642), is used satisfactorily on thousands of acres of diversified crops, but where drainage is impaired salinity conditions develop quickly.

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## APPENDIX

### METHODS OF ANALYSIS

#### ELECTRICAL CONDUCTIVITY

##### APPARATUS

- (a) Wheatstone bridge suitable for electrical conductivity measurements.
- (b) Conductivity cell, either pipette or immersion type. The cell constant should be approximately 1.0 reciprocal centimeter.

##### REAGENTS

- (a) Standard potassium chloride solution, 0.01 N. This is the standard reference solution, and at 25° C. has an electrical conductivity of  $1411.8 \times 10^{-6}$  (0.0014118) (28).

##### PROCEDURE

Place four tubes of the standard potassium chloride solution (a) in a water bath. (For subsequent sets of determinations, discard the first tube of potassium chloride solution, shift the others one place,

and insert a tube of fresh solution.) Place two tubes of each sample in the bath, adjust the temperature to 25° C., and hold at this temperature for 20 to 30 minutes. If the room temperature is very far from 25° C., it is better to adjust the temperature of the bath to approximately that of the room and hold at that temperature until equilibrium is attained. Rinse the electrode in three of the tubes of potassium chloride solution, transfer it to the fourth, and read the resistance. This resistance multiplied by the known electrical conductivity of the standard reference solution at 25° C. (0.0014118) gives the cell constant,  $C_t$ , corresponding to the temperature of the observation. Rinse the electrode several times in one tube of the sample, transfer it to the other tube, and read the resistance,  $R_t$ . The electrical conductivity (EC) at 25° C. of the sample is calculated from the equation:

$$EC = \frac{C_t}{R_t}$$

This is multiplied by 1,000,000 [ $10^6$ ] and reported as  $EC \times 10^6$  at 25° C., or as EC, micromhos/cm. at 25° C.

#### HYDROGEN ION CONCENTRATION, pH

(1, p. 28)

Electrometric methods using the quinhydrone, hydrogen, or glass electrode or colorimetric methods involving indicators are applicable. The colorimetric procedure is sufficiently accurate for this work.

#### DISSOLVED SOLIDS

(4, p. 629, modified)

#### PROCEDURE

Allow the sample to stand until all the sediment has settled and filter if necessary to obtain a perfectly clear liquid. Evaporate 100 to 250 ml. to dryness in a weighed platinum dish. Dry to constant weight at 105° to 110° C., cool, and weigh. If a 100-ml. aliquot is taken, grams of residue multiplied by 10,000 equals parts per million and this value multiplied by 0.00136 equals tons per acre-foot. Report as t. a. f.

#### BORON

(47; 1, p. 87)

The principle involved in the titration procedure proposed by Foote (18) forms the basis for the electrometric titration method described below. It has long been known that when an unbuffered solution of mixed salts containing boric acid is titrated to a point near pH 7.0 and mannitol then added, the solution becomes acid. Foote observed that the quantity of alkali required to titrate the solution back to the initial pH is an accurate measure of the boron present.

The choice of apparatus for the electrometric titration of boric acid should be determined by the instruments available, the number and kind of analyses to be made, and the frequency of use. If plant material as well as water analyses are to be made, a calomel electrode should be used.

A rather simple set, involving only a galvanometer and shunt in combination with quinhydrone and calomel electrodes, is suitable for ordinary water analyses and is described by Wilcox (1, p. 87). The set described below is recommended where a large number of determinations are to be made on waters of different chloride concentration.

#### APPARATUS

- (a) Potentiometer, or a "pH meter."
- (b) Motor stirrer.
- (c) Electrodes, quinhydrone and 0.1 N calomel. Other electrode pairs that have been found satisfactory: Quinhydrone and saturated calomel; glass and saturated calomel. There are, no doubt, other electrode combinations that might be used, but their suitability should be judged on the basis of sensitivity and stability. The following statements are offered as a guide.

*Sensitivity.*—At the end point, in an unbuffered solution, a single drop of 0.0231 N sodium hydroxide should deflect the galvanometer 5 to 10 scale divisions. The galvanometer used has a sensitivity of 0.025 microampere per scale division.

*Stability.*—The end point should be stable with little, if any, more drift than occurs in the potentiometric measurement of pH. In this connection, it has been observed that traces of iron appearing as a contamination in the quinhydrone cause a slow drift to the acid side.

*Rapid equilibrium.*—Glass electrodes of very high resistance would probably be unsatisfactory, because of the slowness with which equilibrium is reached.

#### REAGENTS

- (a) Quinhydrone, reagent quality, free from heavy metals.
- (b) Bromothymol-blue indicator solution, 1 percent. Methylred may be substituted.
- (c) Sulfuric acid. Approximately 1 N.
- (d) Sulfuric acid. Approximately 0.02 N.
- (e) Sodium hydroxide. Approximately 0.5 N, carbonate-free.
- (f) Sodium hydroxide. Standard 0.0231 N, carbonate-free, 1 ml. is equivalent to 0.25 mg. B.
- (g) Boric acid solution. Dissolve 0.5716 gm. reagent grade, dry  $H_2BO_3$  in distilled water, and dilute to 1 liter. One ml. contains 0.1 mg. B. This solution is used in standardizing the NaOH (f).
- (h) Mannitol (mannite), neutral. The blank titration for 5 gm. of mannitol should not exceed 0.1 ml. of the standard 0.0231 N NaOH (g).

#### PROCEDURE

Transfer 250 ml. of the water to a 400-ml. beaker. (Pyrex borosilicate glassware can be used, but new glassware must be cleaned with acid.) The aliquot should not contain more than the equivalent of 1 mg. of elemental boron. If the sample is high in boron, take a smaller aliquot and dilute to 250 ml. with distilled water. Add a drop of bromothymol-blue indicator (b) and acidify with 1 N sulfuric acid (c), adding about 0.5 ml. in excess. Bring to a boil, stir, cautiously at first, then vigorously, to expel carbon dioxide. Cool to room temperature in a water bath.

Adjust the potentiometer and set it at pH 7.1. With the switch in the electrode circuit open, introduce the electrodes and stirrer into the solution. Start the stirrer and add carbonate-free 0.5 N sodium hydroxide (e) to approximate neutrality as shown by the bromothymol blue. Add about 0.2 gm. quinhydrone. Close the switch in the electrode circuit. The galvanometer should indicate approximate balance. Adjust with either 0.0231 N sodium hydroxide or 0.02 N sulfuric acid until the galvanometer shows no deflection. The galvanometer should be steady, showing at most only very slow drift.

This is the initial point of the titration. Add 5 gm. mannitol. If boric acid is present, the indicator will change to the acid color and the galvanometer will swing to the side indicating an excess of acid. Add standard 0.0231 N sodium hydroxide (*f*) until balance is again indicated on the galvanometer. This is the end point. Record the volume of standard sodium hydroxide used between the initial and end points of the titration.

The burette should be of such accuracy that the volume of standard alkali can be estimated to 0.01 ml. From the gross volume, a blank correction is deducted, which is determined by substituting boron-free distilled water for the sample and proceeding as directed above. The equivalency of the standard sodium hydroxide is establishing by titrating aliquots of the boric acid solution (*g*). The standard sodium hydroxide solution (*f*), if exactly 0.0231 N, is equivalent to 0.25 mg. B per ml. or, if a 250-ml. sample is used, each ml. of sodium hydroxide is equivalent to 1 p. p. m. of B. Report as p. p. m. B.

#### CALCIUM

(6, modified)

#### REAGENTS

- (a) Hydrochloric acid (1+1).
- (b) Oxalic acid solution, 1 N.
- (c) Ammonium hydroxide (1+1).
- (d) Sulfuric acid, concentrated.
- (e) Standard potassium permanganate solution, 0.05 N.

#### PROCEDURE

Acidify 250 ml. of the sample with dilute HCl (*a*) and add 1 ml. oxalic acid solution (*b*). Heat to boiling. Neutralize with ammonium hydroxide. An excess of the oxalic acid is added gradually (10 ml. is usually sufficient) with constant stirring. Add ammonium hydroxide to the hot solution until just alkaline, to methyl orange. Allow to cool for several hours and until the precipitate of calcium oxalate settles, during which time further additions of ammonium hydroxide may be necessary to keep the solution faintly alkaline to methyl orange. Filter through quantitative paper and wash thoroughly with water until free from soluble oxalates. (Designate the filtrate and washings as *solution A* and reserve for the determination of magnesium.) Puncture the tip of the filter paper and wash the precipitate into a clean beaker. (The beaker in which the calcium was precipitated can be used if free from soluble oxalates.)

Dilute 5 ml. concentrated sulfuric acid (*d*) to 50 ml. with water and pour this hot solution through the filter paper, followed by several portions of water or until the volume is approximately 100 ml. Heat nearly to boiling and titrate the liberated oxalic acid with the standard potassium permanganate solution (*e*) to a faint pink color. The filter paper is placed in the beaker toward the end of the titration. Subtract a blank, usually about 0.15 ml. If an aliquot of 250 ml. is used, the volume of standard 0.05 N potassium permanganate solution minus a blank, multiplied by 0.2, will give Ca in e. p. m. Report as Ca in e. p. m.

## MAGNESIUM

(3, p. 642, modified)

## REAGENTS

- (a) Hydrochloric acid (HCl).
- (b) Diammonium hydrogen phosphate solution, 10 percent. A fresh lot of this reagent should be prepared for each set of samples.
- (c) Ammonium hydroxide (1+1).
- (d) Ammonium hydroxide, concentrated.
- (e) Ammonium hydroxide (5+95).

## PROCEDURE

Evaporate *solution A* (see calcium procedure above) to approximately 100 ml. and cool. Acidify with hydrochloric acid (a), adding sufficient excess so that the solution will remain acid after addition of 10 ml. of diammonium hydrogen phosphate solution (b). Add ammonium hydroxide (1+1) (c), drop by drop with constant stirring, until the solution is strongly alkaline. After a few minutes add 10 ml. concentrated ammonium hydroxide (d). On the following day, filter on ashless paper and wash with dilute ammonium hydroxide (5+95) (e). Transfer the paper with the precipitate to a porcelain crucible, dry, ignite, and weigh as  $Mg_2P_2O_7$ . If a 250-ml. aliquot is used, the weight in grams of  $Mg_2P_2O_7$  multiplied by 71.85 equals Mg in e. p. m. Report as Mg in e. p. m.

## SODIUM

(5, modified)

## REAGENTS

- (a) Uranyl zinc acetate: Uranyl acetate ( $2H_2O$ ), 300 gm.; zinc acetate ( $2H_2O$ ), 900 gm.; acetic acid, 30 percent, 270 ml.; water, 2,430 ml. Transfer the salts to a large bottle and add the acetic acid and water. Shake or stir until the salts are dissolved. This may take several days. Ordinarily there is sufficient sodium as an impurity in the salts to saturate the reagent with *sodium* uranyl zinc acetate. If not, add a small quantity of a sodium salt or a gram or more of *sodium* uranyl zinc acetate precipitate. Filter the reagent just before use.
- (b) Ethyl alcohol saturated with *sodium* uranyl zinc acetate precipitate. If 1 percent by volume of concentrated acetic acid is added to the alcohol before it is saturated with the sodium triple salt, the solubility of the salt is reduced and the stability of the reagent is increased.
- (c) Ether, anhydrous, C. P.

## PROCEDURE

Transfer to a Pyrex beaker an aliquot of the sample sufficient to give 50 to 200 mg. of the triple salt (usually 10 to 20 ml.). (Should the residue become dry, silica may be dehydrated and interfere with filtration.) Cool. Add 20 ml. of the filtered uranyl zinc acetate reagent (a). Stir the solution and allow to stand 1 hour or longer, with repeated stirring if the quantity of precipitate is very small. Filter through a crucible of medium porosity. Transfer the precipitate to the filter by means of a rubber policeman and a small wash bottle filled with filtered reagent. Wash the precipitate 5 times with 2-ml. portions of the filtered reagent. It is important to have the crucible and the precipitate free of the reagent before washing with alcohol.

As soon as the reagent has drained away completely, wash the crucible 4 times with 2-ml. portions of the saturated alcohol (b). Remove the alcohol by suction and wash twice with ether (c). Continue the suction until the precipitate is dry. Allow the crucible to stand in a desiccator 1 hour and weigh. Return the crucible to the suction apparatus and wash with small portions of water until all the soluble material is dissolved and has passed through the crucible. Wash with alcohol and ether, dry, and weigh, as before. The difference between the two weighings represents the weight of the sodium precipitate. If a 10-ml. aliquot of the sample is used, the weight of the triple salt in grams multiplied by 65.02 gives Na in e. p. m. Report as Na in e. p. m.

The triple salt is represented by the formula:



The procedure, as described, reduces errors due to small quantities of phosphate.

#### POTASSIUM

(48)

#### REAGENTS

- (a) Nitric acid, N.
- (b) Trisodium cobaltinitrite solution. Prepare an aqueous solution containing 1 gm. of the salt of reagent quality in each 5 ml., allowing 5 ml. for each determination. Filter before use. The solution is stable for some time, but it is preferable to make up a fresh lot before each set of determinations.
- (c) Nitric acid, 0.01 N.
- (d) Ethyl alcohol, 95 percent.

#### PROCEDURE

Transfer 10 to 50 ml. of the sample to a Pyrex beaker. Add a few drops of dilute sodium hydroxide and evaporate to 5 to 10 ml. to eliminate ammonium ion, which interferes with the determination of potassium. Add water to 10-ml. volume and neutralize with nitric acid (a). After the salts are in solution, add 1 ml. of N nitric acid and 5 ml. of the sodium cobaltinitrite solution (b): Mix and allow to stand for 2 hours at not more than 20° C. If the quantity of precipitate is very small, it is desirable to allow the sample to stand for a longer time and at a lower temperature (5° to 15° C.). Filter through a glass or porcelain crucible of fine porosity, the tare weight of which is known, using 0.01 N nitric acid in a wash bottle to make the transfer. Wash 10 times with 2-ml. portions of the dilute nitric acid and 5 times with 2-ml. portions of alcohol. The temperature of the wash solutions should be the same as the samples. Continue the suction until the alcohol is removed and the precipitate is dry. Wipe the outside of the crucible with a cloth, dry for 1 hour at 110° C., cool in a desiccator, and weigh. If a 20-ml. aliquot of the sample is used, the weight of the precipitate in grams multiplied by 220.2 equals K in e. p. m. Report as K in e. p. m. The precipitate is represented by the formula:  $\text{K}_2\text{NaCo}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$ .

#### CARBONATE AND BICARBONATE

(4, p. 640, modified)

This determination is often referred to as "total alkalinity." It may include, in addition to carbonate and bicarbonate, other weak anions such as borate, phosphate, silicate, and other chemicals.

**PROCEDURE**

To 50 ml. of the sample, add a few drops of phenolphthalein, and if a pink color is produced, titrate with 0.05 N sulfuric acid, adding a drop every 2 or 3 seconds until the pink color disappears. Multiply the burette reading in milliliters by 2 to obtain carbonate in equivalents per million. To the colorless solution from this titration, or to the original solution if no color is produced with phenolphthalein, add 1 or 2 drops of methyl orange, and without refilling the burette continue the titration to the first change in methyl orange color and note the total reading. Designate the solution as *B* and reserve for determination of chloride. If carbonate is absent, the total burette reading in milliliters is numerically equal to bicarbonate in e. p. m. If carbonate is present, multiply the reading with phenolphthalein by 2 and subtract this figure from the total reading of the burette. The difference in milliliters is numerically equal to e. p. m. of bicarbonate. Blank determinations should be run with the reagents and corrections made if necessary. Report as  $\text{CO}_3$  and  $\text{HCO}_3$  in e. p. m.

**SULFATE**

(4, p. 642, modified)

**REAGENTS**

- (a) Concentrated hydrochloric acid.
- (b) Barium chloride solution, 10 percent.

**PROCEDURE**

Neutralize an aliquot of 200 ml. of the sample with hydrochloric acid (a) to methyl orange and add 1 ml. in excess. Heat to boiling and add an excess of barium chloride solution (b) drop by drop with constant stirring. Evaporate on the water bath for several hours, during which time the volume should be reduced to about 50 ml. After cooling, filter the precipitate of barium sulfate through fine-textured ashless filter paper and wash with water until free of chloride. Transfer the filter paper to a tared porcelain crucible and place in a cold, well-ventilated muffle furnace, which is slowly brought to a red heat. After complete ignition of the paper, remove the crucible, cool, and weigh. The weight of  $\text{BaSO}_4$  precipitate in grams multiplied by 42.84 gives  $\text{SO}_4$  in e. p. m. Report as  $\text{SO}_4$  in e. p. m.

**CHLORIDE**

(4, p. 632, modified)

**REAGENTS**

- (a) Potassium chromate indicator. Dissolve 5 gm.  $\text{K}_2\text{CrO}_4$  in water and add a solution of silver nitrate until a slight permanent red precipitate is produced. Filter and dilute to 100 ml.
- (b) Standard silver nitrate solution, 0.05 N.

**PROCEDURE**

To solution *B* from bicarbonate determination, add 1 ml. potassium chromate indicator (a) and titrate with standard silver nitrate solution (b) to the first tinge of reddish brown. Correct for the quantity of silver nitrate solution necessary to give, in 50 ml. of chloride-free water with 1 ml. of chromate indicator, the shade obtained at the end of the titration of the sample. If a 50-ml. aliquot of the sample

is taken, the net volume in milliliters is numerically equal to e. p. m. of Cl. Report as Cl in e. p. m.

#### NITROGEN IN THE FORM OF NITRATE

##### I. PHENOLDISULFONIC ACID METHOD

(4, p. 631, modified)

This method is used for water of low chloride content.

##### REAGENTS

(a) Phenoldisulfonic acid solution. Dissolve 25 gm. pure white phenol in 150 ml. of sulfuric acid, add 75 ml. fuming sulfuric acid (13 to 15 percent  $\text{SO}_3$ ), and heat at  $100^\circ\text{C}$ . for 2 hours.

(b) Standard nitrate solution. Dissolve 1.001 gm. pure potassium nitrate in 1 liter of water. This is 0.01 N, or 10 e. p. m. Designate as *solution A*. Dilute 100 ml. of *solution A* to 1 liter. This is 0.001 N. Designate as *solution B*. Evaporate 50 ml. of *solution B* to dryness in a porcelain dish; when cool, treat with 2 ml. of the phenoldisulfonic acid solution, rubbing with a glass rod to insure intimate contact, and dilute to 250 ml. (This solution is permanent.) To prepare a color standard, take 50 ml. of this solution, make alkaline with  $\text{NH}_4\text{OH}$ , and dilute to 100 ml. This standard has 0.1 e. p. m. nitrate.

(c) Standard silver sulfate solution, 0.02 N. Dissolve 3.12 gm. silver sulfate in 1 liter of water.

(d) Ammonium hydroxide (1+1).

(e) Alumina cream (39, p. 411). Dissolve 30 gm. of alum ( $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ) in 1 liter of water and filter. Pour the alum solution into a solution made by diluting 25 ml. of concentrated ammonium hydroxide to 250 ml. with water. The converse method of precipitation yields an unsatisfactory, granular product. The liquid and precipitate are transferred to a gallon bottle and diluted with water to the capacity of the bottle, and the alumina allowed to settle. It is then washed in the bottle by decantation twice a day until the supernatant liquid gives no reaction with barium chloride. This usually takes about a week. Dilute to 1 liter.

##### PROCEDURE

To 20 ml. of the sample containing  $X$  e. p. m. of chloride, as determined independently, add  $X-1$  ml. of standard silver sulfate solution, thus leaving a slight excess of Cl. Add 10 ml. of alumina cream, make to 100 ml., filter through a dry filter, discarding the first portion. Evaporate 50 ml. of the filtrate (equivalent to 10 ml. of the original sample) to dryness in a porcelain dish on a steam bath. Cool, add 2 ml. phenoldisulfonic acid solution, rub with a glass rod to insure intimate contact. Let the reagent react for 10 minutes, then add 25 ml. water, and stir until the residue is in solution. Add slowly (1+1) ammonium hydroxide until alkaline. Check with litmus paper. Make to 50 ml. and filter if necessary. Compare with the standard nitrate solution in the colorimeter in the usual manner. A comparator with a permanent glass standard may be used, but its accuracy should be verified with standard nitrate solution. Report as  $\text{NO}_3$  in e. p. m.

##### II. DEVARDA METHOD

(4, p. 28, modified)

This method is used for water of high chloride content.

##### APPARATUS

(a) Nitrogen distilling apparatus, equipped with efficient scrubber bulbs.

## REAGENTS

- (a) Standard sulfuric acid, 0.05 N.
- (b) Boric acid, 2 percent solution.
- (c) Devarda alloy.
- (d) Sodium hydroxide, saturated solution.
- (e) Bromeresol green-methyl red (BCG-MR) indicator solution.<sup>4</sup> Prepare a 0.1 percent BCG solution, adding 2 ml. 0.1 N NaOH per 0.1 gm. of indicator. Prepare a 0.1 percent MR solution in 95 percent ethyl alcohol, adding 3 ml. 0.1 N NaOH per 0.1 gm. of indicator. Mix 75 ml. BCG, 25 ml. MR, and 100 ml. 95 percent ethyl alcohol. The indicator should be gray in color in a solution containing boric acid and ammonium sulfate in concentrations equal to those encountered in the Devarda procedure. It is often necessary to add a little of one or the other of the indicators until the proper shade is obtained. The color change is from green in alkali, through gray at the end point, to red in acid solution.

## PROCEDURE

Place 50 ml. of the sample, or such volume as will contain not less than 0.2 mg. equivalent  $\text{NO}_3$ , in a Kjeldahl flask and add 2 gm. Devarda alloy. Make up to 300 ml. with distilled water, then add 2 ml. NaOH (d), allowing it to run down the side of the flask so that it does not mix with the contents at once. Connect with the distilling apparatus and rotate the flask to mix. Heat slowly at first and then at such a rate that the 200 ml. of distillate required will pass over in 1 hour. Collect the distillate in 50 ml. of boric acid solution. The ammonia is titrated with standard 0.05 N sulfuric acid, using the BCG-MR indicator. If an aliquot of 50 ml. is used, the volume of standard 0.05 N acid in ml. minus a blank correction is numerically equal to e. p. m.  $\text{NO}_3$ . Report as  $\text{NO}_3$  e. p. m.

## NITROGEN IN THE FORM OF AMMONIA

(1, p. 64)

The distillate can be collected in a boric acid solution and titrated as described under the Devarda procedure for nitrate.

## PHOSPHATE

The Chapman (7) modification of the Truog and Meyer (40) colorimetric method is recommended.

## SILICA

(4, p. 640)

## IRON AND ALUMINUM

(4, p. 640)

## FLUORIDE

A comprehensive study of methods for determining fluoride in water was made by a committee appointed by the American Water Works Association. The results were published (3) in 1941. Both the Sanchis (29) method and the Scott (36) modification of the Sanchis method were found to be reliable.

<sup>4</sup>Chapman, H. D., Univ. of Calif. Private communication.

## FACTORS AND CONSTANTS

To change an analysis reported in parts per million to equivalents per million, the concentration of each radical in parts per million is divided by its equivalent weight. The equivalent (or combining) weight of a radical is the molecular weight divided by its valence. The equivalent weights of the common constituents are:

Cation, or basic radical:	Equivalent weight	Anion, or acidic radical:	Equivalent weight
Calcium (Ca)-----	20.04	Carbonate (CO <sub>3</sub> )-----	30.005
Magnesium (Mg)-----	12.16	Bicarbonate (HCO <sub>3</sub> )-----	61.018
Sodium (Na)-----	22.997	Sulfate (SO <sub>4</sub> )-----	48.03
Potassium (K)-----	39.096	Chloride (Cl)-----	35.457
		Nitrate (NO <sub>3</sub> )-----	62.008

To change an analysis reported in equivalents per million to parts per million, the concentration of each radical in equivalents per million is multiplied by its equivalent weight.

Total hardness is defined as the calcium carbonate (CaCO<sub>3</sub>) equivalent of the calcium and magnesium content of a water. It can be calculated as follows:

As CaCO<sub>3</sub> in p. p. m. =  $50 \times (\text{Ca} + \text{Mg}, \text{ expressed in e. p. m.}), \text{ or}$

As CaCO<sub>3</sub> in grains per U. S. gallon =  $\frac{50}{17.1} \times (\text{Ca} + \text{Mg}, \text{ expressed in e. p. m.}).$

## MEASURES AND EQUIVALENTS

Grains per U. S. gallon  $\times 17.1 =$  parts per million (p. p. m.).

Parts per million  $\times 0.00136 =$  tons per acre-foot (t. a. f.).

Tons per acre-foot  $\times 735 =$  parts per million.

1 mile = 5,280 feet.

1 acre = 43,560 square feet.

Acres-foot = A unit of volume of water that would cover 1 acre to a depth of 1 foot; 43,560 cu. ft. of water.

1 acre-foot of soil weighs 4,000,000 pounds (approximate).

1 acre-foot of water weighs 2,720,000 pounds (approximate).

1 cubic foot of water per second (c. f. s.), or second foot (s. f.) =

50 miner's inches in—

Idaho, Kansas, Nebraska, Nevada, New Mexico, North Dakota, South Dakota, Utah, and southern California.

40 miner's inches in—

Arizona, California (statute), Montana, and Oregon.

38.4 miner's inches in Colorado.

Gallons per minute (g. p. m.)  $\times 0.002228 =$  cubic feet per second (c. f. s.).

1 c. f. s. for 24 hours = 1.98 acre-feet.

1 U. S. gallon =

231 cubic inches.

0.1337 cubic foot.

8.338 pounds water at 59° F. (15° C.).

58,366 grains water at 59° F. (15° C.).

1 cubic foot =

7.4805 gallons.

62.372 pounds water at 59° F. (15° C.).

1 cubic foot of soil in place weighs 70 to 105 pounds.

Soil particles, specific gravity = 2.65.

Electrical conductivity expressed as  $K \times 10^6$  at 25° C. multiplied by 10 =  $EC \times 10^6$  at 25° C.