REPORT OF COMMITTEE

ON

Method of Stating Water-Analyses.

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REPORT OF COMMITTEE ON METHOD OF STATING WATER-ANALYSES.

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To the President and Members of the
Chemical Society of Washington:

GENTLEMEN: Chemists are called upon to make analyses of natural waters, mainly from three points of view, in order to answer one of three questions, viz:

1*st.* Does the water contain any substances that render it useful for medicinal purposes?

2*d.* Does the water contain anything injurious to health?

3*d.* Is the water suitable for certain manufacturing purposes or technical uses?

The first question is asked of mineral waters, the second of potable or drinking waters, and the third of those utilized for economic purposes in the industrial arts.

The universal use of water for drinking would naturally, in the earlier stages of society, lead men to distinguish waters simply as potable or non-potable; but very soon mineral waters would be separated from the others and divided into classes, according to their predominant characters, or to those qualities appealing most strongly to the senses of taste and smell.

Thus, even in the time of Aristotle, mineral waters were classified according to the vapors they contained; and Pliny, in the first century, divides them into acidulous, sulphurous, saline, nitrous, aluminous, and bituminous, very much the same as we do to-day.

Medicinal, or mineral waters, having thus been differentiated long before the dawn of chemical science, it is not surprising to find that the earliest water-analyses are of mineral waters, while potable waters were neglected until the increasing density of population and the necessity of hygienic precaution compelled attention to their chemical characters, and, still later, the growth of industrial arts made the chemical examination of certain waters necessary to the successful prosecution of many manufactures.

Although a comparatively large number of works on mineral springs were published during the fifteenth and sixteenth centuries, none contain any account of accurate chemical examination of the waters.

About the latter part of the seventeenth century hosts of authors all over Europe are found writing enthusiastically of the mineral waters of their respective countries, and some of them detail the early experiments with regard to their analyses.

These attempts were, of course, extremely crude, and were limited mainly to their identification, as either acid or alkaline, and to the determination of such solid substances as iron, sulphur, and common salt.

The principal re-agents in use during the early part of the eighteenth century, as stated by Bergmann, were "infusion or powder of gall," "the juice of the flowers of leffer—iris," "syrup of violets," "martial vitriol," "lemon juice," "sal ammoniac," the "volatile hepar sulphur," and "vitriolic acid."

To trace the progressive advances in water-analyses would be to follow the steps in the growth of chemical analyses in general. A few general remarks in the lines of investigation already indicated will suffice here.

The first treatise relating to the use and quality of water that we find printed in America is one with the following title: *The Curiosities of Common Water, or the Advantages thereof in Curing Cholera, Intemperance, and other Maladies, by John Smith, C. M.*," was reprinted at Boston, Massachusetts, from the London edition of 1712, for Joseph Edwards, at the corner shop on the north side of Town House, in 1725. This book calls especial attention to the excellency of water as a drink, and enumerates as well its therapeutical attributes. It cures gout and hypochondriac melancholy; it benefits gravel and stone in the bladder; it makes the child grow strong in the womb, and increases the mother's milk; it stays hunger; "for there was a certain crack-brained man who, at Leyden, where Dr. Car resided in that University, pretended he could fast as long as Christ did; and it was found that he held out the time of forty days without eating any food, only he drank water and smoked tobacco."

Water is also of great use to strengthen weak children ; it prevents swelling from bruises, sickness of the stomach, shortness of breath, and vomiting ; it cures fluxes, consumptions, flushes, colic, small-pox, &c., &c.

We are instructed in this quaint volume " *How to distinguish water:*" "The way to do this is by the taste and scent; for if it have no taste nor smell, being purely fresh, not salt, nor sweetish, nor ill-scented, it is good, provided it be pure and clear, of which kind is the common water used in London, when well settled or in fair weather.

"As for those who are curious and will be at the charge, they may procure the best water for drink by distillation, either in an alembic or in a cold still used in drawing any cold water from herbs ; for no earthy nor metallic substance, nor any kind of salt, will rise in distillation ; so that the water so distilled will be pure and admirable to drink when cold, and will keep as long from stinking as any of the cold distilled water in the apothecaries' shops, according to what Dr. Quincy hath affirmed about it in his Dispensatory.

" Those who have not the convenience of distillation may boil it a little as they do for tea ; for then, when kept awhile after it is cold, it will become more fine, by suffering any mixture contained in it to settle to the bottom of the vessel wherein it is contained, and that will render it still more pure ; in short, all water that will make good lather with soap is wholesome to drink without boiling, but none else."

This book was written 175 years ago, and we still treat water by distillation, by boiling, and by soap.

In 1771 Dr. Percival made an analysis of the hard pump-water of Manchester, England.

In 1793 and 1794 Dr. Franklin called attention to the necessity of pure water in Philadelphia, because of the ravages of contagious diseases, and in his will (dated 1879) he recommends that at the end of 100 years, if not before, they be supplied by water brought in pipes from the *Wissahickon*.

Dr. Brown, of N. Y., in 1798, reports on the character of the water, and declares it to be the cause of contagious diseases, especially of yellow fever, from which the city had lately suffered.

Thomas Ewell, M. D., of Virginia, in a series of discourses on chemistry, calls attention to the necessity of purification of filthy waters, and recommends filtering.

In France, in 1808, it was decreed that no one should dig a well within 100 metres of any cemetery.

In 1824, Dr. Charles T. Jackson, State assayer of Massachusetts, speaks of examining a specimen of drinking water that contained lead; and similar reports were made by him in the following years.

The water of Cochituate lake, with view to utilizing it to supply Boston, was examined in 1834, at which time only the total residue left on evaporation was reported. In 1837, and three times in 1845, other examinations, more critical, were made, and the reports were much in the general form now used.

Prof. Boyé analyzed the water of Schuylkill river in 1842, and Prof. L. C. Phillips in 1870, and the two results were stated in the same terms.

In 1845 a report was made as to the best method of supplying the city of Boston with water, and examinations made by Dr. Jackson and Mr. Hayes stated the results of their analyses in parts per 100,000.

This report involved the permanent supply of water to Boston. Yet, in reading over the minutes of the proceedings of the water board, while considering this question, it strikes one that the chemical question was a subordinate one. For instance: "The foreign matters in this water are in such small proportions as in no way to impair its healthfulness as a drink, nor will they prove injurious in washing clothes."

In 1849 analyses of the well waters in Brooklyn, N. Y., were made by Drs. Torrey and Chilton.

The analysis of Fresh pond, that now supplies Cambridge, Mass., with water, was first made in 1853, and not again till 1872; but between 1872 and 1880 sixty-three complete examinations are reported.

The Board of Health of Troy, N. Y., in 1856, had the hydrant-water examined by Prof. Wm. Elderhorst, and in 1858 the water of two of the principal wells of that city were also examined. These examinations were conducted with metric weights and measures, but the reports were made in grains per gallon. The results reported in these analyses differ but little from those now made, except in relation to organic matter.

In this same year a chemical report of the waters supplied to London (Eng.) was made by Prof. A. W. Hoffman to the President of the General Board of Health.

In 1859 the waters of an artesian well at Louisville, Ky., were examined, and the result reported in grains per gallon, with a statement in terms of the various salts found.

Although the oldest water company of London was founded in the latter part of the sixteenth century, it was not until 1827 that attention was called to the quality of the water supplied from the Thames. In 1828 a commission was appointed to inquire into its condition, and two chemists were employed, viz., Dr. Pearson and Dr. Gardner, who made analyses of the water.

Analyses were also made in 1834, and in 1844 a royal commission was issued to inquire into the state of large towns and populous districts of England and Wales. The instructions included the examination of the water-supply in such towns and districts. Three distinguished chemists—Professors Graham, Miller, and Hoffman—aided in making the report.

The cholera visitation to England, in 1847, brought forth from the Queen the Public Health Act (11 and 12 Vict., p. 63) of 1848, whereby one-tenth of the inhabitants of any city or town, by petition to the General Board of Health, could secure a thorough sanitary inspection of such city or town. Numerous places were thus brought under observation, and the numerous cases of water pollution from various causes attracted attention everywhere. The epidemic of cholera which so soon followed (1854) was marked by some special facts in regard to water contamination, and the real importance of a close scrutiny of all sources of water supply was clearly established.

There was introduced, in 1864, in Parliament the first River Pollution Prevention Bill, but it failed to pass the Commons. The following year it was amended and again offered, and again it failed; but a royal commission was appointed to inquire into the best means of preventing the pollution of the rivers, which reported the following year. Nothing was effected, and, in 1868, a new commission was appointed, but it was not till 1876 that an act was passed which protected in any way the various sources of water-supply from contamination. At the present time a bill is before Parliament for the better protection of the rivers from pollution.

From 1872 to the present water-analyses have been of common occurrence, and individual cases are not worth especial mention. The interest in this question of the purity of water was excited by the extensive information obtained by the inquiries of the royal commission, and chemists were stimulated to seek more exact methods for determining the presence and character of organic matters. Aside from the determination of the presence of these organic compounds, the results of a chemical analysis of water to-day differs in no material respect from results of fifty years ago.

The industrial applications of water very often require chemical examination of its purity, and amendment of its quality by chemical processes. The principal arts in which the character of the water is of essential importance are dyeing, tanning, paper-making, and the management of steam-boilers. Dyeing is one of the oldest arts, and the importance of pure water is mentioned by every one who has written upon the subject. In the earlier books the terms "soft water," usually meaning rain-water, "fair water," and "clean water," are commonly used. In the later works on dyeing directions are usually given which conform more or less perfectly to the methods described in analytical chemical books of the same or an earlier date, and which are more or less complete, for the examination and purification of water. The same remarks will apply to the arts of tanning and paper-making.

So important, from an industrial point of view, does pure water become, that it is said a large paper-mill built near Holyoke, Mass., found itself unable to carry on its business profitably merely because the water supply contained more impurities than those of neighboring mills; the excess of chemicals required to correct the water costing more than the usual profit amounted to, thus necessitating an abandonment of the enterprise.

Most of the peculiar processes for the purification of water have been adopted to treat the feed-water of steam-boilers, which are so extensively used everywhere. The effect of organic impurities in any quantity is to cause the water to froth and foam, and thereby cause it to be mechanically carried along with the steam, while the presence of earthy salts causes a deposit on the shell of the boiler that prevents the passage of heat to the water, and is technically known as "scale."

The methods of prevention or cure of these difficulties are mechanical or chemical, and necessarily vary according to the nature of the water; those which are mechanical either relating to filters through which the water passes before entering the boiler, or to devices which skim off and remove the scum before it settles.

The processes that are chemical include compositions or treatment for purifying the water before entering the boiler, as the addition of lime, soda, &c., or for softening or holding in solution the scale, so that it may frequently be removed by the process called "blowing-off." For the latter purpose very many singular and arbitrary compounds have been used, such as tan-liquor, potato water, malt extract, &c., and combinations of these or similar substances with alkaline, earthy, or iron salts, for varieties of which more than 100 U. S. patents have been granted.

Bergman, the celebrated Swedish chemist of the 18th century, in his paper published about 1788, was the first to outline a systematic scheme of water-analysis. He examined water in two ways, viz., by precipitants and by evaporation, and says if accuracy is necessary, both should be used, and the analyses should be confirmed by synthesis. He begins with the examination of the physical quantities, and distinguishes the matters held in solution from those mechanically suspended. He also succeeded in making artificial mineral waters by combining the elements similar to those found in well-known springs. Dr. John Murray, in 1816, still further systematized the plan of water-analysis. He published a general formula for the analyses of mineral waters, and took the ground that the salts existing in a water need not be the same as those obtained upon evaporation, for salts viewed as incompatible may co-exist in a state of weak solution. According to Murray, the analysis of a mineral water consists in nothing more than the determination of the several acids and bases it contains, although he combined the acids and bases so found, according to their solubility, into compounds which he supposed to be the most probable actual ingredients in the water.

Berzelius contended that everything beyond the mere statement of the acids and bases being mere matters of hypothesis, nothing should be set down but the respective weights of those acids and bases.

Almost all the modern works on chemical analysis present schemes for water-analyses; among them may be mentioned, "Reid, 1836," "Parnell, 1845," "Rose, 1843–1851," "Noad, 1864," "Fresenius (5th edition), in 1870,"[1] "Sutton (3d edition), 1876," and "Church, 1877."

Although complete instructions for water-analyses are usually given, very little is said as to the method of stating results.

Henry Noad, in his manual of chemical analysis, published in 1864, treats of the arrangements of the results of the analyses. He advises that the electro-negative and electro-positive ingredients be arranged, as established by direct experiment, into binary combinations, in the ratio of their mutual affinities, the strongest acid being combined with the strongest base, paying attention, also, to the fact pointed out by Berthollet, that the force of affinity is considerably modified by the degree of solubility of the salts. He also says that the direct results should be given, and the total amount of the fixed constituents must agree with the joint amounts of the several ingredients. Such examples of analyses as are given are expressed in grains to the imperial gallon.

Perhaps it is not too strong a statement to say that the introduction of the Nessler process, for the determination of ammonia, by Messrs. Hardow and Miller, and its adaptation by Frankland and by Wanklyn, as described in their works on water-analysis, is one of the most important improvements in modern analytical chemistry.[2]

Indeed, the researches of Clark, Frankland, Armstrong, Miller, Wanklyn, and others, within recent years, have brought the subject of water-analysis into such satisfactory form that little seems to be desired in addition, except some uniformity as to the statement of results.

It may be of interest to present here two analyses made by Bergman (1777–90) as showing how some of the earlier analyses were stated. The first, an analysis of sea-water, is as follows:

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[1] The earlier editions do not appear to treat of water-analyses separately. The English edition of 1870–71 contains full instructions.

[2] The test discovered by Nessler was first applied to quantitative determination by the late Profs. Hardow and Miller, and more recently has been adopted by Dr. Frankland and by Professors Wanklyn and Chapman.—*Parkes' Hygiene, 5th edition*, 1878.

	In one Kanne (*Swedish measure*).[1] Ounces.	Grains.
Of common salt	2	433
Of salited magnesia	0	380
Of gypsum	0	48
Total	3	378

The second is of the water from a mineral spring in Denmark Parish, near Upsola, in Sweden, and is expressed as follows:

	In one Kanne.
Of aerial acid	7 cubic inches.
Of aerated iron	0¼ grains.
Of vitriol of iron	14 "
Of Glauber's salt	3½ "
Of selenite	14 "
Of common salt, at most	0¾ "
Of siliceous, nearly	0¼ "
Total	32¾ grains.

Which, as Bergman says, "considerably exceeded the weight of the residuum, which was 20½ grains;" the difference, he says, arising from the water of crystallization. The majority of the earlier analyses are expressed in the form of the most probable combination of these elements, and in many cases the entire process of the analysis is given in detail. The following list of 42 methods of statement or expression is based upon an inspection of about a thousand analyses:

With no statement as to the meaning of the figures.
As per cent.
" Parts in 100.
" Parts in 1,000.
" Parts in 10,000.
" Parts in 100,000.
" Parts in 1,000,000.
" Parts in 100 grains.
" Parts in 1,000 centimetres.
" Parts in 100 grammes, or 1 hectogram.
" Grains in 64 cubic inches.
" Grains in 100 cubic inches.
" Grains in 200 cubic inches.
" Grains to the pint.
" Grains in wine pint.
" Grains in imperial pint.
" Troy grains in pint.
" Grains in 5 pints.
" Grains in 28 Parisian pints.
" Grains in 16 ounces of water.
" Grains in 20 ounces of water.
As Grains in one quart.
" Grains in three quarts.
" Grains in gallon.
" Grains in gallon of 231 cu. in.
" Grains in wine gallon.
" Grains in U. S. gallon.
" Grains in American gallon.
" Grains in standard gallon.
" Grains in gal. of 70,000 grains.
" Grains in imperial gallon.
" Grains in about 7 gallons.
" Grains in 1,000 parts.
" Grains in 1,000.
" Grains in 6,000.
" Grains in 8,000.
" Grains in 50,000, or nearly 7 pts.
" Grains per litre.
" Pounds in 100,000 U. S. gallons.
" Grammes per litre.
" Grammes to 1,000 grammes.
" Milligrammes per litre.

1 A Swedish kanne is given as about 6 English pints, 100 cubic inches, or 3 quarts.

In some places three scales were found in the same table, a part expressed as grains per gallon, another part as milligrammes per litre and the hardness in Clark's degrees. These can nearly all be reduced to one or another of four common methods of expression as detailed by Nichols, viz:

1st. Grains per English or imperial gallon (277 cubic inches or 10 lbs. = 70,000 grains of pure water).

2d. In grains to the U. S. or wine gallon (231 cubic inches = 58,372+ grains of pure water).

3d. On a decimal basis as parts per 100, 1,000, 1,000,000, &c. This is generally used in France and Germany, also in the reports of the "Rivers Pollution Committee of Great Britain," and in this country in reports of the "National Board of Health," and of many State Boards of Health.

4th. As so many milligrammes to the litre. (This would be the same as parts in 1,000,000 if the water had the same density as pure water, *i. e.*, if the litre actually weighed 1,000 grammes).

The variation of specific gravity in the case of potable waters would be of little account, but in the case of waters more highly mineralized the difference between parts per million and milligrammes per litre would be too great to be disregarded, and precludes the combination in the same analyses of measure by weight and measure by volume in any way, if analyses are to be made exact and mutually comparable. Of about eight hundred analyses of mineral waters of the United States, 60% were expressed according to the second method, about 7% in the English or first method, and about 3% according to the fourth method, while 22% are expressed in the decimal or third method.

After careful consideration the Committee would recommend the following conclusions, viz:

1st. That water analyses be uniformly reported in parts per million or milligrammes per kilogramme, with the temperature stated, and that Clark's scale and all other systems be abandoned.[a]

2d. That all analyses should be stated in terms of the radicals found, whether elementary or compound.[b]

3d. The constituent radicals should be arranged in electro-chemical series, the positive radicals first.

4th. The combinations deemed most probable by the chemist making the analysis should be stated, both by symbols and by name.[c]

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WASHINGTON, D. C., *Feb. 11th*, 1886.

NOTES ON RECOMMENDATIONS.

a. The Committee were unable to agree with the recommendation of the Society of Public Analysts of London, that water analyses should be reported in grains per gallon, because the Committee believe that parts per million will be better understood by non-professional readers than grains per gallon, which, in themselves, are incommensurable quantities, because not of the same denomination; while to professional chemists the decimal form of report is much preferable. The general form recommended by the London society is herewith appended for the benefit of those to whom their reports are not readily accessible:

Form in which analyses should be reported.

(As recommended by committee of the Society of Public Analysts of London.—*The Analyst*, London, vol. 6, 1881, p. 139).

	Grains per gallon
Description of sample,	
Drawn,	
Temperature when drawn,	
Appearance in two-foot tube,	
Smell when heated to 100° F.	
Chlorine in chlorides,	
Phosphoric acid in phosphates,	
Nitrogen in nitrates,	
Ammonia,	
Albuminoid ammonia,	
Oxygen absorbed in fifteen minutes at 80° F.	
Oxygen absorbed in four hours at 80° F.	
Hardness before boiling (Clark's scale),	
Hardness after boiling (Clark's scale),	
Total solid matters dried at 212° F.	
Microscopical appearance of deposit,	
Remarks,	

b. By terms of the radical *found* is to be understood the immediate results of the actual analysis. For example: It is usual to determine ammonia as such, and it should be stated as ammonia (NH_3); if nitrogen (N) alone for any reason is found as an element, it should be so stated; if carbonic acid (CO_2) is found as such, put it down so, in order that any one examining the analytical results may have the same facts as the chemist who made the analyses.

c. The Committee have been careful to avoid any recommendation as to the manner of combination of the analytical results, because the views of chemists would probably differ so much that uniformity in this respect could not at present be obtained. The use of symbols is recommended to avoid obscurity in compounds, such as the salts of iron, etc.