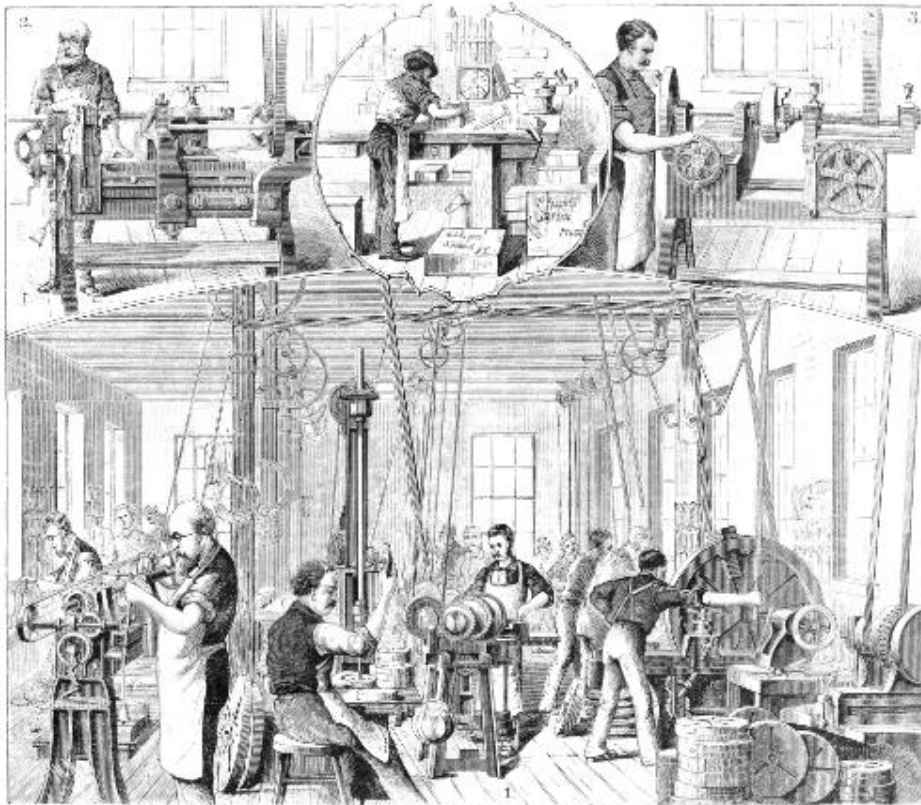


Consensus Organizations – Before EPA and the Path to Today

William Lipps
Analytical and Measurement Division
August 2020

Prior to the industrial age, manufacturing was a craftsman approach

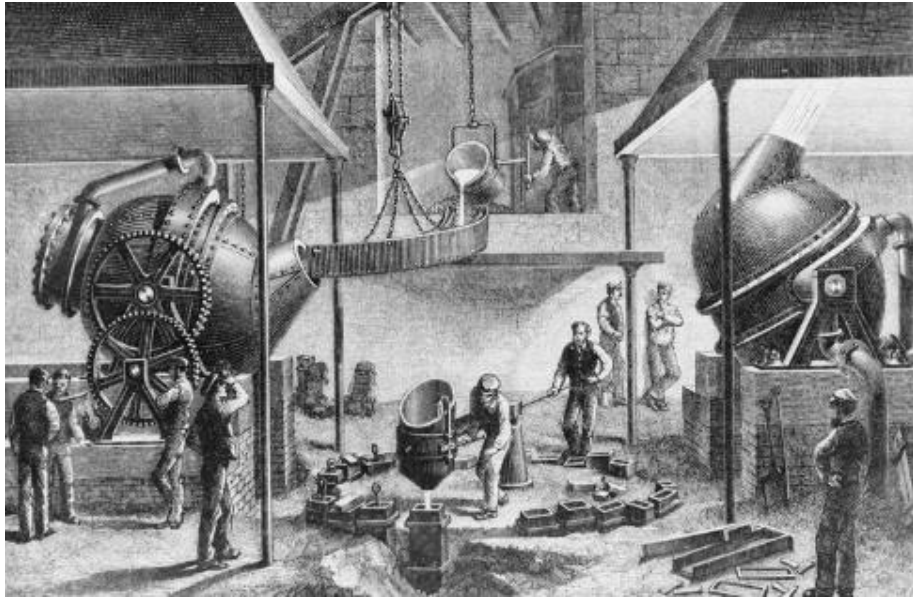


THE MANUFACTURE OF UNIVERSAL CHUCKS—THE E. HORTON & SON COMPANY WINDSOR LOCKS, CONN.

Artisans had no need or equipment to:

- Measure tensile strength
- Chemical composition
- Meet pre-defined specifications

The industrial age opened the need for specifications and standardization



Universal History Archive/Getty Images



Mass production  Craftsman



Manufacturers encountered quality problems with raw materials and end products



Each manufacturer issued detailed descriptions of required materials needed.



Pages and pages of required physical or chemical properties



Testing between labs may provide different results



Samples provided could result in lots being rejected because of differences in methods or expectations

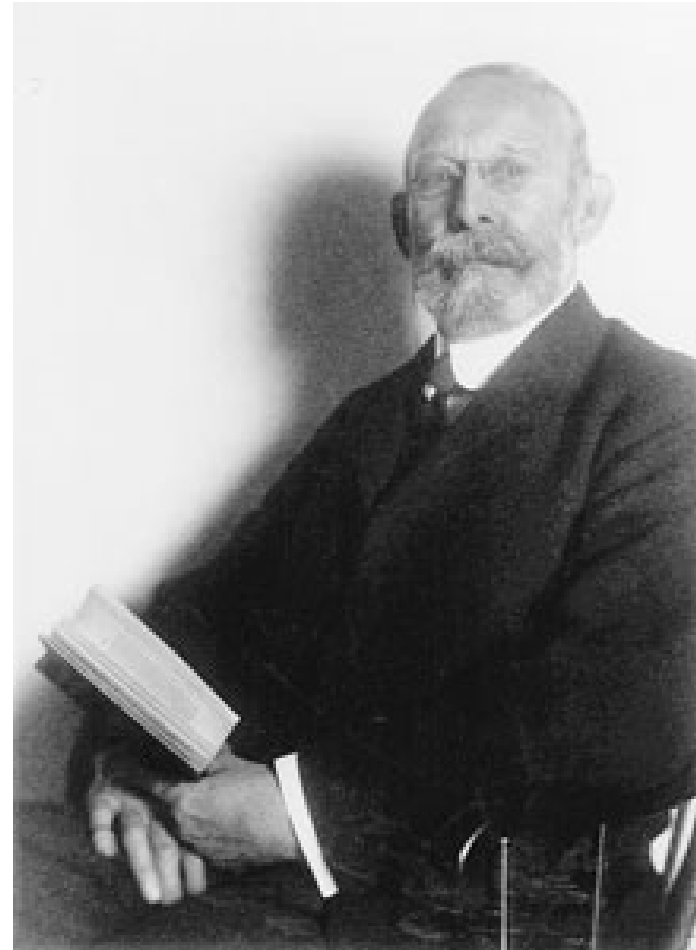
Suppliers resisted standard specifications and test methods for fear of customer rejection

- Industrywide specifications were unheard of or highly customized
- Buyers were unable to ensure uniformity
- Buyers could find reasons to complain – no pre-agreed specifications

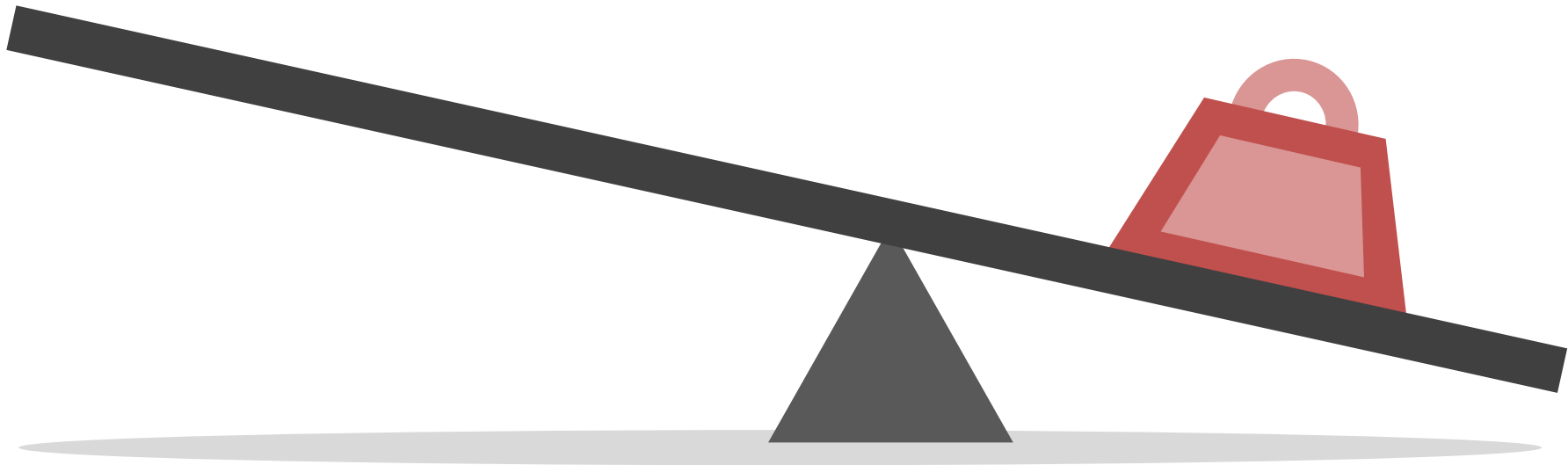


Enter Charles Benjamin Dudley and the formation of ASTM

- **ASTM established in 1898 to bring together suppliers and customers in Technical Committees**
- **Committees provide representatives of every interested party**
- **Specifications and Methods established by consensus**
- **Created periodic review, revisions and updates as part of the process**



In 1908, ASTM set rules regarding committee balance, 2/3 majority vote, and weighting of negatives



The basic structure of checks and balances, designed to ensure fairness of standards, is still in place today

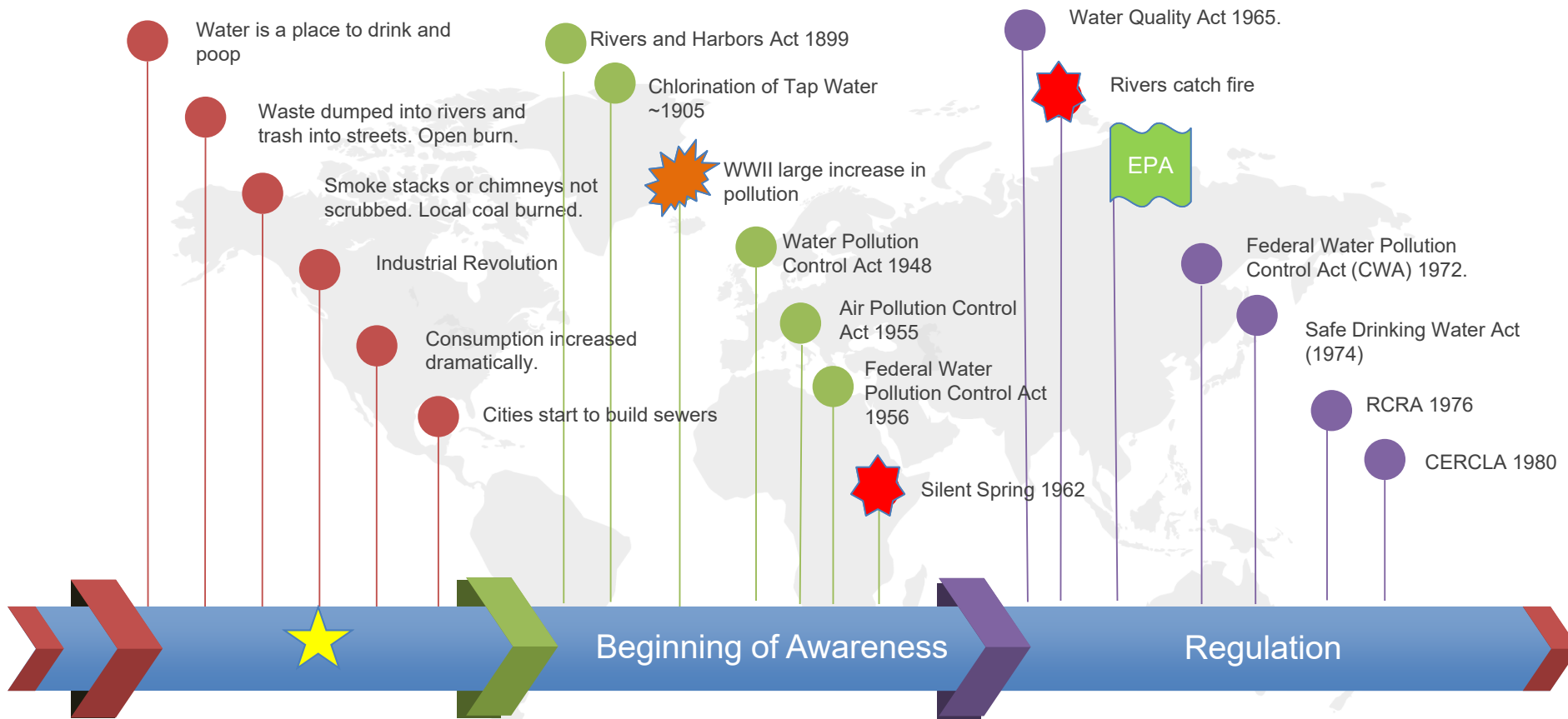
Interesting to note is that the NBS, established in 1901, met greater resistance with industry



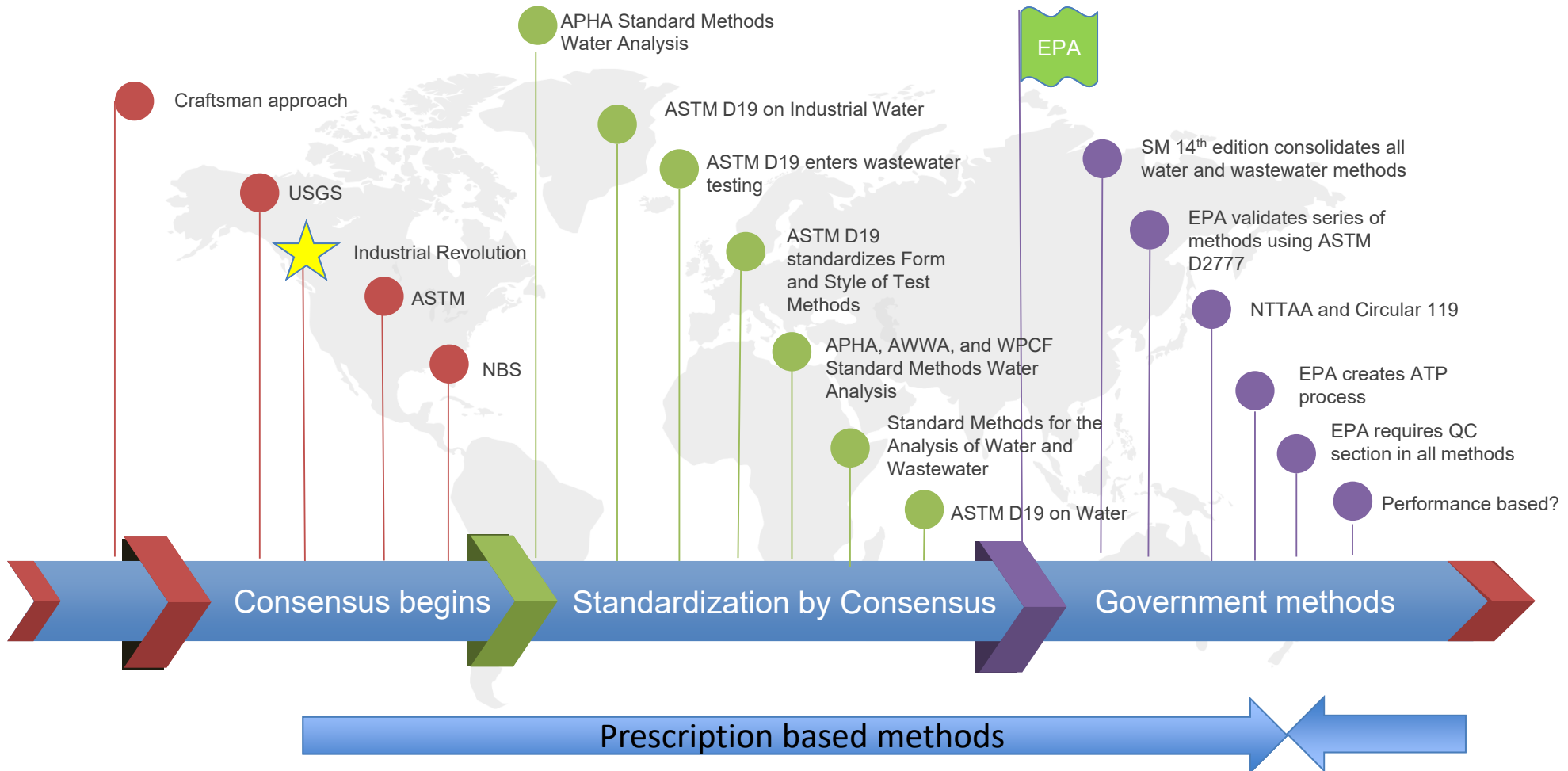
Manufacturers and Engineers
resisted US plan to duplicate
European government forced
national standards

Result = **uniquely American**
system of Voluntary Consensus
Standard Development

Timeline for awareness of environmental issues in the US



Timeline for Standards Development for the Analysis of water in the environment



Progression of Standard Methods over time



EPA

SUSPENDED MATTER. 50 110

DETERMINATION WITH GOOCH CRUCIBLE.

Reagent.—Prepare a dilute cream of asbestos fibre which has been finely shredded, thoroughly ignited, treated with strong hydrochloric acid for at least 12 hours, and washed with distilled water till free from acid.

Procedure.—1. Prepare a mat of the asbestos fibre 1/16 inch thick in a Gooch crucible. Dry it in an oven at 103 or 180° C., cool and weigh. Filter 1,000 cc. of samples having a turbidity of 50 parts per million or less. If the turbidity is higher use sufficient water to obtain 50 to 100 mg. of suspended matter. Dry for one hour at 103 or 180° C., cool and weigh. Report the temperature at which the residue was dried. If 1,000 cc. is filtered the increase in weight expressed in milligrams is equal to parts per million of suspended matter.



Sample holding time, then and now

INTERVAL BEFORE ANALYSIS.

In general, the shorter the time elapsing between the collection and the analysis of a sample the more reliable will be the analytical results. Under many conditions analyses made in the field are to be commended, as data so obtained are frequently preferable to data obtained in a distant laboratory after the composition of the water has changed.

The time that may be allowed to elapse between the collection of a sample and the beginning of its analysis cannot be stated definitely. It depends on the character of the sample, the examinations to be made, and other conditions. The following are suggested as fairly reasonable maximum limits.

Physical and chemical analysis.

Ground waters	72 hours
Fairly pure surface waters	48 "
Polluted surface waters	12 "
Sewage effluents	6 "
Raw sewages	6 "

Microscopical examination.

Ground waters	72 hours
Fairly pure surface waters	24 "
Waters containing fragile organisms	Immediate examination

Bacteriological examination.

Samples kept at less than 10°C.	24 hours
---	----------

TABLE 10011. Summary of Water Sampling and Retention Requirements*

Determinative	Container†	Maximum Sample Size, mL	Sample Type‡	Preservation	Minimum Storage	Regulatory§
Acidity	P, GBU, TP	100	f	Cool, 0-6°C	24 h	14 d
Alkalinity	P, G, TP	250	g	Cool, 0-6°C	24 h	14 d
BOD	P, G, TP	1000	g, c	Cool, 0-6°C	6 h	48 h
Boron	F, P (PTEE) or quartz	1000	g, c	HNO ₃ to pH<2	28 d	6 months
Bromide	P, G, TP	100	g, c	None required	28 d	28 d
Carbon, organic, total	GBU, P, TP	100	g, c	Analyze immediately, or cool to 0°C and add HCl, H ₂ O ₂ , or H ₂ SO ₄ to pH<2	7 d	28 d
Carbon dioxide	P, G	100	g	Analyze immediately	0.25 h	N.S.
COO	P, G, TP	100	g, c	Analyze as soon as possible, or add H ₂ SO ₄ to pH<2; Cool, 0-6°C	7 d	28 d
Chloride	P, G, TP	20	g, c	None required	N.S.	28 d
Chlorine, free, residual	P, G	500	g	Analyze immediately	0.25 h	0.25 h
Chlorine dioxide	P, G	500	g	Analyze immediately	0.25 h	N.S.
Chlorophyll	P, G	500	g	Chilled, dark, 0-6°C (Do not store in frost-free freezer)	24-48 h	N.S.
Color	P, G, TP	500	g, c	Cool, 0-6°C	24 h	48 h
Specific conductance	P, G, TP	500	g, c	Cool, 0-6°C	24 h	24 h
Cyanide						
Total	P, G, TP	1000	g, c	Analyze within 15 min. Add NaOH to pH>12 if sample is to be stored; Cool, 0-6°C, in dark. Add free chlorine if residual chlorine present.	24 h	14 d, 24 h if residue present
Arsenite to chlorite	P, G, TP	1000	g, c	Barium acetate chloride with thioacetate and cool 0-6°C	none	14 d, 24 h if residue present
Fluoride	P	100	g, c	None required	28 d	28 d
Hardness	P, G, TP	100	g, c	Add HNO ₃ or H ₂ SO ₄ to pH<2	6 months	6 months
Iron	P, G	500	g	Analyze immediately	0.25 h	N.S.
Merch	PVA, G(A), TP (A)	1000	g, c	For dissolved metals filter immediately, add HNO ₃ to pH<2	6 months	6 months
Chemical VI	HA, G(A), TP (A)	250	g	Cool, 0-6°C; pH 5.5-9.2; ammonium sulfate buffer procedure as specified in method 500.0; to cool to 0-6°C	28 d	28 d
Copper by colorimetry	— ^a	—	g, c	—	—	—
Mercury	PVA, G(A), TP(A)	500	g, c	Add HNO ₃ to pH<2; Cool, 0-6°C	28 d	28 d
Nitrogen						
Ammonia	P, G, TP	500	g, c	Analyze as soon as possible or add H ₂ SO ₄ to pH<2; Cool, 0-6°C	7 d	28 d
Nitrite	P, G, TP	100	g, c	Analyze as soon as possible; Cool, 0-6°C	48 h	48 h (14 d for chlorinated samples)
Nitrate + nitrite	P, G, TP	250	g, c	Add H ₂ SO ₄ to pH<2; Cool, 0-6°C	1-2 d	28 d
Nitrate	P, G, TP	100	g, c	Analyze as soon as possible; Cool, 0-6°C	none	48 h
Organic phosphorus	P, G, TP	500	g, c	Cool, 0-6°C; add H ₂ SO ₄ to pH<2	7 d	28 d
Oxide	G	500	g	Analyze as soon as possible; Cool, 0-6°C	6 h	24 h (EPA Method for drinking water)
Oil and grease	G, wide-mouth cardboard	1000	g	Add HCl to H ₂ SO ₄ to pH<2; Cool, 0-6°C	28 d	28 d

* EPA 816/0-80-010-10115-01M/RW 7837-008

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Turbidity with a Pt wire, or do you prefer candles?

PLATINUM WIRE METHOD.⁴

This method requires a rod with a platinum wire 1 mm. in diameter inserted in it about 1 inch from one end of the rod and projecting from it at a right angle at least 25 mm. Near the other end of the rod, at a distance of 1.2 meters from the platinum wire, a small ring shall be placed directly above the wire through which, with his eye directly above the ring, the observer shall look when making the examination.

The rod shall be graduated as follows: The graduation mark of 100 shall be placed on the rod at a distance of 100 mm. from the center of the wire. Other graduations shall be made according to Table 1, which is based on the best obtainable data. The distances recorded in Table 1 are intended to be such that when the water is diluted the turbidity readings will decrease in the same proportion as the percentage of the original water in the mixture. These graduations are those on what is known as the U. S. Geological Survey Turbidity Rod of 1902.¹⁰⁸

TURBIDIMETRIC METHOD.

Several forms of turbidimeter or diaphanometer⁷³ have been suggested for use. The simplest and most satisfactory form is the candle turbidimeter.¹⁰⁸ This consists of a graduated glass tube with a flat polished bottom, enclosed in a metal case. This is supported over an English standard candle and so arranged that one may look vertically down through the tube at the flame of the candle. The observation is made by pouring the sample of water into the tube until the image of the flame of the candle just disappears from view. Care shall be taken not to allow soot or moisture to accumulate on the lower side of the glass bottom of the tube so as to interfere with the accuracy of the observations. The graduations on the tube correspond to turbidities produced in distilled water by certain numbers of parts per million of silica standard. In order to insure uniform results it is necessary to have the distance between the top rim of the candle and the bottom of the tube constant, and this distance shall be 7.6 cm. or 3 inches. The observations shall be made in a darkened room or with a black cloth over the head.

It is allowable to substitute for the candle an electric light. Calibrate the apparatus to correspond with the United States Geological Survey scale. The figures in Table 2 on page 8 are believed to be approximately correct for the candle turbidimeter but should be checked by the experimenter. It is allowable to calibrate the tube of the instrument with waters of known turbidity prepared by making a series of dilutions of the silica standard with distilled water. From the figures obtained in calibrating plot a curve from which the turbidity of a sample may be read when the depth of water in the tube has been obtained.

Pt-Co Color from 1912 to present

COLOR 9

COLOR.

The "color," or the "true color," of water shall be considered the color that is due only to substances in solution; that is, it is the color of the water after the suspended matter has been removed. In stating results the word "color" shall mean the "true color" unless otherwise designated.

The "apparent color" shall be considered as including not only the true color but also any color produced by substances in suspension. It is the color of the original unfiltered sample.

The platinum-cobalt method of measuring color shall be considered as the standard, and the unit of color shall be that produced by 1 part per million of platinum.

COMPARISON WITH PLATINUM-COBALT STANDARDS.*

Reagents.—Dissolve 1.246 grams of potassium platonic chloride ($\text{PtCl}_2\cdot 2\text{KCl}$), containing 0.5 gram platinum, and 1.00 gram crystallized cobalt chloride ($\text{CoCl}_2\cdot 6\text{H}_2\text{O}$), containing 0.25 gram of cobalt, in water with 100 cc. concentrated hydrochloric acid, and dilute to 1 liter with distilled water. This solution has a color of 500. Dilute this solution with distilled water in 50 cc. Nessler tubes to prepare standards having colors of 0, 5, 10, 15, 20, 25, 30, 35, 40, 50, 60, and 70. Keep these standards in Nessler tubes of such diameter that the graduation mark is between 20 and 25 cm. above the bottom and of such uniformity that they match within such limit that the distance from the bottom to the graduation mark of the longest tube shall not exceed that of the shortest tube by more than 6 mm. Protect the tubes from dust and light when not in use.

Procedure.—The color of a sample shall be observed by filling a standard Nessler tube to the height equal to that in the standard tubes with the sample and by comparing it with the standards. The observation shall be made by looking vertically downward through the tubes upon a white or mirrored surface placed at such angle that light is reflected upward through the column of liquid.

Water that has a color greater than 70 shall be diluted before making the comparison, in order that no difficulties may be encountered in matching the hues.

Water containing matter in suspension shall be filtered, before the color observation is made, until no visible turbidity remains.

2120 COLOR*

2120 A. Introduction

Color in surface and ground waters results primarily from the presence of natural organic matter, particularly aquatic humic matter. Humic matter consists of humic and fulvic acids; both cause a yellow-brown color. Humic acids give a more intense color, and the presence of iron intensifies the color through the formation of soluble ferric humates. Suspended particles, especially colloidal-size particles such as clays, algae, iron and manganese oxides, give waters an appearance of color; they should be removed before measurement. Industrial wastewaters can contain lignins, tannins, dyes, and other organic and inorganic chemicals that cause color. Humic materials and the color caused by these materials are removed from potable water supplies for aesthetic reasons and for health reasons because they are precursors in the formation of disinfection by-products. Color also is removed to make water suitable for industrial applications. Colored industrial wastewaters may require color removal before discharge into watercourses.

1. Terminology

The term "color" is used here to mean true color, that is, the color of water from which turbidity has been removed. Colloidal and larger suspended particles scatter light interfering with the determination of true color measurements in Method 2120B and in the spectrophotometric procedures of Methods 2120C-F. The term "apparent color" includes not only color due to substances

in solution, but also that due to suspended matter. Apparent color is determined on the original sample without filtration. In some waters and wastewaters, apparent color is contributed principally by colloidal or suspended matter.

2. Selection of Method

Methods 2120B and C are applicable to measurement of color caused primarily by natural organic matter. The measurements apply to all surface and ground waters; wastewaters, both domestic and industrial, and especially potable waters. While all methods (2120B-F) are suitable for true color measurements, for apparent color measurements use only 2120B; in such cases, determine both true color and apparent color. For comparison among laboratories, correlate 2120B with 2120C. Methods 2120D-F allow color measurement for any dissolved chemical that gives the appearance of color in the visible-light wavelength range. They are especially applicable to colored waters and wastewaters having color characteristics different from, but not excluding, platinum-cobalt standards.

3. Bibliography

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CHRISTMAN, R.F. & M. GUSTAFSON. 1966. Chemical nature of organic color in water. *J. Amer. Water Works Assoc.* 58:723.
FRISMAN, L.M. 1965. Organic Geochemistry of Natural Waters. MartinusNijhoffDr. W. Junk Publishers, Dordrecht, Netherlands.
SWEENEY, C.N., P.O. MCCURRY & G.F. FOSTER. 1991. Chemistry for Environmental Engineering, 4th ed. McGraw-Hill, Inc., New York, N.Y.

2120 B. Visual Comparison Method

1. General Discussion

a. Principle. Color is determined by visual comparison of the sample with known concentrations of colored solutions. Comparison also may be made with special, properly calibrated glass color disks. The platinum-cobalt method of measuring color is the standard method, the unit of color being that produced by 1 mg platinum/L in the form of the chloro-platinate ion. The ratio of cobalt to platinum given (2120B.4) matches the color of natural waters.

b. Application. The platinum-cobalt method is applicable to natural waters, potable waters, and to wastewaters, both domestic and industrial.

c. Interference. Even a slight turbidity causes the apparent color to be noticeably higher than the true color; therefore remove turbidity by the filtration procedure described in 2120C.

The color value of water is extremely pH-dependent and invariably increases as the pH of the water is raised. When reporting a color value, specify the pH at which color is

determined. For research purposes, or when color values are to be compared among laboratories, determine the color response of a given water over a wide range of pH values.¹

d. Field method. Because the platinum-cobalt standard method is not convenient for field use, compare water color with that of glass disks held at the end of metal tubes containing glass comparator tubes filled with sample and colorless distilled water. Match sample color with the color of the tube of clear water plus the calibrated colored glass when viewed by looking toward a white surface. Calibrate each disk to correspond with the colors on the platinum-cobalt scale. The glass disks give results in substantial agreement with those obtained by the platinum-cobalt method and their use is recognized in a standard field procedure.

e. Nonstandard laboratory methods. Using glass disks or liquids other than water as standards for laboratory work is permissible only if these have been individually calibrated against platinum-cobalt standards. Waters of highly unusual color, such as those that may occur by mixtures with certain

* Approved by Standard Methods Committee, 2001. Editorial revision, 2011.
Joint Task Group: 21st Edition—James R. Edwards (chair), Perry J. Brant, Brian A. Donney, Dennis A. Lopic, David J. Pezansky, Mike J. Saito, Jeff Truesdell.

<https://doi.org/10.2105/2010MWW.282.011>

Hardness by the soap method anyone?

TOTAL HARDNESS BY CALCULATION.

The most accurate method of ascertaining total hardness is to compute it from the results of determinations of calcium and magnesium in the sample. (See methods, pp. 57-58.) Iron and other metals must be included in the calculation if they are present in significant amounts. Total hardness as CaCO_3 equals 2.5 Ca plus 4.1 Mg.

TOTAL HARDNESS BY SOAP METHOD.^{1,11b}

The determination of hardness by the soap method roughly approximates the amount of calcium and magnesium in a water, though it actually measures the soap-consuming power of the water.

Reagents.—1. Standard calcium chloride solution. Dissolve 0.2 gram of pure calcite (calcium carbonate) in a little dilute hydrochloric acid, being careful to avoid loss of solution by spattering. Evaporate the solution to dryness several times with distilled water to expel excess of acid. Dissolve the residue in distilled water and dilute the solution to 1 liter. One cc. of this dilution is equivalent to 0.2 mg. of calcium carbonate.

2. Standard soap solution. Dissolve 100 grams of dry white Castile soap in 1 liter of 80 per cent alcohol, and allow this



2340 HARDNESS*

2340 A. Introduction

1. Terminology

Originally, water hardness was understood to be a measure of the capacity of water to precipitate soap. Soap is precipitated chiefly by the calcium and magnesium ions present. Other polyvalent cations also may precipitate soap, but they often are in complex forms, frequently with organic constituents, and their role in water hardness may be minimal and difficult to define. In conformity with current practice, total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate, in milligrams per liter.

When hardness numerically is greater than the sum of carbonate and bicarbonate alkalinity, that amount of hardness equivalent to the total alkalinity is called "carbonate hardness"; the amount of hardness in excess of this is called "noncarbonate hardness." When the hardness numerically is equal to or less than the sum of carbonate and bicarbonate alkalinity, all hard-

ness is carbonate hardness and noncarbonate hardness is absent. The hardness may range from zero to hundreds of milligrams per liter, depending on the source and treatment to which the water has been subjected.

2. Selection of Method

Two methods are presented. Method B, hardness by calculation, is applicable to all waters and yields the higher accuracy. If a mineral analysis is performed, hardness by calculation can be reported. Method C, the EDTA titration method, measures the calcium and magnesium ions and may be applied with appropriate modification to any kind of water. The procedure described affords a means of rapid analysis.

3. Reporting Results

When reporting hardness, state the method used, for example, "hardness (calc.)" or "hardness (EDTA)."

* Approved by Standard Methods Committee, 1997. Editorial revision, 2011.

2340 B. Hardness by Calculation

1. Discussion

The preferred method for determining hardness is to compute it from the results of separate determinations of calcium and magnesium.

2. Calculation

Hardness, as equivalent CaCO_3 , L =
 $2.497[\text{Ca, mg/L}] + 4.118[\text{Mg, mg/L}]$

2340 C. EDTA Titrimetric Method

1. General Discussion

a. Principle: Ethylenediaminetetraacetic acid and its sodium salts (abbreviated EDTA) form a chelated soluble complex when added to a solution of certain metal cations. If a small amount of a dye such as Eriochrome Black T or Calmagite is added to an aqueous solution containing calcium and magnesium ions at a pH of 10.0 ± 0.1 , the solution becomes wine red. If EDTA is added as a titrant, the calcium and magnesium will be complexed, and when all of the magnesium and calcium has been complexed the solution turns from wine red to blue, marking the endpoint of the titration. Magnesium ion must be present to yield a satisfactory endpoint. To ensure this, a small amount of complexometrically neutral magnesium salt of EDTA is added to the buffer; this automatically introduces sufficient magnesium and obviates the need for a blank correction.

The sharpness of the endpoint increases with increasing pH. However, the pH cannot be increased indefinitely because of the

danger of precipitating calcium carbonate, CaCO_3 , or magnesium hydroxide, $\text{Mg}(\text{OH})_2$, and because the dye changes color at high pH values. The specified pH of 10.0 ± 0.1 is a satisfactory compromise. A limit of 5 min is set for the duration of the titration to minimize the tendency toward CaCO_3 precipitation.

b. Interference: Some metal ions interfere by causing fading or indistinct endpoints or by stoichiometric consumption of EDTA. Reduce this interference by adding certain inhibitors before titration. MgCDDTA [see 2340C.2b3)], selectively complexes heavy metals, releases magnesium into the sample, and may be used as a substitute for toxic or malodorous inhibitors. It is useful only when the magnesium substituted for heavy metals does not contribute significantly to the total hardness. With heavy metal or polyphosphate concentrations below those indicated in Table 2340.I, use Inhibitor I or II. When higher concentrations of heavy metals are present, determine calcium and magnesium by a non-EDTA method (see Sections 3500-Ca and 3500-Mg) and obtain hardness by calculation. The values in Table 2340.I are

<https://doi.org/10.2195/SMWW.2882.025>

In the old days, you distilled ammonia-N and did TKN for organic nitrogen. Oh, wait..... almost the same

ORGANIC NITROGEN, 4500-N_{org}

Procedure for water.—Boil 500 cc. of the sample in a round-bottomed flask to remove ammonia nitrogen. This usually causes the loss of 200 cc. of the sample, which may be collected for the determination of ammonia nitrogen. Add 5 cc. of nitrogen-free concentrated sulfuric acid and a small piece of ignited pumice. Mix by shaking and place over a flame under a hood. Digest until copious fumes of sulfuric acid are given off and the liquid finally becomes colorless or pale straw color. Remove from the flame, and add potassium permanganate crystals in small portions until a heavy green precipitate persists in the liquid. Cool. Dilute to about 300 cc. with ammonia-free water. Make alkaline with 10 per cent ammonia-free sodium hydroxide. Distill the ammonia, collect the distillate in Nessler tubes, Nesslerize, and compare with standards as described (pp. 16-18).

First procedure for sewage¹.—Distill the ammonia nitrogen directly from 100 cc. or less of the sample, diluted to 500 cc. with nitrogen-free water. Collect the distillate and determine the ammonia nitrogen in it. Add 5 cc. of nitrogen-free sulfuric acid and 1 cc. of 10 per cent nitrogen-free copper sulfate, and digest the liquid for half an hour after it has become colorless or pale straw color. Add 0.5 gram of potassium permanganate crystals to the hot acid solution, and dilute to 500 cc. with ammonia-free water. Dilute 10 cc. or more of this liquid, in a Kjeldahl distilling flask, to about 300 cc. with ammonia-free water. Make alkaline with 10 per cent sodium hydroxide, distill, and Nesslerize. With some samples direct Nesslerization may be used. (See p. 19.)

In this determination care must be taken to digest thoroughly, to add potassium permanganate to the point of precipitation, to sample carefully after dilution, and to add enough sodium hydroxide to insure the separation of the ammonia from the precipitated manganese hydroxide. Potassium permanganate should not be added during digestion because it causes loss of nitrogen.

Second procedure for sewage.—Omit the separation of ammonia nitrogen and determine the ammonia nitrogen and organic nitrogen together. Determine the ammonia nitrogen in a separate sample

4500-N_{org} NITROGEN (ORGANIC)*

4500-N_{org} A. Introduction

1. Selection of Method

The Kjeldahl methods (4500-N_{org} B and C) determine nitrogen in the inorganic state. They fail to account for nitrogen in the form of azide, uric, urea, hydrazine, nitrate, nitrite, nitrile, nitro, nitroso, oxime, and semi-carbazone. "Kjeldahl nitrogen" is the sum of organic nitrogen and ammonia nitrogen.

The major factor that influences the selection of a macro- or semi-micro-Kjeldahl method to determine organic nitrogen is its concentration. The macro-Kjeldahl method is applicable for samples containing either low or high concentrations of organic nitrogen but requires a relatively large sample volume for low concentrations. In the semi-micro-Kjeldahl method, which is applicable to samples containing high concentrations of organic nitrogen, the sample volume should be chosen to contain organic plus ammonia nitrogen in the range of 0.2 to 2 mg.

The block digestion method (4500-N_{org} D) is a micro method with an automated analysis step capable of measuring organic nitrogen as low as 0.1 mg/L when blanks are carefully controlled.

2. Storage of Samples

The most reliable results are obtained on fresh samples. If an immediate analysis is not possible, preserve samples for Kjeldahl digestion by acidifying to pH 1.5 to 2.0 with concentrated H₂SO₄ and storing at 4°C. Do not use HgCl₂ because it will interfere with ammonia removal.

3. Interferences

a. **Nitrate:** During Kjeldahl digestion, nitrate in excess of 10 mg/L can oxidize a portion of the ammonia released from the digested organic nitrogen, producing N₂O and resulting in a negative interference. When sufficient organic matter in a low state of oxidation is present, nitrate can be reduced to ammonia, resulting in a positive interference. The conditions under which significant interferences occur are not well defined and there is no proven way to eliminate the interference with the Kjeldahl methods described herein.

b. **Inorganic salt and solids:** The acid and salt content of the Kjeldahl digestion reagent is intended to produce a digestion

temperature of about 380°C. If the sample contains a very large quantity of salt or inorganic solids that dissolve during digestion, the temperature may rise above 400°C, at which point pyrolytic loss of nitrogen begins to occur. To prevent an excessive digestion temperature, add more H₂SO₄ to maintain the acid-salt balance. Not all salts cause precisely the same temperature rise, but adding 1 mL H₂SO₄/g salt in the sample gives reasonable results. Add the extra acid and the digestion reagent to both sample and reagent blank. Too much acid will lower the digestion temperature below 380°C and result in incomplete digestion and recovery. If necessary, add sodium hydroxide-sodium thio-sulfate before the final distillation step to neutralize the excess acid.

Large amounts of salt or solids also may cause bumping during distillation. If this occurs, add more dilution water after digestion.

c. **Organic matter:** During Kjeldahl digestion, H₂SO₄ oxidizes organic matter to CO₂ and H₂O. If a large amount of organic matter is present, a large amount of acid will be consumed, the ratio of salt to acid will increase, and the digestion temperature will increase. If enough organic matter is present, the temperature will rise above 400°C, resulting in pyrolytic loss of nitrogen. To prevent this, add to the digestion flask 10 mL conc H₂SO₄/3 g COD. Alternately, add 50 mL more digestion reagent/g COD. Additional sodium hydroxide-sodium thio-sulfate reagent may be necessary to keep the distillation pH high. Because reagents may contain traces of ammonia, treat the reagent blank identically with the samples.

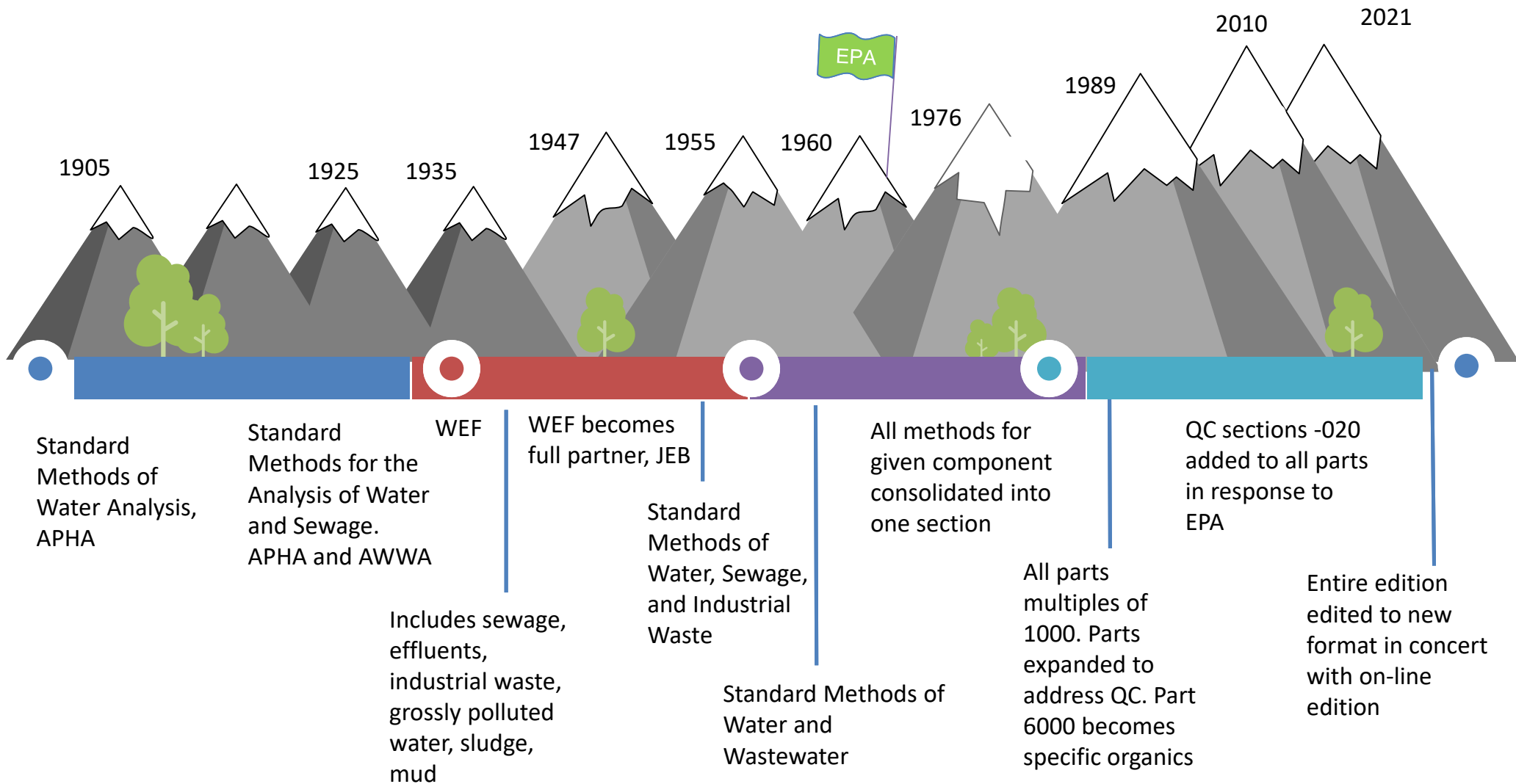
4. Use of a Catalyst

Mercury has been the catalyst of choice for Kjeldahl digestion. Because of its toxicity and problems associated with legal disposal of mercury residues, a less toxic catalyst is recommended. Digestion of some samples may be complete or nearly complete without the use of a catalyst. Effective digestion results from the use of a reagent having a salt:acid ratio of 1 g/mL with copper as catalyst (4500-N_{org} B.3a), and specified temperature (4500-N_{org} B.2a) and time (4500-N_{org} B.4c). If a change is made in the reagent formula, report the change and indicate percentage recovery relative to the results for similar samples analyzed using the previous formula.

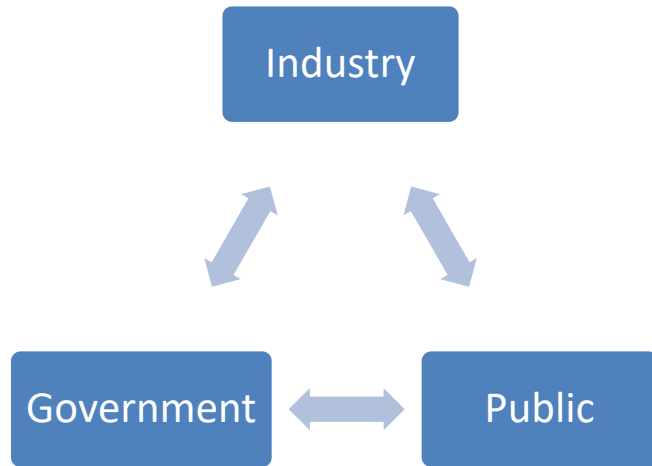
Before results are considered acceptable, determine nitrogen recovery from samples with known additions of nicotinic acid, to test completeness of digestion, and with ammonium chloride to test for loss of nitrogen.

* Approved by Standard Methods Committee, 1997. Editorial revisions, 2011. Joint Task Group: 20th Edition—(4500-N_{org} D)—Scott Steg (chair), Bradford B. Fisher, Owen H. Maden, Theresa M. Wright.

Progression and Growth of Standard Methods



ASTM D19 on Industrial Water before EPA

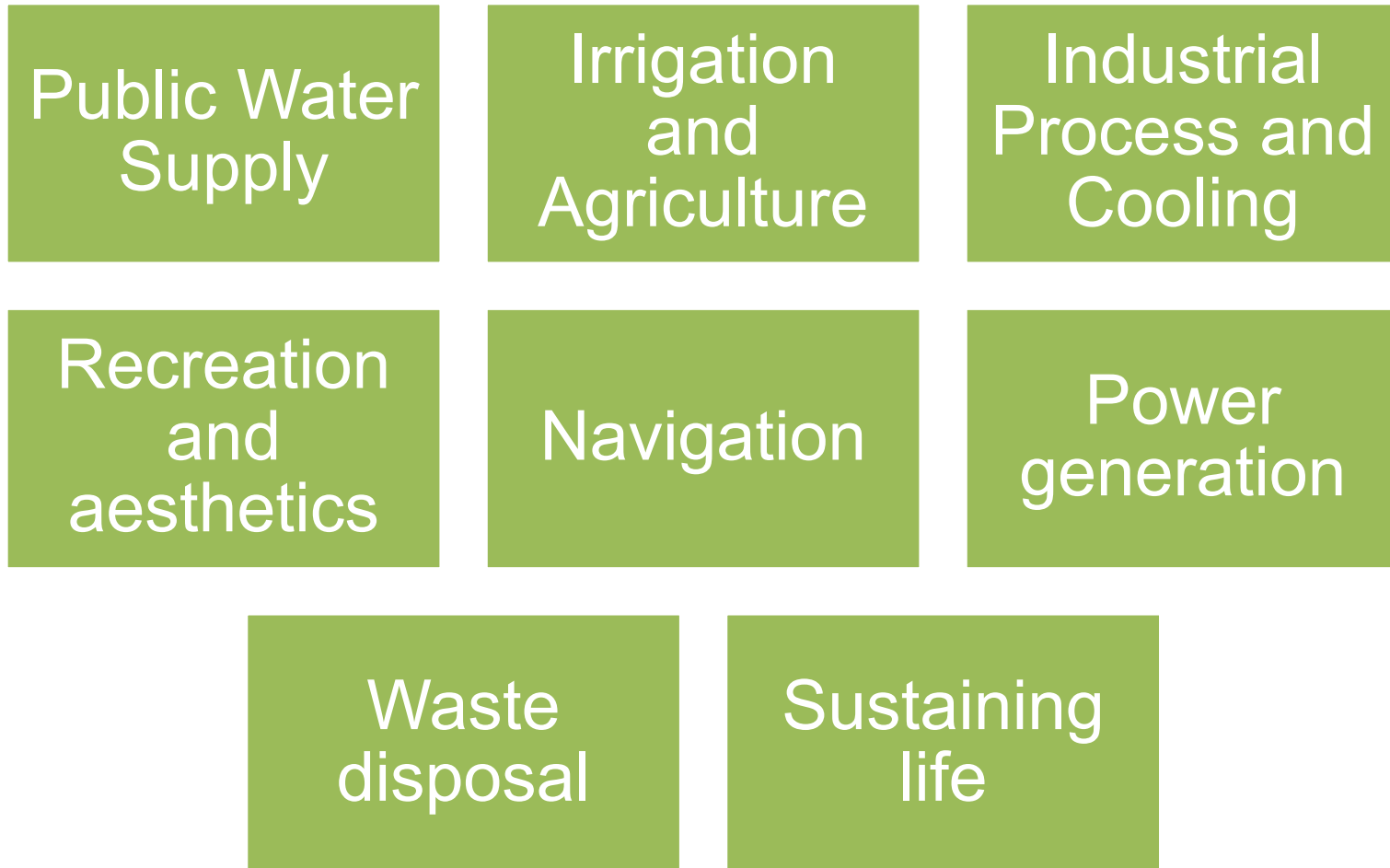


Cooperative effort to find solutions to common problems

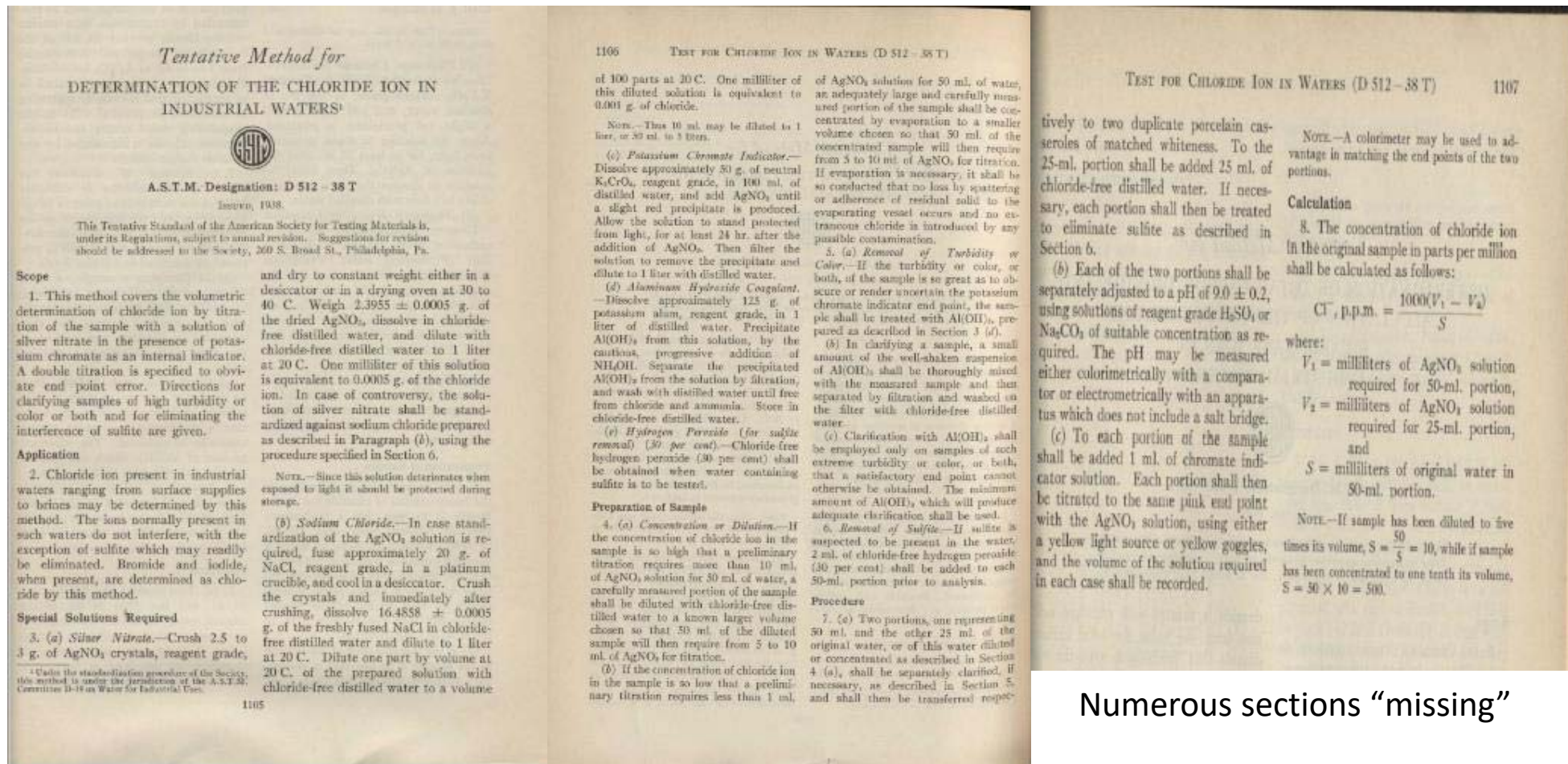
Committed to Standardization of test methods:

- Common language to express results
- Quality Control
- Minimum limits (no such thing as zero)
- Negative and positive interferences
- Interpretation based on scope
- Known precision and accuracy

ASTM D19 on Industrial Water defined water based on ultimate use



First ASTM D19 Chloride method



Tentative Method for
DETERMINATION OF THE CHLORIDE ION IN INDUSTRIAL WATERS¹



A.S.T.M. Designation: D 512 - 38 T
 Issued, 1938.

This Tentative Standard of the American Society for Testing Materials is under its Regulations, subject to annual revision. Suggestions for revision should be addressed to the Society, 260 S. Broad St., Philadelphia, Pa.

Scope

1. This method covers the volumetric determination of chloride ion by titration of the sample with a solution of silver nitrate in the presence of potassium chromate as an internal indicator. A double titration is specified to obviate end point error. Directions for clarifying samples of high turbidity or color or both and for eliminating the interference of sulfite are given.

Application

2. Chloride ion present in industrial waters ranging from surface supplies to brines may be determined by this method. The ions normally present in such waters do not interfere, with the exception of sulfite which may readily be eliminated. Bromide and iodide, when present, are determined as chloride by this method.

Special Solutions Required

3. (a) *Silver Nitrate*.—Crush 2.5 to 3 g. of AgNO₃ crystals, reagent grade,

¹Under the standardization procedure of the Society, this method is under the jurisdiction of the A.S.T.M. Committee D-19 on Water for Industrial Uses.

and dry to constant weight either in a desiccator or in a drying oven at 30 to 40 C. Weigh 2.3955 ± 0.0005 g. of the dried AgNO₃, dissolve in chloride-free distilled water, and dilute with chloride-free distilled water to 1 liter at 20 C. One milliliter of this solution is equivalent to 0.0005 g. of the chloride ion. In case of controversy, the solution of silver nitrate shall be standardized against sodium chloride prepared as described in Paragraph (b), using the procedure specified in Section 6.

NOTE.—Since this solution deteriorates when exposed to light it should be protected during storage.

(b) *Sodium Chloride*.—In case standardization of the AgNO₃ solution is required, fuse approximately 20 g. of NaCl, reagent grade, in a platinum crucible, and cool in a desiccator. Crush the crystals and immediately after crushing, dissolve 16.4858 ± 0.0005 g. of the freshly fused NaCl in chloride-free distilled water and dilute to 1 liter at 20 C. Dilute one part by volume at 20 C. of the prepared solution with chloride-free distilled water to a volume

1105 TEST FOR CHLORIDE ION IN WATERS (D 512 - 38 T)

of 100 parts at 20 C. One milliliter of this diluted solution is equivalent to 0.001 g. of chloride.

NOTE.—This 10 ml. may be diluted to 1 liter, or 50 ml. to 5 liters.

(c) *Potassium Chromate Indicator*.—Dissolve approximately 50 g. of neutral K₂CrO₄, reagent grade, in 100 ml. of distilled water, and add AgNO₃ until a slight red precipitate is produced. Allow the solution to stand protected from light, for at least 24 hr. after the addition of AgNO₃. Then filter the solution to remove the precipitate and dilute to 1 liter with distilled water.

(d) *Aluminum Hydroxide Coagulant*.—Dissolve approximately 125 g. of potassium alum, reagent grade, in 1 liter of distilled water. Precipitate Al(OH)₃ from this solution, by the cautious, progressive addition of NH₄OH. Separate the precipitated Al(OH)₃ from the solution by filtration, and wash with distilled water until free from chloride and ammonia. Store in chloride-free distilled water.

(e) *Hydrogen Peroxide (for sulfite removal) (30 per cent)*.—Chloride-free hydrogen peroxide (30 per cent) shall be obtained when water containing sulfite is to be tested.

Preparation of Sample

4. (a) *Concentration or Dilution*.—If the concentration of chloride ion in the sample is so high that a preliminary titration requires more than 10 ml. of AgNO₃ solution for 50 ml. of water, a carefully measured portion of the sample shall be diluted with chloride-free distilled water to a known larger volume chosen so that 50 ml. of the diluted sample will then require from 5 to 10 ml. of AgNO₃ for titration.

(b) If the concentration of chloride ion in the sample is so low that a preliminary titration requires less than 1 ml.

of AgNO₃ solution for 50 ml. of water, an adequately large and carefully measured portion of the sample shall be concentrated by evaporation to a smaller volume chosen so that 50 ml. of the concentrated sample will then require from 5 to 10 ml. of AgNO₃ for titration. If evaporation is necessary, it shall be so conducted that no loss by spattering or adherence of residual solid to the evaporating vessel occurs and no extraneous chloride is introduced by any possible contamination.

5. (a) *Removal of Turbidity or Color*.—If the turbidity or color, or both, of the sample is so great as to obscure or render uncertain the potassium chromate indicator end point, the sample shall be treated with Al(OH)₃, prepared as described in Section 3 (d).

(b) In clarifying a sample, a small amount of the well-shaken suspension of Al(OH)₃ shall be thoroughly mixed with the measured sample and then separated by filtration and washed on the filter with chloride-free distilled water.

(c) Clarification with Al(OH)₃ shall be employed only on samples of such extreme turbidity or color, or both, that a satisfactory end point cannot otherwise be obtained. The minimum amount of Al(OH)₃ which will produce adequate clarification shall be used.

6. *Removal of Sulfite*.—If sulfite is suspected to be present in the water, 2 ml. of chloride-free hydrogen peroxide (30 per cent) shall be added to each 50-ml. portion prior to analysis.

Procedure

7. (a) Two portions, one representing 50 ml. and the other 25 ml. of the original water, or of this water diluted or concentrated as described in Section 4 (a), shall be separately clarified, if necessary, as described in Section 5, and shall then be transferred respec-

TEST FOR CHLORIDE ION IN WATERS (D 512 - 38 T) 1107

tively to two duplicate porcelain casseroles of matched whiteness. To the 25-ml. portion shall be added 25 ml. of chloride-free distilled water. If necessary, each portion shall then be treated to eliminate sulfite as described in Section 6.

(b) Each of the two portions shall be separately adjusted to a pH of 9.0 ± 0.2, using solutions of reagent grade H₂SO₄ or Na₂CO₃ of suitable concentration as required. The pH may be measured either colorimetrically with a comparator or electrometrically with an apparatus which does not include a salt bridge.

(c) To each portion of the sample shall be added 1 ml. of chromate indicator solution. Each portion shall then be titrated to the same pink end point with the AgNO₃ solution, using either a yellow light source or yellow goggles, and the volume of the solution required in each case shall be recorded.

NOTE.—A colorimeter may be used to advantage in matching the end points of the two portions.

Calculation

8. The concentration of chloride ion in the original sample in parts per million shall be calculated as follows:

$$Cl^-, \text{ p.p.m.} = \frac{1000(V_1 - V_2)}{S}$$

where:

V₁ = milliliters of AgNO₃ solution required for 50-ml. portion,

V₂ = milliliters of AgNO₃ solution required for 25-ml. portion, and

S = milliliters of original water in 50-ml. portion.

NOTE.—If sample has been diluted to five times its volume, $S = \frac{50}{5} = 10$, while if sample has been concentrated to one tenth its volume, $S = 50 \times 10 = 500$.

Numerous sections "missing"

New ASTM D19 Chloride method, includes Precision and Bias among other required sections

This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guidelines and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.



Designation: D512 - 12

Standard Test Methods for Chloride Ion in Water¹

This standard is issued under the fixed designation D512; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last approval. A superscript letter (a) indicates an editorial change since the last revision or approval.

This standard has been approved for use by agencies of the U.S. Department of Defense.

1. Scope²

1.1 These test methods cover the determination of chloride ion in water, wastewater (Test Method C only), and brines. The following three test methods are included:

Section	Section
Test Method A (Mercuric Nitrate)	7 to 4
Test Method B (Silver Nitrate Titration)	15 to 21
Test Method C (Ion-Selective Electrode Method)	22 to 28

1.2 Test Methods A, B, and C were validated under Practice D2777 - 77, and only Test Method B conforms also to Practice D2777 - 86. Refer to Sections 14, 21, and 29 for further information.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. For a specific hazard statement, see 26.1.1.

1.5 A former colorimetric test method was discontinued. Refer to Appendix X1 for historical information.

2. Referenced Documents

- 2.1 *ASTM Standards*³
- D1066 Practice for Sampling Seawater
 - D1120 Terminology Relating to Water
 - D1191 Specification for Reagent Water
 - D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
 - D3770 Practice for Sampling Water from Closed Circuits

¹ These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.08 on Inorganic Constituents in Water.

² Former edition approved June 15, 2012; published July 2012. Originally approved in 1978. Last previous edition approved in 2010 as D512 - 13, DOI: 10.1520/D512-13.

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

- D4127 Terminology Used with Ion-Selective Electrodes
- D5810 Guide for Spiking into Aqueous Samples
- D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
- E2000 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test methods, refer to Terminologies D1129 and D4127.

4. Significance and Use

4.1 Chloride ion is under regulation in waste water, and most, therefore, is measured accurately. It is highly detrimental to high-pressure boiler systems and to stainless steel, so monitoring is essential for the prevention of damage. Chloride analysis is widely used as a test for estimating the cycles of concentration, such as in cooling tower applications. Precipitating reactions and pickling solutions used in the food processing industries also require dependable methods of analysis for chloride.

5. Purity of Reagents

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Purity of Water—Unless otherwise indicated, reference to water shall be understood to mean Type I reagent water conforming to Specification D1193. Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely

⁴ Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see Analytical Standards for Laboratories Chemicals, REE 1st ed., Reels, Pinner, H.C., and the District Sales Representatives and National Formulary, U.S. Pharmaceutical Companies, Inc. (USPC), Rockville, MD.

¹A Summary of Changes section appears at the end of this standard.

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affecting the precision and bias of the test method. Type II water was specified at the time of round robin testing of this test method.

6. Sampling

6.1 Collect the sample in accordance with Practice D1066 and Practices D5501, as applicable.

TEST METHOD A—MERCURIMETRIC TITRATION⁴

7. Scope

7.1 This test method can be used to determine chloride ion in water, provided interferences are absent (see Section 9).

7.2 Though not specified in the research report, the precision statement is presumed to have been obtained using Type II reagent water. It is the responsibility of the analyst to assure the validity of this test method for untreated matrices.

7.3 This test method was validated for the concentration range 0.0 to 250 mg/L Cl⁻.

8. Summary of Test Method

8.1 Dilute mercuric nitrate solution is added to an acidified sample in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.

9. Interferences

9.1 The anions and cations generally found in water offer no interference. Zinc, lead, nickel, and ferrous and chromous ions affect solution and end-point color, but do not reduce the accuracy of the titration when present in concentrations up to 100 mg/L. Copper is tolerable up to 50 mg/L. Thioacetamide in the presence of chromate ion requires indicator with extra background color (alpha-naphthyl) and prior reduction for concentrations above 100 mg/L. Ferric ion above 10 mg/L must be reduced before titration, and sulfide ion must be oxidized. Sulfamate, iodide, and thiosulfate will be titrated or partially titrated with the chloride. Quaternary ammonium salts also interfere if present in significant amounts (1 to 2 mg/L). Soap color may also interfere.

10. Apparatus

10.1 *Microburet*, 1 or 5-mL, with 0.01-mL graduation increments.

11. Reagents and Materials

11.1—Consult the manufacturer Material Safety Data Sheet for safe work practices before working with reagents.

11.1.1 Hydrogen Peroxide (30% H₂O₂)

11.1.1.1 *Hydrogen Peroxide Solution* (10 g/L) Dissolve 1 g of purified hydrogen peroxide in water and dilute to 100 mL.

⁴ For information of interest in connection with this test method, and supporting data, refer to Chalk, R. E., "Standardization of Chloride Ion Reagent," Analytical Chemistry, Vol. 22, April 1950, pp. 593-595, and Vol. 23, November 1950, p. 1458.

11.3 *Mercuric Nitrate Solution, Standard* (0.0125M, 0.025N) Dissolve 4.2810 g of mercuric nitrate (Hg(NO₃)₂·H₂O) in 50 mL of water acidified with 0.5 mL of concentrated nitric acid (HNO₃, sp gr 1.42). Dilute the acidified Hg(NO₃)₂ solution with water to 1 L. Filter if necessary, and standardize against the standard sodium chloride (NaCl) solution, using the procedure described in Section 12 (see Note 2).

Note 2—Sharpness of End Point—The end point, while sharp, can be improved somewhat for certain types of water by adding several drops of a 0.05-g/L solution of yellow crystalline PO or alphanaphthyl blue-green dye color index 114) to the titration sample.

11.4 *Mixed Indicator Solution*⁵ Dissolve 0.5 g of crystalline diphenylcarbazone and 0.05 g of bromophenol blue powder in 75 mL of ethyl alcohol (95%), and dilute to 100 mL with the alcohol (Note 3). Store in a brown bottle and discard after 6 months (Note 4).

Note 3—Methanol, isopropanol, or ethanol dissolved with either methanol or isopropanol (Formula 3A) may be used if pure ethyl alcohol is not available. Other denatured ethanol formulas are not suitable.

Note 4—Liquid indicator generally deteriorates to the point that it yields an end-point color after 12 to 18 months of storage. High concentrations (above 0.2%) (100%) and exposure to bright light may shorten storage life. A dry powder mixture of the two indicator ingredients is stable for much longer periods. Both the powder mixture (capsule form) and the liquid indicator are available commercially.

11.5 *Nitric Acid* (2 + 997)—Mix 3 volumes of concentrated nitric acid (HNO₃, sp gr 1.42) with 997 volumes of water.

11.6 *pH Indicating Paper*, long-range type, covering a pH range 1 to 11.

11.7 *Sodium Chloride Solution, Standard* (0.025N)—Purchase a commercially available standard or prepare as follows: Dry several grams of reagent grade sodium chloride (NaCl) for 2 h at 110°C. Dissolve 1.6613 g of the dry salt in water, and dilute to 1 L at 25°C in a volumetric flask.

11.8 *Sodium Hydroxide Solution* (10 g/L) Dissolve 10 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

12. Procedure

12.1 Use a volume of sample such that it will contain not more than 20 mg of chloride ion, diluting the sample with water to approximately 20-mL volume if necessary. Determine an indicator blank on 50 mL of chloride free water, applying the same procedure followed for the sample.

12.2 Add 5 to 10 drops of mixed indicator solution, and shake or swirl the flask. If a blue-violet or red color develops, add HNO₃ (3 + 997) dropwise until the color changes to yellow. Add 1 mL of excess acid. If a yellow or orange color forms immediately on addition of the mixed indicator, add NaOH solution (10 g/L) dropwise until the color changes to blue-violet; then add HNO₃ (3 + 997) dropwise until the color changes to yellow and further add 1 mL excess of acid (Note 3).

Note 5—The prescribed acidification provides a satisfactory pH range

⁵ This diphenylcarbazone-1-bromophenol blue indicator is covered by U.S. Patent No. 2,764,064.

Bias Statement—The precision of this method is as follows:

$$S_p = 0.023X + 0.43$$

$$S_o = 0.002X + 0.46$$

- = overall precision, mg/L,
- = single-operator precision, mg/L, and
- = concentration of chloride ion determined.

14.2 Bias Statement—Recoveries of known amounts of chloride were as follows:

Amount Added, mg/L	Amount Found, mg/L	% Bias	Statistically Significant (95% Confidence Level)
250	248	-0.80	no
80.0	79.3	-0.88	no
8.00	7.51	-6.13	yes

14.3 The information presented in 14.1 and 14.2 is derived from round-robin testing in which five laboratories, including seven operators, participated. Though not clearly specified in the test report, the matrix is presumed to be Type II reagent water. Of seven data sets ranked as described in Practice D2777, none was rejected, nor were any data points determined to be "outliers." Three sample levels were run on at least three days. The method of "least squares" was used to determine the precision statement, with correlation of 0.7394 for S_o and 0.9993 for S_p .

14.4 It is the responsibility of the analyst to assure the accuracy of this test method for untreated matrices.

Precision and bias for this test method conform to Practice D2777 - 77, which was in place at the time of the testing. Under the allowances made in Practice D2777 - 08, these precision and bias data are acceptable for interlaboratory studies.

from 1.0 to 7.5. Adjusted results have been made available on request. pH check 88 was used and a double jacketed 18 solution. Also available on sample request for the chloride test.

12.3 Titrate the solution until light, perceptible reddition of the solution.

Note 6. The natural line color determination is bright blue in acidic, and yellow in neutral, green in alkaline. The end-point is a yellowish green.

12.4 If the concentration of the sample is less than 2.5 mg/L, add 5 mL of sodium chloride to the sample.

12.5 If the concentration of hydrochloric acid is less than 1.0 N, use 12.5 mL of the acid.

12.6 If ferric chromate and/or ferric chloride are present in more than 2.5 mg/L of the sample, use 12.5 mL of the acid.

12.7 If the volume of the sample is less than 20 mL, use 20 mL of the sample.

13. Calculation

13.1 Calculate the chloride concentration in mg/L in the original sample as follows:

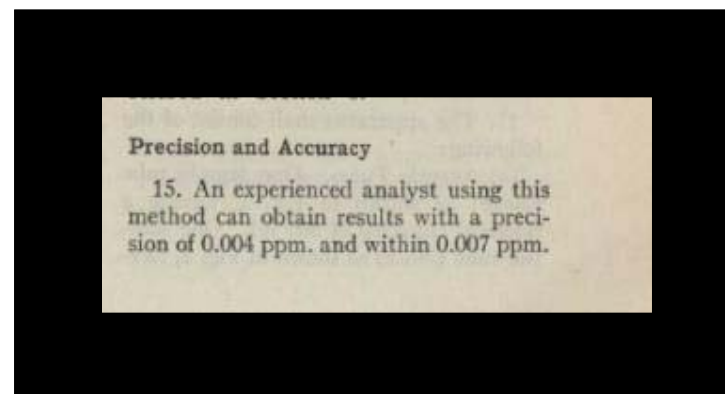
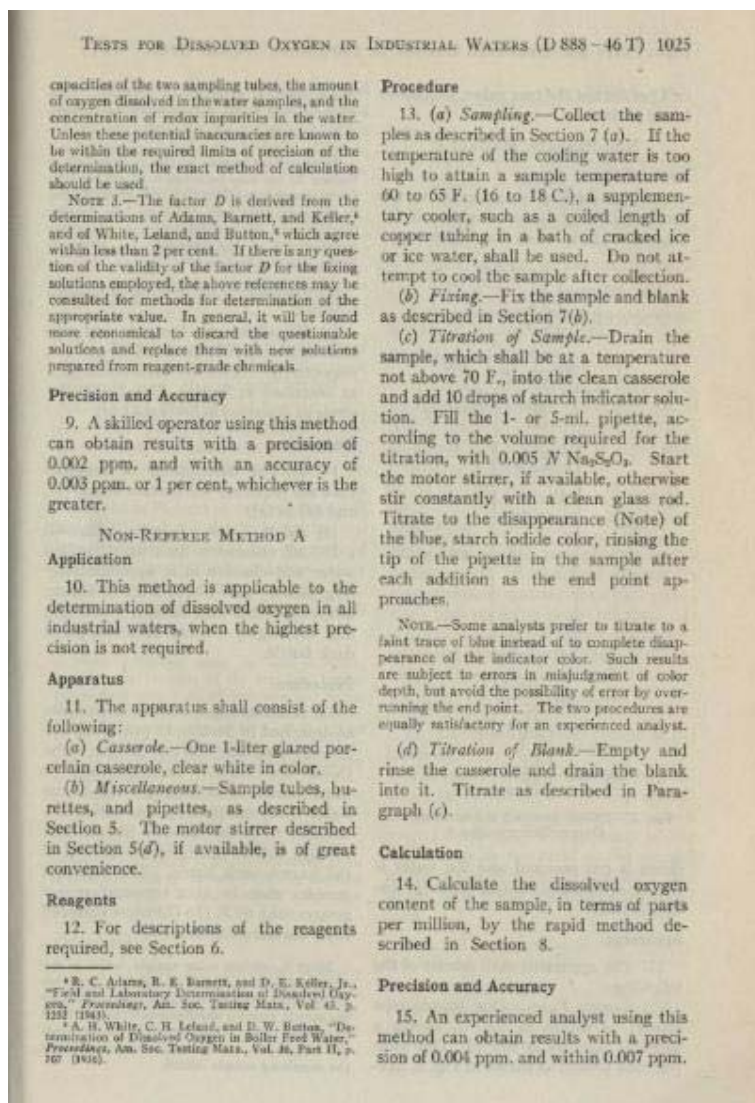
$$\text{Chloride, mg/L} = (V - V_b) \times N \times 35.453$$

where:
 V_b = standard Hg(NO₃)₂ solution of the blank, mL
 V_s = standard Hg(NO₃)₂ solution required for the sample, mL
 N = normality of the Hg(NO₃)₂ solution (see Note 5)
 35.453 = 35.453 grams chlorine × 1000 mg/g

Note 7—The normality of the mercuric nitrate solution standard is based on a 2:1 (Cl:Hg) reaction.

¹ Engineering data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR-010-1076. Contact ASTM Customer Service at service@astm.org. (March 9, 2012, 11:15 AM)

ASTM D19 original DO method, with limited precision and bias section



ASTM D19 current DO method, with all sections

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must be qualified with an indication that they do not fall within the performance criteria of the test method.

22.6 Matrix Spike (MS):
25.6.1 Dissolved oxygen is not an analyte that can be readily spiked into samples.

25.7 Duplicate:
25.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. The values obtained must fall within the control limits established by the laboratory.

25.7.2 Calculate the standard deviation of the duplicate values and compare to the precision determined by the laboratory or in the collaborative study using an *F* test. Refer to 8.4.2 of Practice D5437 for information on applying the *F* test.
25.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

25.8 Independent Reference Material (IRM):
25.8.1 Independent reference water samples may be obtained from commercial sources. The value obtained from these samples must fall within the control limits established by the laboratory.

25.8.2 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

25.8.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

TEST METHOD C INSTRUMENTAL PROBE PROCEDURE — LUMINESCENCE-BASED SENSOR

26. Scope
26.1 This test method is applicable to water containing dissolved oxygen in the range from 0.1 to 20.00 mg/L. It is the user's responsibility to assess the validity of this test method for waters of unknown nature.

26.2 This test method is for an instrumental probe-luminescence-based sensor using the technology of frequency-domain lifetime-based luminescence quenching and signal processing for analysis of dissolved oxygen. This test method is applicable to all water and wastewater analyses that are free from interferences of normal solids and subject to treatment and final effluent wastewater concentrations.

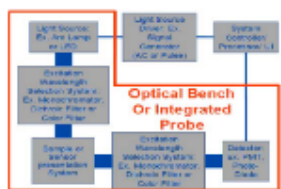


FIG. 1 Optical Bench or Integrated Probe

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water-saturated air. Consequently, the calibration and verification of the instrumental probe-luminescence based sensor may be performed in air as well as water. The data presented in this test method was based on instruments with a single-point calibration.

29.4 Preparation of Water-Saturated Air Sample:
29.4.1 Add 1 mL of reagent water to a clean 300 mL BOD bottle and seal with stopper.

29.4.2 Shake vigorously for approximately 30 seconds.

29.4.3 Allow 30 minutes for the BOD bottle and its contents to equilibrate to room temperature.

29.4.4 The water-saturated air sample is now ready to use for calibration purposes.

29.5 Preparation of Air-Saturated Water:
29.5.1 Add approximately 1500 mL of reagent water to a 2-L beaker.

29.5.2 Allow the water to equilibrate to room temperature (±2°C).

29.5.3 Using a steady stream of clean compressed air (approximately 30 to 40 mL per minute flow rate) across the water for a minimum of 30 minutes.

29.5.4 Allow the water to re-equilibrate to room temperature (±2°C) for 45 to 60 minutes.

29.5.5 Transfer a small water to clean BOD bottles until overflowing, then seal with stopper.

29.5.6 Note the laboratory barometric pressure and sample temperature and save values from Table X1.1 to calculate the theoretical dissolved oxygen concentration.

29.5.7 Analyze within 4 hours of preparation.

29.6 Provide for suitable ambient flow past the sensor cap.

29.7 Verify calibration with water-saturated air or air-saturated water and the completion of matrix samples.

29.7.1 Calibration verification should be within 97 to 104 % of theoretical dissolved oxygen concentration.

29.7.2 If calibration verification is outside of theoretical recovery range, re-calibrate sensor and re-analyze matrix samples.

29.8 Two-point calibrations are acceptable; however, inter-laboratory data included in this standard was collected using a single-point calibration.

29.8.1 It is the users responsibility to demonstrate acceptability of calibration. Data must meet the method requirements in Table 1 and Table 2.

29.8.2 Steps and supporting data for a two-point calibration can be found in Appendix X2.

29.9 Preparation of Nitrogen-Saturated Water (for 0 Point or a Two-Point Calibration):
29.9.1 Add approximately 1500 mL of reagent water to a 2-L beaker.

29.9.2 Using a steady stream of clean compressed nitrogen (approximately 10 to 40 mL per minute flow rate) across the water for a minimum of 30 minutes.

29.10 Preparation of Saturated Sodium Sulfite Solution:
29.10.1 Add approximately 252.08 g/L of sodium sulfite (Na₂SO₃) to reagent water for a 2 M solution. Alternatively, add approximately 50 g of anhydrous sodium sulfite (Na₂SO₃) to 1 L of reagent water for a solution of about 0.4 M.

29.10.2 The sodium sulfite sample is now ready to use for calibration purposes.

30. Precision and Bias
30.1 The precision of the test method was determined by eight laboratories using four saturated samples of reagent water at a reference dissolved oxygen concentration of 1.74 mg/L. The mean concentration was 1.77 mg/L, and the pooled single operator precision in these samples was 0.02 mg/L.

30.2 Precision and bias for this test method conform to Practice D2777-03, which was in place at the time of collaborative testing. Under the allowance made in 1.4 of Practice D2777-13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

Note 10—The data presented in this test method was based on instruments with a single-point calibration. The calibration was performed in air and verified in water.

30.3 Quality Control (QC)
30.3.1 To ensure that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing dissolved oxygen.

30.3.2 Collaborative and Collaborative Verification:
30.3.2.1 Use water-saturated air and air-saturated water reference samples described in 29.4 and 29.5. Calibration values should fall within values in Table 1.

30.3.2.2 Analyze four replicates of air-saturated water.

30.3.2.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in 30.1 and recovery and precision in Table 1. This study should be repeated until the recoveries are within the limits given in 30.1.

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TABLE 2 Method Performance of DO Measurements from Air-Saturated Water Reference Samples

Lab No.	Data Set 1			Data Set 2		
	Method A Water % Rec.	Method B Recovery % Rec.	Method C LOO % Rec.	Method A Water % Rec.	Method B Recovery % Rec.	Method C LOO % Rec.
1	102.2	95.7	95.7	96.1	96.4	96.0
2	97.6	96.9	95.2	97.5	96.9	96.9
3	97.0	95.0	101.0	95.7	98.0	99.0
4	99.8	96.1	98.2	97.4	97.7	98.5
6	98.7	96.6	100.0	91.0	96.8	101.0
7	94.0	94.0	101.0	94.5	94.5	98.4
8	94.0	96.1	101.0	96.0	96.0	96.0
9	100.0	104.0	101.0	100.0	100.0	104.0
10	93.2	95.0	93.6	93.8	94.0	94.0
11	100.0	104.0	100.0	100.0	91.0	100.0
Average	97.5	97.7	101.0	97.6	97.4	99.0
SDMV	3.8	4.3	2.8	4.7	3.8	3.7
NRMSD	5.8	4.1	2.0	4.8	3.0	2.7
Precision Data Only						
Average	97.6	97.5	100.0			
SDMV	4.0	3.3	2.7			
NRMSD	6.2	3.9	2.7			

31.4 Laboratory Control Sample (LCS):
31.4.1 Air-saturated reference water samples may be used for laboratory control samples. The values obtained must fall within the control limits established by the laboratory.

31.5 Matrix Spike (MS):
31.5.1 Dissolved oxygen is not an analyte that can be readily spiked into matrix samples.

31.6 Duplicate:
31.6.1 To check the precision of sample analyses, analyze an air-saturated water reference sample in duplicate with each batch. The values obtained must fall within the control limits established by the laboratory.

31.6.2 Calculate the standard deviation of the duplicate values and compare to the precision determined by the laboratory or in the collaborative study.

31.6.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

31.7 Independent Reference Material (IRM):
31.7.1 Independent reference water samples may be obtained from commercial sources. The values obtained from these samples must fall within the control limits established by the commercial source.

31.8 Tables 1 and 2 reflect round robin results that a typical user of this test method should achieve.

32. Keywords
32.1 analysis; dissolved oxygen; frequency domain; lifetime-based; luminescence; probe; titrimetric; water

APPENDICES

(Nonmandatory Information)

XI. OXYGEN SATURATION VALUES

X1.1 Oxygen Saturation Values in Water and Air/Water—The solubility of oxygen in water at various temperatures and elevations under an atmospheric pressure of 760 mm is shown in Table X1.1.

X1.2 Oxygen Saturation Values in Water and Salt Waters—The solubility of oxygen in water exposed to water saturated

air under an atmospheric pressure of 760 mm is shown in Table X1.2 at several temperatures and concentrations of sea water to illustrate the effects of salt concentration and temperature. The solubility versus dissolved salt concentration can vary considerably with the nature of the salts in solution.

TABLE 1 Pooled Round Robin Recovery and Precision Criteria for Luminescence-Based Sensor

Reference Water DO Range	DO Conc. (mg/L)	97.5 % Lower Limit of Recovery (%)	97.5 % Upper Limit of Recovery (%)	95 % Upper Limit of Precision (%)
Low	1.00 ± 0.04	96.4	104.6	1.75
High	7.00 ± 0.28	96.2	104.6	1.10

Excerpts of the current ASTM D19 DO method showing QC and precision and bias sections

30. Precision and Bias

30.1 The precision of the test method was determined by eight laboratories using four saturated samples of reagent water at a reference dissolved oxygen concentration of 1.74 mg/L. The mean concentration was 1.73 mg/L, and the pooled single operator precision in these samples was 0.02 mg/L.

30.2 Precision and bias for this test method conform to Practice D2777 – 03, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

Note: 18—The data presented in this test method was based on instruments with a single-point calibration. The calibration was performed in air and verified in water.

31. Quality Control (QC)

31.1 To ensure that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing dissolved oxygen.

31.2 Calibration and Calibration Verification:

31.2.1 Use water-saturated air and air-saturated water reference samples described in 29.4 and 29.5. Calibration values should fall within values in Table 1.

31.3 Initial Demonstration of Laboratory Capability:

31.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

31.3.2 Analyze four replicates of air-saturated water.

31.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in 30.1 and recovery and precision in Table 1. This study should be repeated until the recoveries are within the limits given in 30.1.

D660 – 19

TABLE 2 Method Performance of DO Measurements from Air-Saturated Water Reference Samples

Lab No.	Data Set 1			Data Set 2		
	Method A Water % Rec	Method B Water % Rec	Method C DO % Rec	Method A Water % Rec	Method B Water % Rec	Method C DO % Rec
1	99.2	99.7	99.7	99.1	99.4	99.9
2	99.5	99.9	99.9	99.5	99.9	99.9
3	99.9	99.9	100.0	99.7	99.9	99.9
4	99.9	99.9	99.9	99.4	99.7	99.9
5	99.7	99.8	99.9	99.9	99.9	99.9
6	99.9	99.9	99.9	99.9	99.9	99.9
7	99.9	99.9	99.9	99.9	99.9	99.9
8	99.9	99.9	99.9	99.9	99.9	99.9
9	99.9	99.9	99.9	99.9	99.9	99.9
10	99.9	99.9	99.9	99.9	99.9	99.9
11	99.9	99.9	99.9	99.9	99.9	99.9
Average	99.9	99.9	99.9	99.9	99.9	99.9
Stdev	0.8	0.8	0.8	0.7	0.8	0.7
%RSD	0.8	0.8	0.8	0.7	0.8	0.7

Pooled Data Set			
Average	99.9	99.9	99.9
Stdev	0.8	0.8	0.7
%RSD	0.8	0.8	0.7

31.4 Laboratory Control Sample (LCS):

31.4.1 Air-saturated reference water samples may be used for laboratory control samples. The value obtained must fall within the control limits established by the laboratory.

31.5 Matrix Spike (MS):

31.5.1 Dissolved oxygen is not an analyte that can be readily spiked into matrix samples.

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31.6.2 Calculate the standard deviation of the duplicate values and compare to the precision determined by the laboratory or in the collaborative study.

31.6.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

31.7 Independent Reference Material (IRM):

31.7.1 Independent reference water samples may be obtained from commercial sources. The value obtained from these samples must fall within the control limits established by the commercial source.

31.8 Tables 1 and 2 reflect round robin results that a typical user of this test method should achieve.

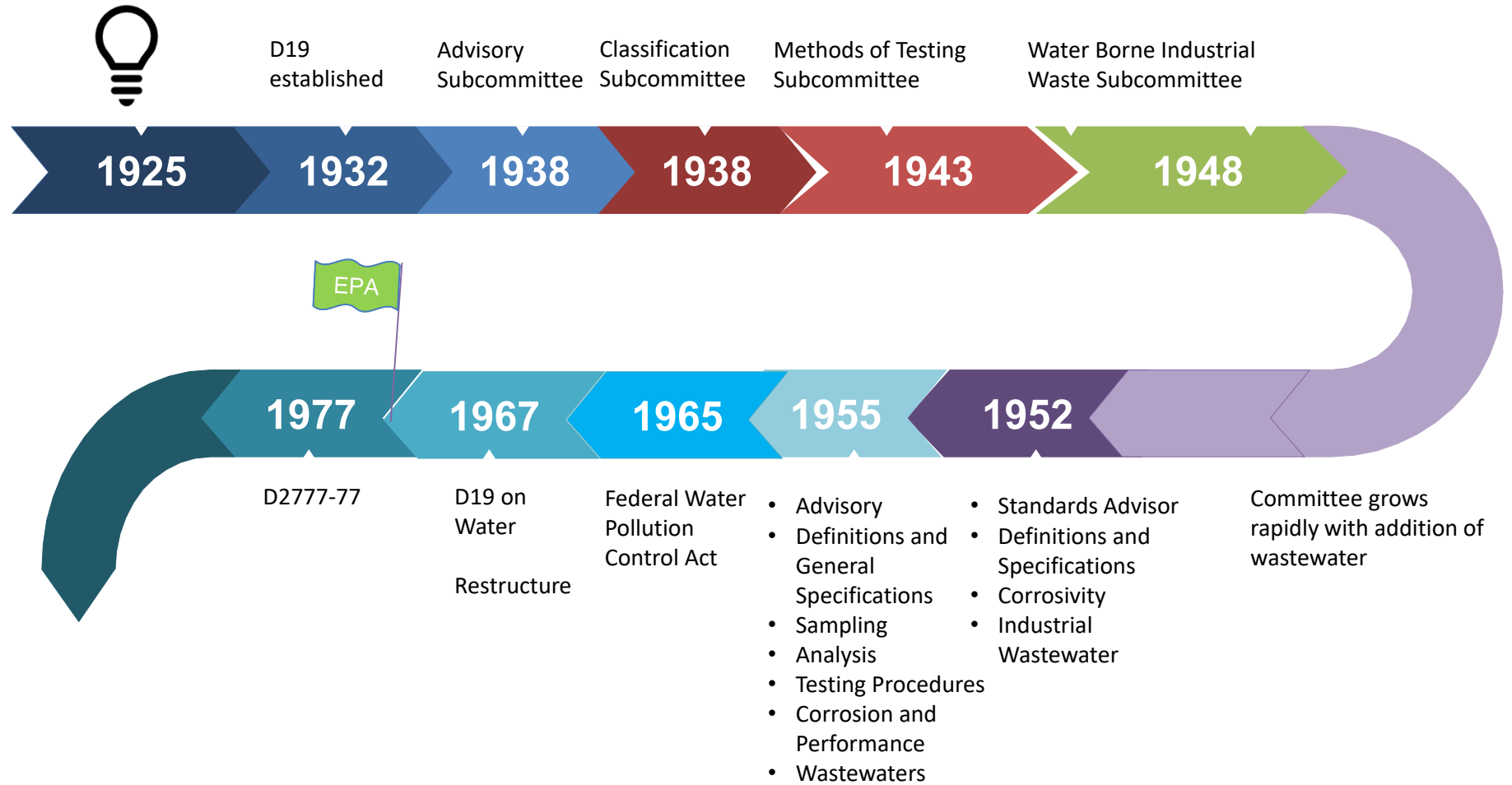
32. Keywords

32.1 analysis; dissolved oxygen; frequency domain; lifetime-based; luminescence; probe; kinetics; water

TABLE 1 Pooled Round Robin Recovery and Precision Criteria for Luminescence-Based Sensor

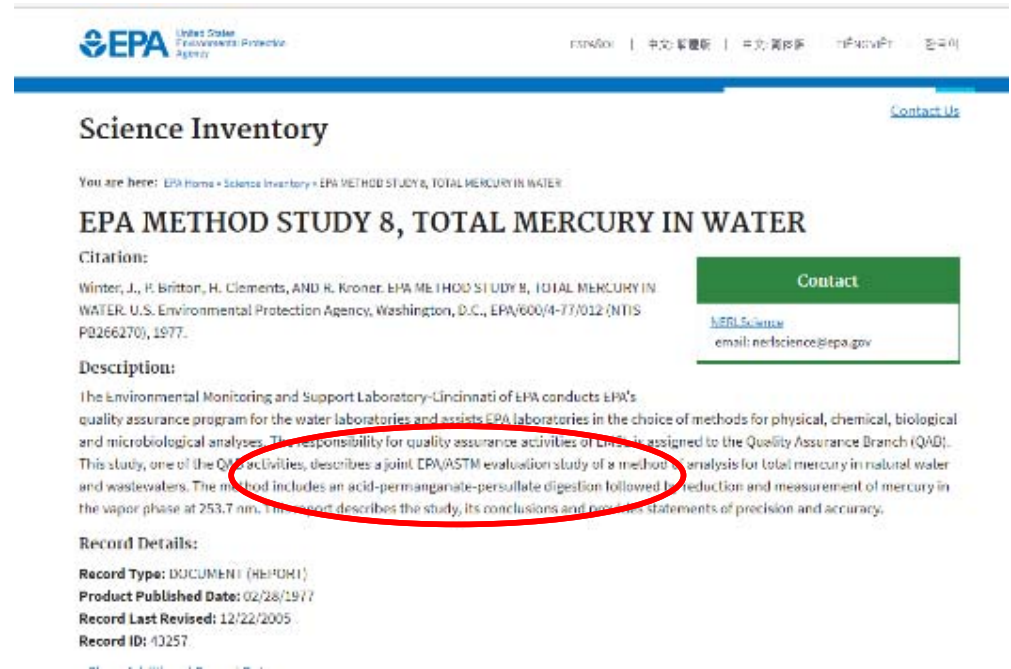
Reference Water DO Range	DO Conc. (mg/L)	97.5 % Lower Limit of Recovery (%)	97.5 % Upper Limit of Recovery (%)	95 % Upper Limit of Precision (%)
Low	1.72 – 1.74	95.4	104.0	1.75
High	7.22 – 9.23	96.2	104.0	1.10

Progression and growth of ASTM D19



There was a rapid growth in development of new methods, EPA methods validated using D2777-77

- Method Study 7 Trace Metals by AA
- Method Study 8 Mercury
- Methods Study 15 Method 605
- Method Study 18 Method 608
- Method Study 24 Method 601
- Method Study 25 Method 602
- Method Study 27 Method 200.7
- Method Study 29 Method 624
- Method Study 30 Method 625
- Method Study 35 Method 3005



EPA United States Environmental Protection Agency

Science Inventory [Contact Us](#)

You are here: EPA Home > Science Inventory > EPA METHOD STUDY 8, TOTAL MERCURY IN WATER

EPA METHOD STUDY 8, TOTAL MERCURY IN WATER

Citation:
Winter, J., R. Britton, H. Clements, AND R. Kroner. EPA METHOD STUDY 8, TOTAL MERCURY IN WATER. U.S. Environmental Protection Agency, Washington, D.C., EPA/600/4-77/012 (NTIS P0266270), 1977.

Description:
The Environmental Monitoring and Support Laboratory-Lincinnati of EPA conducts EPA's quality assurance program for the water laboratories and assists EPA laboratories in the choice of methods for physical, chemical, biological and microbiological analyses. The responsibility for quality assurance activities of EPA is assigned to the Quality Assurance Branch (QAB). This study, one of the QAB activities, describes a joint EPA/ASTM evaluation study of a method analysis for total mercury in natural water and wastewaters. The method includes an acid-permanganate-persulfate digestion followed by reduction and measurement of mercury in the vapor phase at 253.7 nm. The report describes the study, its conclusions and provides statements of precision and accuracy.

Record Details:
Record Type: DOCUMENT (REPORT)
Product Published Date: 02/28/1977
Record Last Revised: 12/22/2005
Record ID: 43257

Contact
[NEPL Science](#)
email: neplscience@epa.gov

~ 1974 - 1984

EPA and ASTM collaborate freely in method validation and sharing data

1. REPORT NO. EPA-600/3-94-050	2. REPORT DATE June 1994	3. RECEIVED ACCESSION NO. PB 94 209915
4. TITLE AND SUBTITLE EPA METHOD STUDY 29, METHOD 624-- PURGEABLES	5. PERFORMING ORGANIZATION CODE	6. PERFORMING ORGANIZATION REPORT NO.
7. AUTHOR(S) Radian Corporation	10. PROGRAM ELEMENT NO. CBL1A	11. CONTROLLING NUMBER 68-03-3102
8. PERFORMING ORGANIZATION NAME AND ADDRESS Radian Corporation P.O. Box 9948 Austin, TX 78766	12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring and Support Laboratory U.S. Environmental Protection Agency 26 N. St. Clair Street Cincinnati, OH 45268	13. TYPE OF REPORT AND PERIOD COVERED 1-87 to 6-88
14. SUPPLEMENTARY NOTES	15. ABSTRACT The work which is described in the report was performed for the purpose of validating, through an interlaboratory study, Method 624 for the analysis of the volatile organic priority pollutants. This method is based on purging and concentration of the various analytes on an adsorbent followed by thermal desorption onto a gas chromatographic column. A low resolution mass spectrometer serves as the measuring device. Participating laboratories were selected based upon technical evaluation of proposals and upon the analyses results of prestudy samples. The laboratories were supplied with ampuls containing various concentrations of the pollutant compounds. These solutions were aliquoted into four different water types which were subsequently analyzed according to the appropriate methods. In addition to the sample concentrates, each laboratory was supplied with an industrial effluent which was known to contain various pollutants and which was used to estimate false positive and false negative data. The data obtained from the interlaboratory study were analyzed employing a series of computer programs known as the Interlaboratory Method Validation Study (IMVS) system which was designed to implement ASTM procedure D2777.	16. SECURITY CLASS (This Report) Unclassified
17. KEY WORDS AND DOCUMENT ANALYSIS		
18. SECURITY CLASS (This Paper) Unclassified	19. NO. OF PAGES 246	20. PRICE
21. DISTRIBUTION STATEMENT Release to Public		

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITIONS OBSOLETE

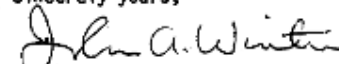
samples for trace elements to D19.05.04 for use in conducting a round robin study on inductively-coupled plasma (ICP) methodology.

However, as was suggested, the recent completion by U.S. Environmental Protection Agency (USEPA) of a very comprehensive collaborative study on trace metals by ICP, provides a large data base for your consideration. I am enclosing a copy of the very extensive report. Please review it and if the study meets your needs, feel free to utilize the statistics or reference any part of the report.

Our agency is very pleased to work with D-19 and other American Society for Testing and Materials (ASTM) committees and to search out common methodologies, in the spirit of Office of Management and Budget (OMB) Circular A-119.

Good luck in review of the data. If you have any questions, don't hesitate to call.

Sincerely yours,



John A. Winter
Chief

Quality Assurance Branch

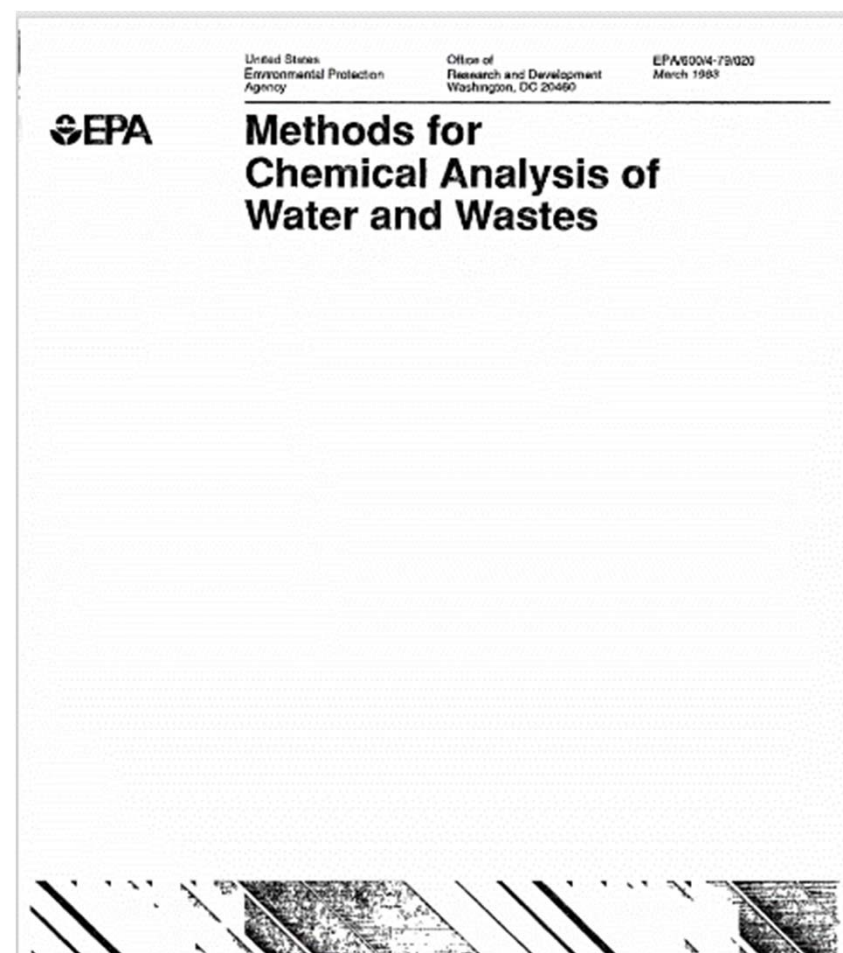
Attachment (1):
As Stated

So what changed regarding consensus standards around 1980?

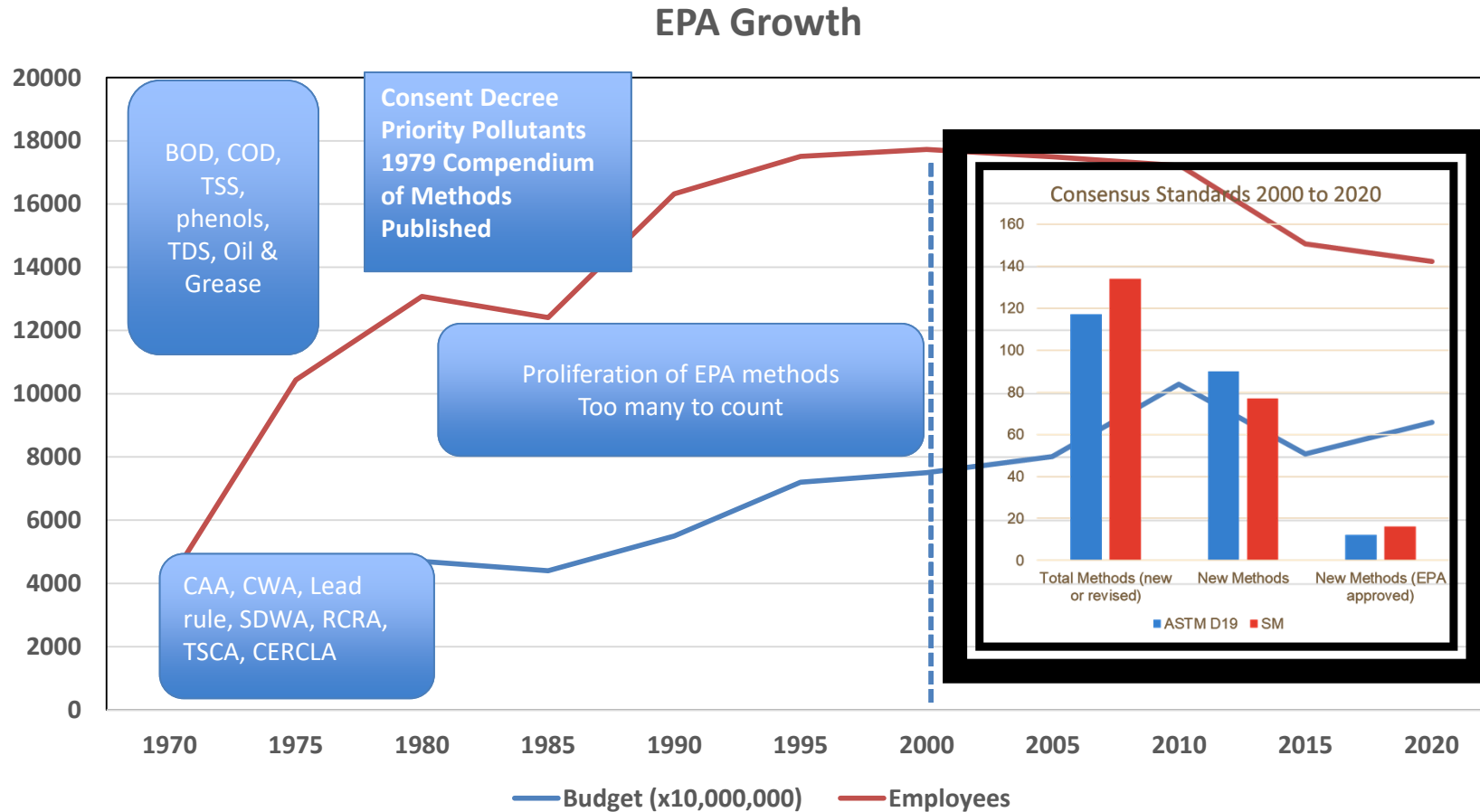
USEPA SW-846 Methods

The US EPA publication SW-846, entitled Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, is the Office of Solid Waste's (OSW's) official compendium of analytical and sampling methods that have been evaluated and approved for use in complying with the RCRA regulations. SW-846 functions primarily as a guidance document setting forth acceptable, although not required, methods for the regulated and regulatory communities to use in responding to RCRA-related sampling and analysis requirements.

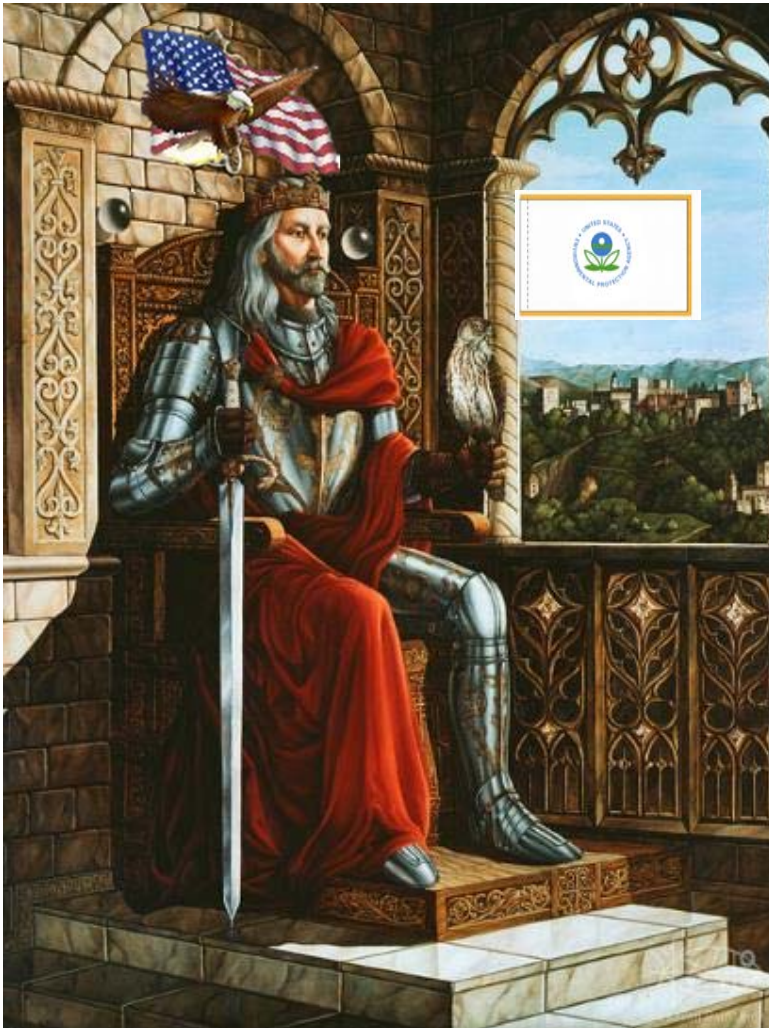
SW-846 is a multi-volume document that changes over time as new information and data are developed. It has been issued by EPA since 1980 and is currently in its third edition. Advances in analytical instrumentation and techniques are continually reviewed by OSW and incorporated into periodic updates to SW-846 to support changes in the regulatory program and to improve method performance and cost effectiveness. To date, EPA has finalized Updates I, II, IIA, IIB, III and IIIA to the SW-846 manual, and the updated and fully integrated manual contains approximately 3500 pages. The Methods Team of OSW has also made Draft Updates IVA and IVB for public use.



Paradigm shift from populace resisting government standards to massive growth (with resulting standards)



The shift resulted in American acceptance of national standards development by a regulatory agency



EPA and other federal agencies now develop regulatory methods used to set “specifications”

Result = **minimal input from public until after the methods are published.**

The National Technology Transfer and Advancement Act (NTTAA) – Legislation to take us back to before?

Public Law 104-113
104th Congress

An Act

To amend the Stevenson-Wylder Technology Innovation Act of 1980 with respect to inventions made under cooperative research and development agreements, and for other purposes.

Be it enacted by the Senate and House of Representatives of the United States of America in Congress assembled,

SECTION 1. SHORT TITLE.

This Act may be cited as the "National Technology Transfer and Advancement Act of 1995".

SEC. 2. FINDINGS.

The Congress finds the following:

(1) Bringing technology and industrial innovation to the marketplace is central to the economic, environmental, and social well-being of the people of the United States.

(2) The Federal Government can help United States business to speed the development of new products and processes by entering into cooperative research and development agreements which make available the assistance of Federal laboratories to the private sector, but the commercialization of technology and industrial innovation in the United States depends upon actions by business.

(3) The commercialization of technology and industrial innovation in the United States will be enhanced if companies, in return for reasonable compensation to the Federal Government, can more easily obtain exclusive licenses to inventions which develop as a result of cooperative research with scientists employed by Federal laboratories.

SEC. 3. USE OF FEDERAL TECHNOLOGY.

Subparagraph (B) of section 11(e)(7) of the Stevenson-Wylder Technology Innovation Act of 1980 (15 U.S.C. 3710(e)(7)(B)) is amended to read as follows:

"(B) A transfer shall be made by any Federal agency under subparagraph (A), for any fiscal year, only if the amount so transferred by that agency (as determined under such subparagraph) would exceed \$10,000."

SEC. 4. TITLE TO INTELLECTUAL PROPERTY ARISING FROM COOPERATIVE RESEARCH AND DEVELOPMENT AGREEMENTS.

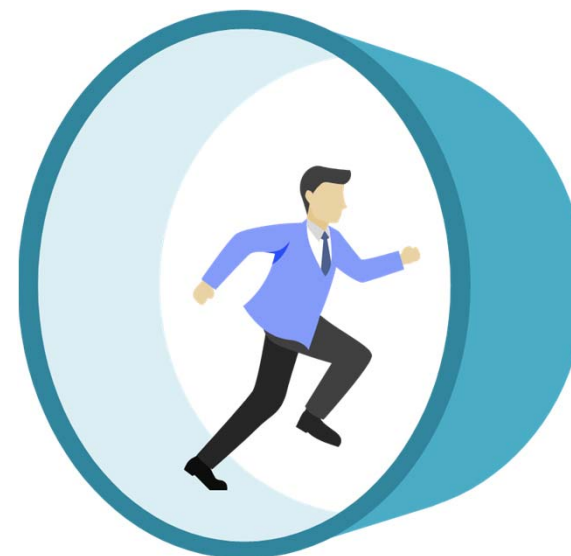
Subsection (b) of section 12 of the Stevenson-Wylder Technology Innovation Act of 1980 (15 U.S.C. 3710a(b)) is amended to read as follows:

"(b) ENUMERATED AUTHORITY.—(1) Under an agreement entered into pursuant to subsection (a)(1), the laboratory may grant, or

Mar. 7, 1995
[H.R. 2196]

National
Technology
Transfer and
Advancement Act
of 1995.
15 USC 3701
note.
15 USC 3701
note.

1995 – NTTAA encourages formal adoption of National Consensus Standards for American regulatory agencies.



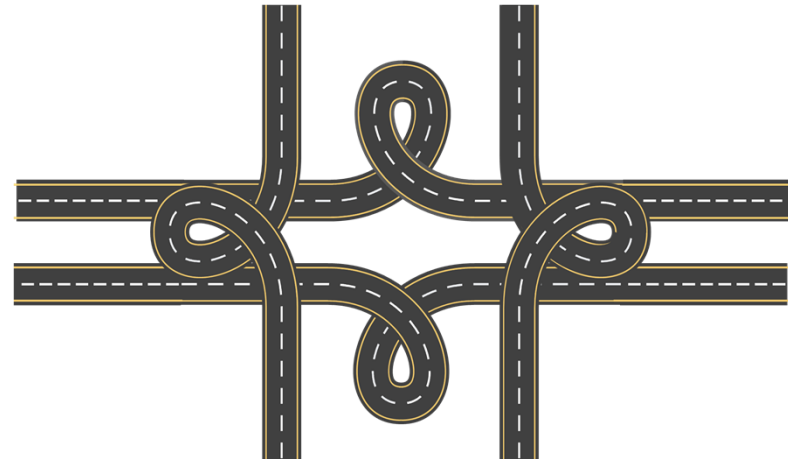
OMB Circular A-119 directs agencies to use consensus standards in place of government standards

BACKGROUND

1. What Is The Purpose Of This Circular?

This Circular establishes policies to improve the internal management of the Executive Branch. Consistent with Section 12(d) of P.L. 104-113, the "National Technology Transfer and Advancement Act of 1995" (hereinafter "the Act"), this Circular directs agencies to use voluntary consensus standards in lieu of government-unique standards except where inconsistent with law or otherwise impractical. It also provides guidance for agencies participating in voluntary consensus standards bodies and describes procedures for satisfying the reporting requirements in the Act. The policies in this Circular are intended to reduce to a minimum the reliance by agencies on government-unique standards. These policies do not create the bases for discrimination in agency procurement or regulatory activities among standards developed in the private sector, whether or not they are developed by voluntary consensus standards bodies. Consistent with Section 12(b) of the Act, this Circular directs the Secretary of Commerce to issue guidance to the agencies in order to coordinate conformity assessment activities. This Circular replaces OMB Circular No. A-119, dated October 20, 1993.

- Provides guidance for agencies participating in VCSBs
- **Reduce** reliance by agencies on government standards



A Voluntary Consensus Standard Body (VCSB):



- A VCSB operates according to:
 - Openness
 - Balance of Interest
 - Due Process
 - Appeals Process
 - Consensus

Examples of VCSB's in US Regulation

VCSB's include:

1. Standard Methods
2. ASTM
3. AOAC

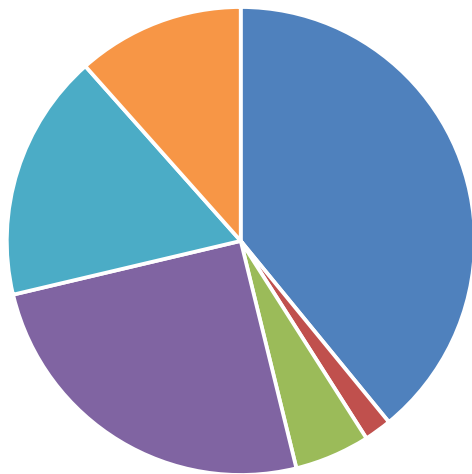
TABLE IB - LIST OF APPROVED INORGANIC TEST PROCEDURES

Parameter	Methodology ²⁵	EPA ²⁶	Standard methods	ASTM	USGS/AOAC/other
1. Acidity, as CaCO ₃ , mg/L	Electrometric endpoint or phenolphthalein endpoint		2310 B-2011	D1067-11	1-1030-85. ²
2. Alkalinity, as CaCO ₃ , mg/L	Electrometric or Colorimetric titration to pH 4.5, Manual		2320 B-2011	D1067-11	973.43, ³ 1-1030-85. ²
	Automatic	310.2 (Rev. 1974) ¹			1-2030-85. ²
3. Aluminum - Total, ²⁷ mg/L	Digestion, ⁴ followed by any of the following:				
	AA direct aspiration ²⁸		3111 D-2011 or 3111 E-2011		1-3051-85. ²
	AA furnace		3113 B-2010.		
	STGFAA	200.9, Rev. 2.2 (1994)			
	ICP/AES ²⁹	200.5, Rev. 4.2 (2003); ²⁸ 200.7, Rev. 4.4 (1994)	3120 B-2011	D1978-12	1-4471-97. ²⁸

Incorporation by reference is used primarily to make privately developed technical standards Federally enforceable

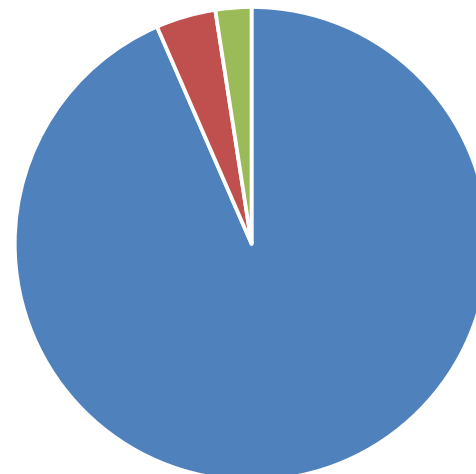
Incorporation of VCSB in Federal Environmental Regulations

All CFRs



- ASTM
- AOAC
- ISO
- Standard Methods
- ANSI
- API

40 CFR



- ASTM
- Standard Methods
- AOAC

Any Questions?

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