



**Techniques of Water-Resources Investigations
of the United States Geological Survey**

Chapter A1

**METHODS FOR DETERMINATION
OF INORGANIC SUBSTANCES
IN WATER
AND FLUVIAL SEDIMENTS**

By Marvin J. Fishman and Linda C. Friedman, Editors

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Book 5
LABORATORY ANALYSIS

Sodium, atomic absorption spectrometric, direct

Parameters and Codes:

Sodium, dissolved, I-1735-85 (mg/L as Na): 00930
Sodium, total recoverable, I-3735-85 (mg/L as Na): none assigned
Sodium, recoverable-from-bottom-material, dry wt, I-5735-85 (mg/kg as Na): 00934

1. Application

1.1 This method may be used to analyze atmospheric precipitation, water, brines, and water-suspended sediment.

1.2 Two analytical ranges for sodium are included: from 0.01 to 1.0 mg/L and from 0.10 to 80 mg/L. Sample solutions containing sodium concentrations greater than 80 mg/L need to be diluted.

1.3 This method may be used to analyze bottom material containing at least 10 mg/kg of sodium.

1.4 Total recoverable sodium in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable sodium in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

2. Summary of method

2.1 Sodium is determined by atomic absorption spectrometry by direct aspiration of the sample solution into an air-acetylene flame (Fishman and Downs, 1966).

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer.

3. Interferences

None of the substances commonly occurring in natural water interfere with this method.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout and automatic zero and concentration controls.

4.2 Refer to the manufacturer's manual to optimize instrument for the following:

Grating -----	Visible
Wavelength -----	588.8 nm
Source (hollow-cathode lamp) -----	Sodium
Oxidant -----	Air
Fuel -----	Acetylene
Type of flame -----	Oxidizing

4.3 The 50-mm (2-in.), flathead, single-slot burner, rotated 90°, allows working ranges of 0.01 to 1.0 mg/L and 0.1 to 80 mg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Sodium standard solution*, 1.00 mL = 1.00 mg Na: Dissolve 2.542 g NaCl in demineralized water and dilute to 1,000 mL.

5.2 *Sodium working standards*: Prepare a series of at least six working standards containing either from 0.01 to 1.0 mg/L or from 0.10 to 80 mg/L sodium by appropriate dilutions of sodium standard solution. The preparation of an intermediate standard solution is desirable when preparing working solutions of extreme dilution.

6. Procedure

While aspirating the blank use the automatic zero control to set the digital display to read zero concentration. While aspirating standards use the automatic concentration control to set the digital display to read concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

7.1 Determine the milligrams per liter of dissolved or total recoverable sodium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing sodium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine milligrams per kilogram of sodium in bottom-material samples, first determine the milligrams per liter of sodium as in paragraph 7.1, then:

$$\text{Na (mg/kg)} = \frac{\text{mg/L Na} \times \frac{\text{mL original digest}}{1000}}{\text{wt of sample (kg)}}$$

8. Report

8.1 Report sodium, dissolved (00930), and total-recoverable (none assigned), concentrations as follows: less than 1.0 mg/L, two decimals; 1.0 to 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

8.2 Report sodium, recoverable-from-bottom-material (00934), concentrations as follows: less than 1,000 mg/kg, nearest 10 mg/kg; 1,000 mg/kg and above, two significant figures.

9. Precision

9.1 Precision for dissolved sodium for 33 samples within the range of 0.20 to 222 mg/L may be expressed as follows:

$$S_T = 0.046X + 0.186$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of sodium, milligrams per liter.

The correlation coefficient is 0.9461.

9.2 Precision for dissolved sodium for six of the 33 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
22	0.20	35
36	2.76	13
25	15.4	6
35	56.0	5
31	96.9	5
19	222	6

9.3 Precision for dissolved sodium within the range of 0.01 to 1.0 mg/L in terms of the percent relative standard deviation by a single operator is as follows:

Number of replicates	Mean (mg/L)	Relative standard deviation (percent)
8	0.009	26.5
8	.028	16.8
8	.136	3.8
8	.540	1.0

9.4 It is estimated that the percent relative standard deviation for total recoverable sodium and for recoverable sodium from bottom material will be greater than that reported for dissolved sodium.

Reference

Fishman, M. J., and Downs, S. C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 38-41.

Sodium, atomic absorption spectrometric, direct-EPA

Parameter and Code:

Sodium, total recoverable, I-3736-85 (mg/L as Na): 00929

1. Application

1.1 This method may be used to analyze water-suspended sediment containing from 0.1 to 80 mg/L of sodium. If the sodium concentration exceeds 80 mg/L, the sample solution needs to be diluted. The method is very sensitive and can be extended to much lower sodium concentrations.

1.2 For ambient water, analysis may be made on an aliquot of the acidified water-suspended sediment sample.

1.3 For all other water, including domestic and industrial effluent, the atomic absorption procedure must be preceded by a digestion-solubilization as specified below. In cases where the analyst is uncertain of the type of sample, this procedure must be followed.

2. Summary of method

2.1 Sodium is determined by atomic absorption spectrometry by direct aspiration of the filtered or digested and filtered sample into an air-acetylene flame (Fishman and Downs, 1966).

2.2 Effluent samples must undergo a preliminary nitric acid digestion followed by a hydrochloric acid solubilization.

3. Interferences

None of the substances commonly occurring in natural water interfere with this method.

4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout and automatic zero and concentration controls.

4.2 Refer to the manufacturer's manual to optimize instrument for the following:

Grating -----	Visible
Wavelength -----	588.8 nm
Source (hollow-cathode lamp) -----	Sodium
Oxidant -----	Air
Fuel -----	Acetylene
Type of flame -----	Oxidizing

4.3 The 50-mm (2-in.), flathead, single-slot burner, rotated 90°, allows a range of 0.1 to 80 mg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Hydrochloric acid 6M*: Dilute 500 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.2 *Hydrochloric acid, 0.3M*: Dilute 25 mL concentrated HCl (sp gr 1.19) to 1 L with demineralized water.

5.3 *Nitric acid, concentrated* (sp gr 1.41).

5.4 *Sodium standard solution, 1.00 mL = 1.00 mg Na*: Dissolve 2.542 g NaCl in demineralized water and dilute to 1,000 mL.

5.5 *Sodium working standards*: Prepare a series of at least six working standards containing from 0.1 to 80 mg/L sodium by appropriate dilutions of sodium standard solution. The preparation of an intermediate standard solution is desirable when preparing working solutions of extreme dilution.

6. Procedure

6.1 When analyzing samples of ambient waters, begin the analysis at step 6.9.

6.2 Transfer the entire sample to a beaker.

6.3 Rinse the sample bottle with 3 mL concentrated HNO₃ for each 100 mL of sample and

add to the beaker. Prepare a blank using 3 mL concentrated HNO_3 per 100 mL demineralized water.

6.4 Evaporate samples and blank to dryness on a hotplate, making sure the samples do not boil.

6.5 Cool and add an additional 3 mL concentrated HNO_3 to the beaker. Cover with a watchglass, return to the hotplate, and gently reflux the solution.

6.6 Continue heating, adding more acid as necessary until the digestion is complete (indicated by a light-colored residue). Evaporate just to dryness.

6.7 Add 6 mL 6M HCl solution per 100 mL original sample and warm the solution to dissolve the residue.

6.8 Filter (Whatman No. 41 or equivalent) the sample and wash the watchglass and beaker with demineralized water. Rinse the filter with hot 0.3M HCl. Dilute to the original volume with demineralized water.

6.9 While aspirating the blank use the automatic zero control to set the digital display to read zero concentration. While aspirating standards use the automatic concentration control to set the digital display to read concentration of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

7. Calculations

Determine the milligrams per liter of total recoverable sodium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing sodium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

8. Report

Report sodium, total-recoverable (00929), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

It is estimated that the percent relative standard deviation for total recoverable sodium is greater than 13 percent at 2.76 mg/L and greater than 5 percent at 96.9 mg/L.

References

- Fishman, M. J., and Downs, S.C., 1966, Methods for analysis of selected metals in water by atomic absorption: U.S. Geological Survey Water-Supply Paper 1540-C, p. 38-41.
- U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, p. 273.1-1.

Sodium, atomic emission spectrometric, ICP

Parameter and Code:

Sodium, dissolved, I-1472-85 (mg/L as Na): 00930

2. Summary of method

Sodium is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric

method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

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Sodium, total-in-sediment, atomic absorption spectrometric, direct

Parameters and Codes:

Sodium, total, I-5473-85 (mg/kg as Na): none assigned

Sodium, total, I-5474-85 (mg/kg as Na): none assigned

2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized. The sample is then treated and analyzed by one of the following techniques.

2.1.1 The sample is fused with a mixture of lithium metaborate and lithium tetraborate in a graphite crucible in a muffle furnace at 1,000°C. The resulting bead is dissolved in acidified, boiling, demineralized water, and sodium is determined by atomic absorption

spectrometry. See method I-5473, metals, major, total-in-sediment, atomic absorption spectrometric, direct.

2.1.2 The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200°C. Sodium is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.

Sodium adsorption ratio, calculation

Parameter and Code:
Sodium adsorption ratio, I-1738-85: 00931

1. Application

This method may be applied to any sample for which measured values for sodium, calcium, and magnesium are available.

2. Summary of method

The sodium adsorption ratio (SAR) is computed from the individual determination of sodium, calcium, and magnesium after conversion of each to milliequivalents per liter (me/L).

7. Calculations

$$\text{SAR} = \frac{\text{me/L Na}}{\sqrt{\frac{\text{me/L Ca} + \text{me/L Mg}}{2}}}$$

8. Report

Report sodium adsorption ratio, calculation (00931), as follows: less than 1.0, one decimal; 1.0 and above, whole numbers.

9. Precision

Precision data are not available for this method, but reproducibility should be comparable to that of the individual determinations.

Sodium, percent, calculation

Parameter and Code:
Sodium, percent, I-1740-85: 00932

1. Application

This method may be applied to any sample for which measured values for sodium, potassium, calcium, and magnesium are available.

2. Summary of method

Percent sodium is computed from the milliequivalent per liter (me/L) of sodium, potassium, calcium, and magnesium.

7. Calculations

$$\text{Sodium (percent)} = \frac{\text{me/L Na}}{\sum \text{me/L (Na + K + Ca + Mg)}} \times 100$$

8. Report

Report sodium, percent, calculation (00932), as whole numbers.

9. Precision

Precision data are not available for this method, but reproducibility should be comparable to that of the individual determinations.

Solids, residue on evaporation at 180°C, dissolved, gravimetric

Parameter and Code:

Solids, residue on evaporation at 180°C, dissolved I-1750-85 (mg/L): 70300

1. Application

The residue-on-evaporation method is applicable to all water regardless of concentration, provided that the residue layer in the evaporation dish is kept sufficiently thin.

2. Summary of method

2.1 A volume of filtered sample that will yield less than 200 mg residue is evaporated just to dryness on a steam bath. The residue is then dried at 180°C for exactly 2 hours, cooled in a desiccator, and immediately weighed.

2.2 The weight of the residue is limited to 200 mg to ensure subjection of all the residue to the full effects of drying at 180°C. Voluminous residues will often seal over during the evaporation process and entrap pockets of water that will not be completely vaporized during the drying process. Massive residues also release their water of crystallization more slowly than do thin films of residue. The chemical composition of the sample has a marked effect on the dissolved-solids value obtained, but the percentage of error incurred for any given chemical type of water is independent of the total concentration if the residue film is kept thin.

2.3 Bicarbonate is converted to carbonate in the evaporation and drying process. The following general observations have been reported by Howard (1933). The residues of carbonate-type water that contain considerable magnesium chloride can be expected to lose some weight (as much as 50 or 100 mg/L) during the drying process; however, such loss of weight is usually more than offset by the water of crystallization tightly held by the salts. Most of the water of crystallization is driven off from sulfates of sodium and magnesium when the

residue is heated at 180°C, but this temperature is insufficient to dehydrate calcium sulfate completely. Residues of water with a high nitrate content may lose as much as 30 mg/L on heating.

2.4 Because many of the salts in the residue are hygroscopic, an efficient desiccant must be used. Silica gel (indicating), anhydrous $Mg(ClO_4)_2$ or $CaSO_4$, and $Mg(ClO_4)_2 \cdot 3H_2O$ are satisfactory and recommended. $CaCl_2$ is not suitable. Under no circumstances should the dried residues be allowed to stand for long periods of time before weighing.

3. Interferences

There are no known interferences to this method.

4. Apparatus

4.1 *Desiccator*, charged with indicating silica gel or other efficient desiccant.

4.2 *Oven*, 180°C, uniform temperature throughout.

4.3 *Platinum evaporating dishes*, 75- to 125-mL capacity, weighing less than 50 g, or zirconium dishes. Platinum or zirconium are recommended for precise work because the change in weight of glass or porcelain dishes may introduce appreciable error into the determination.

4.4 *Steam bath*.

5. Reagents

None required.

6. Procedure

6.1 Pipet a volume of filtered sample containing 10 to 200 mg dissolved solids (500 mL max) into a tared platinum dish.

6.2 Evaporate the sample just to dryness on a steam bath.

6.3 Dry in an oven at 180°C for 2.0 h.

6.4 Cool in a desiccator and immediately weigh. Record the weight to the nearest 0.1 mg.

7. Calculations

Dissolved solids (mg/L) =

$$\frac{1,000}{\text{mL sample}} \times \text{mg residue}$$

8. Report

Report solids, residue on evaporation at 180°C, dissolved (70300), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

9.1 Precision for dissolved solids for 22 samples within the range of 60 to 1760 mg/L may be expressed as follows:

$$S_T = 0.024X + 11.3$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of dissolved solids, milligrams per liter.

The correlation coefficient is 0.7633.

9.2 Precision for dissolved solids for six of the 22 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
27	59.2	8
28	267	4
39	524	11
28	558	2
29	1160	4
49	1760	3

Reference

Howard, C. S., 1933, Determination of total dissolved solids in water analysis: Industrial Engineering Chemistry, Analytical Edition, v. 5. p. 4.

Solids, residue on evaporation at 105°C, dissolved, gravimetric

Parameter and Code:

Solids, residue at 105°C, dissolved, I-1749-85 (mg/L): 00515

1. Application

The residue-on-evaporation method is applicable to all water regardless of concentration, provided that the residue layer in the evaporating dish is kept sufficiently thin.

2. Summary of method

2.1 A volume of filtered sample that will yield less than 200 mg residue is evaporated just to dryness on a steam bath. The residue is dried at 105°C for 2.0 h, cooled in a desiccator, and immediately weighed.

2.2 The weight of the residue is limited to 200 mg to ensure subjection of all the residue to the full effects of drying at 105°C. Voluminous residues will often seal over during the evaporation process and entrap pockets of water that will not be completely vaporized during the drying process. Massive residues also release their water of crystallization more slowly than do thin films of residue. The chemical composition of the sample has a marked effect on the dissolved-solids value obtained, but the percentage of error incurred for any given chemical type of water is independent of the total concentration if the residue film is kept thin.

2.3 Because many of the salts in the residue are hygroscopic, an efficient desiccant must be used. Silica gel (indicating), anhydrous $Mg(ClO_4)_2$ or $CaSO_4$, and $Mg(ClO_4)_2 \cdot 3H_2O$ are satisfactory and recommended. $CaCl_2$ is not suitable. Under no circumstances should the dried residues be allowed to stand for long periods of time before weighing.

3. Interferences

There are no known interferences to this method.

4. Apparatus

4.1 *Desiccator*, charged with indicating silica gel or other efficient desiccant.

4.2 *Oven*, 105°C, uniform temperature throughout.

4.3 *Platinum evaporating dishes*, 75- to 125-mL capacity, weighing less than 50 g, or zirconium dishes. Platinum or zirconium is recommended for precise work because the change in weight of glass or porcelain dishes may introduce appreciable error into the determination.

4.4 *Steam bath*.

5. Reagents

None required.

6. Procedure

6.1 Pipet a volume of filtered sample containing 10 to 200 mg dissolved solids (500 mL max) into a tared platinum dish.

6.2 Evaporate the sample just to dryness on a steam bath.

6.3 Dry in an oven at 105°C for 2.0 h.

6.4 Cool in a desiccator and immediately weigh. Record the weight to the nearest 0.1 mg.

7. Calculations

$$\text{Dissolved solids (mg/L)} = \frac{1,000}{\text{mL sample}} \times \text{mg residue}$$

8. Report

Report solids, residue on evaporation at 105°C, dissolved (00515), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

It is estimated that the percent relative standard deviation of this method is greater than 8 percent at 59 mg/L and greater than 3 percent at 1760 mg/L.

Reference

American Public Health Association and others, 1980, Standard methods for the examination of water and wastewater [15th ed]: Washington, D.C., p. 92-4.

Solids, residue on evaporation at 105°C, total, gravimetric

Parameter and Code:

Solids, residue on evaporation at 105°C, total, I-3750-85 (mg/L): 00500

1. Application

1.1 This method may be used to determine the total-solids concentration of any natural or treated water or industrial waste.

1.2 Total residue represents the sum of both dissolved and suspended (including colloidal) material in a sample. The determination is not exact, because of the compromise that must be made in selecting the temperature at which the evaporated residue is to be dried. At temperatures sufficient to release water of hydration of the hydrated salts that form on evaporation, there is risk of volatilization of the more volatile dissolved or suspended materials in the sample. On the other hand, drying at a sufficiently low temperature to conserve volatiles fails to remove much of the entrapped water and ordinary water of hydration. Because of these factors, the determination must be considered as providing only an approximation of the sum of dissolved and suspended matter.

1.3 The determination is not very useful; determination of dissolved solids (method I-1749) and suspended solids (method I-3765) provides more useful information.

2. Summary of method

A volume of well-mixed sample is evaporated to dryness. The residue is dried at 105°C for 2.0 h, cooled in a desiccator, and immediately weighed.

3. Interferences

Care must be taken to ensure that a representative sample is provided. Usually, large, floating particles are excluded from the sample.

4. Apparatus

4.1 *Desiccator*, charged with indicating silica gel or other efficient desiccant.

4.2 *Oven*, 105°C, uniform temperature throughout.

4.3 *Platinum evaporating dishes*, 75- to 125-mL capacity, weighing less than 50 g, or zirconium dishes. Platinum or zirconium is recommended because the change in weight of glass or porcelain dishes may introduce appreciable error into the determination.

6. Procedure

6.1 Shake the sample vigorously and rapidly pipet a suitable aliquot of unfiltered sample.

6.2 Transfer the sample to a tared platinum evaporating dish.

6.3 Rinse the pipet with demineralized water to ensure transfer of all particulate matter to the evaporating dish.

6.4 Evaporate the sample just to dryness on a steam bath.

6.5 Dry in an oven at 105°C for 2.0 h.

6.6 Cool in a desiccator and immediately weigh. Record the weight to the nearest 0.1 mg.

7. Calculations

$$\text{Total solids (mg/L)} = \frac{1,000}{\text{mL sample}} \times \text{mg residue}$$

8. Report

Report solids, residue on evaporation at 105°C, total (00500), concentrations as follows:

less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

It is estimated that the percent relative standard deviation of this method is greater than 8

percent at 59 mg/L and greater than 3 percent at 1760 mg/L.

Reference

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, p. 160.3.

Solids, residue at 105°C, suspended, gravimetric

Parameter and Code:

Solids, residue at 105°C, suspended, I-3765-85 (mg/L): 00530

1. Application

This method may be used to determine the suspended-solids concentration of any natural or treated water or industrial waste.

2. Summary of method

2.1 Suspended solids are those that are retained on a glass-fiber filter. The determined value is fairly representative of the sample but does not accurately represent the suspended-sediment concentration of a stream; suspended-solids values should not be confused with sediment concentration, which is the more accurate measure of material in suspension.

2.2 The unfiltered sample is mixed thoroughly and an appropriate volume is rapidly poured into a graduated cylinder. The suspended solids are collected on a glass-fiber filter, and the insoluble residue is dried and weighed.

3. Interferences

Precipitation in the sample during storage, such as iron, will produce erroneously high results.

4. Apparatus

4.1 *Desiccator*, charged with indicating silica gel or other efficient desiccant.

4.2 *Filtration apparatus*, consisting of suction flask, gooch crucible, glass-fiber filter disk, and suitable holder.

4.3 *Oven*, 105°C, uniform temperature throughout.

6. Procedure

6.1 Shake the sample bottle vigorously and rapidly pour a suitable volume into a graduated cylinder. Record the volume.

6.2 Quantitatively collect the suspended material from the sample on a tared glass-fiber filter disk. A blank should be determined with each set of samples.

6.3 Wash the suspended material on the filter sparingly with demineralized water.

6.4 Dry the residue and filter disk overnight at 105°C.

6.5 Cool in a desiccator and weigh the filter disk containing the dry residue to the nearest 0.1 mg. Record the weight.

7. Calculations

7.1 Apply a correction for any loss shown by the blank.

7.2 Determine suspended solids in milligrams per liter as follows:

Suspended solids, mg/L =

$$\frac{1000}{\text{mL sample}} \times \text{mg residue}$$

8. Report

Report solids, residue at 105°C, suspended (00530), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

Precision data are not available for this method.

Reference

Guy, H. P., 1969, Laboratory theory and methods for sediment analysis: Techniques of Water-Resources Investigations of the U.S. Geological Survey, book 5, chapter C1, 58 p.

Solids, volatile-on-ignition, dissolved, gravimetric

Parameter and Code:

Solids, volatile-on-ignition, dissolved, I-1753-85 (mg/L): 00520

1. Application

This method may be used to analyze any natural, treated, or industrial water and other wastewater.

2. Summary of method

The residue obtained after determination of dissolved solids (method I-1750) is ignited at 550°C. The loss in weight of residue represents a measure of dissolved volatile solids.

3. Interferences

3.1 None of the substances commonly occurring in natural waters interfere with this method.

3.2 Because of the great variability in the nature of the compounds that can be present in the sample, particularly in samples of industrial and other wastes, the determination can be considered only an approximation of the amount of volatile material present. Some of the volatile material may have been released during the determination of dissolved solids. Moreover, ignition at 550°C volatilizes water of hydration from the hydrated salts present.

4. Apparatus

4.1 *Muffle furnace*, 550°C.

4.2 For additional items of required apparatus, see solids, dissolved (method I-1750).

5. Reagents

None required.

6. Procedure

6.1 Determine dissolved solids as directed in method I-1750.

6.2 Place the weighed evaporating dish in a muffle furnace at 550°C; heat for 1 h.

6.3 Remove and cool in a desiccator; weigh and record the weight to the nearest 0.1 mg.

7. Calculations

Solids, volatile on ignition, dissolved, mg/L =

$$\frac{1000}{\text{mL sample}} \times (ER - IR)$$

where

ER = weight of dissolved solids, milligrams,

IR = weight of ignited residue, milligrams.

8. Report

Report solids, volatile-on-ignition, dissolved (00520), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

Precision data are not available for this method.

Solids, volatile-on-ignition, total, gravimetric

Parameter and Code:

Solids, volatile-on-ignition, total, I-3753-85 (mg/L): 00505

1. Application

This method may be used to analyze any natural, treated, or industrial water and other waste.

2. Summary of method

A measured volume of well-mixed, unfiltered sample is evaporated to dryness. The residue is dried at 105 °C for 2.0 h, cooled in a desiccator, and immediately weighed. See solids, total (method I-3750). The residue is then ignited at 550 °C and weighed, the difference in weight representing total volatile solids.

3. Interferences

3.1 Care must be taken to ensure that a representative sample is provided. Usually, large, floating particles are excluded from the sample.

3.2 Because of the great variability in the nature of the compounds that can be present in the sample, particularly in samples of industrial and other wastes, the determination can be considered only an approximation of the amount of volatile material present. Much of the volatile material may have been released during the determination of total residue. Moreover, ignition at 550 °C certainly volatilizes water of hydration from the hydrated salts present.

4. Apparatus

4.1 *Muffle furnace*, 550 °C.

4.2 For additional items of required apparatus, see solids, dissolved (method I-3750).

5. Reagents

None required.

6. Procedure

6.1 Determine the total solids as directed in solids, total (method I-3750).

6.2 Place the weighed evaporating dish in a muffle furnace at 550 °C; heat for 1 h.

6.3 Remove and cool in a desiccator. Weigh and record the weight to the nearest 0.1 mg.

7. Calculations

Solids, volatile-on-ignition, total mg/L =

$$\frac{1000}{\text{mL sample}} \times (ER - IR)$$

where

ER = weight of evaporated total residue, milligrams,

IR = weight of ignited total residue, milligrams.

8. Report

Report solids, volatile-on-ignition, total (00505), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

Precision data are not available for this method.

Solids, volatile-on-ignition, suspended, gravimetric

Parameter and Code:

Solids, volatile-on-ignition, suspended, I-3767-85 (mg/L): 00535

1. Application

This method may be used to analyze any natural or treated water or industrial waste.

2. Summary of method

The dry residue obtained for the determination of suspended solids (method I-3765) is ignited at 550°C for 1 h. The loss on ignition corresponds to the amount of volatile suspended solids.

3. Interferences

3.1 None of the substances commonly occurring in natural waters interfere with this method.

3.2 Because of the great variability in the nature of the compounds that can be present in the sample, particularly in samples of industrial waste, the determination can be considered only an approximation of the amount of volatile material present. Some of the volatile material may have been released during the determination of suspended solids. Moreover, ignition at 550°C certainly volatilizes water of hydration from the hydrated salts present.

4. Apparatus

4.1 *Muffle furnace*, 550°C.

4.2 For additional items of required apparatus, see solids, suspended (method I-3765).

5. Reagents

None required.

6. Procedure

6.1 Determine suspended solids as directed in method I-3765.

6.2 Place the weighed gooch crucible containing the dry suspended solids in a muffle furnace at 550°C; heat for 1 h. A blank should be determined with each set of samples.

6.3 Remove and cool in a desiccator. Weigh and record the weight to the nearest 0.1 mg.

7. Calculations

Solids, volatile-on-ignition, suspended, mg/L =

$$\frac{1000}{\text{mL sample}} \times (ER - IR)$$

where

ER = weight of dry suspended solids, milligrams,

IR = weight of ignited suspended solids, milligrams.

8. Report

Report solids, volatile-on-ignition, suspended (00535), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

Precision data are not available for this method.

Solids, volatile-on-ignition, total-in-bottom-material, gravimetric

Parameter and Code:

Solids, volatile-on-ignition, total-in-bottom-material, dry wt, I-5753-85 (mg/kg): 00496

1. Application

This method may be used to analyze samples of bottom material. Usually, only the material that will pass a 2-mm sieve is taken for analysis.

2. Summary of method

A portion of well-mixed sample is dried at 105°C. A portion of dry, well-mixed sample is carefully weighed and then ignited at 550°C. The loss of weight on ignition represents the amount of volatile solids in the sample.

3. Interferences

None.

4. Apparatus

4.1 *Desiccator*, charged with indicating silica gel or other efficient desiccant.

4.2 *Muffle furnace*, 550°C.

4.3 *Oven*, 105°C, uniform temperature throughout.

4.4 *Platinum evaporating dishes*, 75- to 125-mL capacity, weighing less than 50 g. Platinum is recommended because the change in weight of glass or porcelain dishes may introduce appreciable error into the determination.

5. Reagents

None required.

6. Procedure

6.1 Spread approx 1 g of sample in the

bottom of a platinum evaporating dish. Place in an oven at 105°C and heat overnight.

6.2 Place the dish containing the dry sample in a desiccator, cool, and weigh to the nearest 0.1 mg.

6.3 Ignite the weighed dry residue at 550°C for 1 h, cool in a desiccator, and weigh to the nearest 0.1 mg.

7. Calculations

Solids, volatile-on-ignition (mg/kg) =

$$\frac{(DR-IR) \times 10^6}{DR}$$

where

IR = weight of ignited residue, milligrams, and

DR = weight of dry residue, milligrams.

8. Report

Report solids, volatile-on-ignition, total-in-bottom-material (00496), concentrations as follows: less than 1,000 mg/kg, whole numbers; 1,000 mg/kg and above, three significant figures.

9. Precision

Precision data are not available for this method.

Solids, nonvolatile-on-ignition, dissolved, calculation

Parameter and Code:

Solids, nonvolatile-on-ignition, dissolved, I-1752-85 (mg/L): 00525

1. Application

This method may be used to calculate nonvolatile dissolved solids on any sample for which the dissolved solids (method I-1750) and the volatile dissolved solids (method I-1753) have been determined.

2. Summary of method

The nonvolatile solids are determined by subtracting the volatile dissolved solids (method I-1753) from the dissolved solids (method I-1750).

7. Calculations

Solids, nonvolatile-on-ignition,
dissolved, mg/L = $DS - DV$

where

DS = dissolved solids, milligrams per liter,
and

DV = solids, volatile on ignition, dissolved,
milligrams per liter.

8. Report

Report solids, nonvolatile-on-ignition, dissolved (00525), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

Precision data are not available for this method.

Solids, nonvolatile-on-ignition, total, calculation

Parameter and Code:

Solids, nonvolatile-on-ignition, total, I-3752-85 (mg/L): 00510

1. Application

This method may be used to calculate total nonvolatile solids on any sample for which the total solids (method I-3750) and the total volatile solids (method I-3753) have been determined.

2. Summary of method

Total nonvolatile solids are determined by subtracting the total volatile solids (method I-3753) from the total solids (method I-3750).

7. Calculations

Solids, nonvolatile-on-ignition,
total, (mg/L) = $TS-TV$

where

TS = total solids, milligrams per liter,
and

TV = solids, volatile on ignition, total, milli-
grams per liter.

8. Report

Report solids, nonvolatile-on-ignition, total (00510), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

Precision data are not available for this method.

Solids, nonvolatile-on-ignition, suspended, calculation

Parameter and Code:

Solids, nonvolatile-on-ignition, suspended, I-3766-85 (mg/L): 00540

1. Application

This method may be used to calculate non-volatile suspended solids on any sample for which the suspended solids (method I-3765) and volatile suspended solids (method I-3767) have been determined.

2. Summary of method

The nonvolatile suspended solids are determined by subtracting the volatile suspended solids (method I-3767) from the suspended solids (method I-3765).

7. Calculations

Solids, nonvolatile on ignition,
suspended, mg/L = $SS - VS$

where

SS = suspended solids, milligrams per liter,
and

VS = solids, volatile on ignition, suspended,
milligrams per liter.

8. Report

Report solids, nonvolatile-on-ignition, suspended (00540), concentrations as follows: less than 1,000 mg/L, whole numbers; 1,000 mg/L and above, three significant figures.

9. Precision

Precision data are not available for this method.

Solids, sum of constituents, calculation

Parameter and Code:

Solids, dissolved, I-1751-85 (mg/L): 70301

1. Application

The calculation method is applicable only to those analyses that include determinations of all major constituents. Such analyses are considered to be complete for all practical purposes. The chemist can never be certain of the completeness of the analysis, but for most alkaline waters other than brines, the determination of silica, calcium, magnesium, sodium, potassium, alkalinity, sulfate, chloride, and nitrate is sufficient. The wide range of metals possible in acid water precludes assumptions as to the completeness of the analysis.

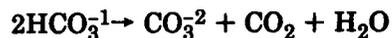
2. Summary of method

2.1 The concentrations of all determined constituents are converted mathematically into the forms in which they would normally exist in an anhydrous residue. These quantities are then added. If the water is grossly polluted, it is usually necessary to determine the nitrogen components. Concentration of carbonaceous material can be estimated by redissolving the residue on evaporation and successively treating it with several amounts of hydrogen peroxide. The difference in weight between the nonoxidized residue and the oxidized residue is an indication of the carbonaceous solids. The estimated carbonaceous solids are not included in the calculated dissolved solids, but are one measure of the differences to be expected between dissolved solids determined by residue on evaporation and by calculation (Howard, 1933).

2.2 The conversion of the constituents in the analysis to the forms in which they would normally exist in an anhydrous residue involves many unknown variables. Consequently, summarizing the constituents requires the arbitrary

assumption that all material present in the theoretical anhydrous residue be in the same form as reported in the analysis, with the exception of bicarbonate.

All bicarbonate in solution is assumed to exist as carbonate in the residue:



Therefore, the bicarbonate in solution is mathematically converted to its equivalent weight as carbonate in the residue.

2.3 The accuracy of the result is dependent on the completeness of the analysis and on the validity of each reported constituent concentration.

7. Calculations

7.1.1 If a field bicarbonate determination was made, convert bicarbonate concentration to carbonate concentration as follows:

$$\text{mg/L CO}_3^{-2} = \frac{\text{mg/L HCO}_3^{-1}}{2.03}$$

7.1.2 Alternatively, convert alkalinity concentration reported as mg/L CaCO₃ to carbonate concentration:

$$\text{mg/L CO}_3^{-2} = \text{mg/L CaCO}_3 \times 0.60$$

7.2 Add all determined dissolved constituents reported in the analytical statement. The

following constituents must be included: calcium, magnesium, sodium, potassium, alkalinity, chloride, nitrate, sulfate, and silica.

8. Report

Report solids, dissolved, calculated (70301), concentrations as follows: less than 100 mg/L, whole numbers; 100 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method, but reproducibility should be comparable to that of the individual determinations.

Reference

Howard, C. S., 1933, Determination of total dissolved solids in water analysis: Industrial Engineering Chemistry, Analytical Edition, v. 5, p. 4.

Specific conductance, electrometric, Wheatstone bridge

Parameters and Codes:

Specific conductance, lab, I-1780-85 ($\mu\text{S}/\text{cm}$ at 25°C): 90095
Specific conductance, lab, automated, I-2781-85 ($\mu\text{S}/\text{cm}$ at 25°C): 90095

1. Application

This method may be applied to all natural, treated, and industrial water.

2. Summary of method

2.1 Specific conductance is determined by using a Wheatstone bridge in which a variable resistance is adjusted so that it is equal to the resistance of the unknown solution between platinized electrodes of a standardized conductivity cell. The ability of a solution to conduct an electric current is a function of the concentration and charge of the ions in the solution and also depends on the rate at which the ions can move under the influence of an electrical potential. As the number of ions per unit volume of solution increases, the rate at which individual ions can move decreases, because of interionic attraction and other effects. For this reason, a graph of total-ion concentration versus specific conductance, even for solutions of a single salt, is a simple straight line only for rather dilute solutions. As specific conductance increases beyond about $5,000 \mu\text{S}/\text{cm}$ at 25°C , the regression line curves, and beyond $50,000 \mu\text{S}/\text{cm}$, the specific conductance is generally an unsatisfactory index of solute-ion concentration.

2.2 The temperature of the electrolyte affects the ionic velocities and, consequently, the conductance. Conductance increases about 2 percent per degree Celsius, which is about the same as the temperature coefficient of viscosity of water.

2.3 In the determination of the specific conductance, preparing a cell having electrodes exactly 1 cm^2 in area and exactly 1 cm apart would be difficult. Moreover, such an exact cell

is unnecessary because a factor called the cell constant (C) can be determined. The cell constant is determined experimentally with a standard solution of known conductance. A $0.00702N$ potassium chloride solution has a specific conductance of $0.001000 \text{ S}/\text{cm}$ at 25°C . The relation between resistance (R), cell constant (C), and specific conductance (K) is shown in the following equation, where K is known and R is determined:

$$RK = C$$

Thus, if the resistance of the cell, when filled with $0.00702N$ KCl, is, for example, 350 ohms, the cell constant would be 0.35 for the conductivity cell used. If the conductivity cell having a cell constant of 0.35 is filled with a sample at 25°C and the observed resistance is 865 ohms, the specific conductance of the sample could be derived from the cell-constant equation:

$$\frac{C}{R} = K$$

Substituting values from the example yields the following:

$$\frac{0.35}{865} = 0.00405 \text{ S at } 25^\circ\text{C}$$

2.4 Unless a constant-temperature room or bath is available, adjustment of sample temperature (T) to exactly 25°C is difficult. For most work, specific conductance is computed from the following equation: $\mu\text{S}/\text{cm} = (R \text{ of } 0.00702N$

KCl at T of sample measurement $\times 1,000) \times (1/R$ of the sample).

2.5 New conductivity cells should be visually checked for cleanliness and platinum uniformity before use. Subsequently, they should be cleaned and replatinized whenever the readings become erratic or indistinct or inspection shows that any platinum black has flaked off. One platinization will usually suffice for a period of several months. To platinize the electrodes, clean them in chromic acid solution and rinse thoroughly in several changes of water. Place the electrodes in a solution of chloroplatinic acid and lead acetate (dissolve 3 g H_2PtCl_6 in 10 mL water to which 20 mg $Pb(C_2H_3O_2)_2$ is added; commercial platinizing solutions are also available). Connect the electrodes to two dry cells ($1\frac{1}{2}$ -V each) in parallel and reverse the direction of the current once per minute for 6 min, or until the shiny platinum surface is covered. Avoid deposition of amorphous platinum on the electrodes.

Repeat the electrolytic process, using 10-percent sulfuric acid to remove chlorine. When not in use, the cell should be kept immersed in distilled water.

2.6 The accuracy and reproducibility of results obtainable depend largely on the type of bridge used, but can approach 2 percent with this equipment. Close attention to temperature is essential for reliable work.

2.7 Additional information on the theory and practice of specific conductance measurements can be found in Daniels and Alberty (1966), and in Scofield (1932).

2.8 This procedure may be automated by the addition of commercially available instrumentation.

3. Interferences

None.

4. Apparatus

4.1 *Conductivity cell:* Cells of at least two different cell constants should be available to measure a wide range of conductivities. The table below provides a general guide to the selection of an appropriate cell constant.

Specific conductance ($\mu S/cm$ at 25°C)	Cell constant (cm^{-1})
20-1,000	0.2
40-2,000	.5
100-4,000	1.0
200-10,000	2.0
400-20,000	5.0
1,000-40,000	10.0

4.2 *Conductivity meter,* Wheatstone-bridge type or equivalent direct-reading meter.

4.3 *Thermometer,* 0 to 50°C, graduated in 0.1°C. Some direct-reading conductivity meters have automatic temperature compensation built into the meter. Alternatively, a thermistor device as described by Hughes (1966) provides a convenient means of directly computing the necessary temperature correction.

5. Reagent

Potassium chloride solution, 0.00702N: Dissolve 0.5234 g KCl, dried at 180°C for 1 h, in demineralized water and dilute to 1,000 mL.

6. Procedure

6.1 Meters measuring resistance: The manufacturer's instructions for operation of the bridge should be followed explicitly. A constant-temperature room or 25°C bath simplifies temperature consideration. Where such facilities are not available, the sample should be brought to approximately room temperature before the determination. However, samples in the laboratory are seldom at exactly the same temperature because of the influence of drafts, sunlight, radiators, ovens, and open flames. The temperature of each sample should be determined at the time of measurement.

6.1.1 Prepare a graph of resistance of 0.00702N KCl throughout the operating-temperature range.

6.1.2 Rinse the cell with sample.

6.1.3 Measure the resistance of the sample and record the temperature at the time of measurement. Record temperature to the nearest 0.1°C.

6.1.4 Determine the resistance of 0.00702N KCl at the temperature at which the sample resistance was measured from the graph prepared in step 6.1.1.

6.2 Direct-reading meters with built-in temperature compensators:

6.2.1 Prepare a table of conductance of 0.00702*N* KCl throughout the operating-temperature range. Calculate and enter in table the correction factors where measured conductance deviates from correct conductance.

6.2.2 Immerse probe-type cell in sample. (Cell will have been immersed in deionized water and blotted dry with tissue just before use.)

6.2.3 Measure conductance and temperature, and record both measurements.

6.2.4 Refer to table prepared in 6.2.1 and apply appropriate correction factors to conductance measurements as necessary.

7. Calculations

Specific conductance ($\mu\text{S}/\text{cm}$ at 25 °C)

$$= \frac{R \text{ of } 0.00702N \text{ KCl}}{R \text{ of sample}} \times 1,000$$

where

R = resistance in ohms.

NOTE 1. Further calculations are unnecessary when measurements are made with a direct-reading meter with builtin temperature compensator.

8. Report

Report specific conductance, $\mu\text{S}/\text{cm}$ at 25 °C (90095), as follows: less than 1,000 $\mu\text{S}/\text{cm}$, whole numbers; 1,000 $\mu\text{S}/\text{cm}$ and above, three significant figures.

9. Precision

9.1 Precision for specific conductance for 36

samples within the range of 9.0 to 2080 $\mu\text{S}/\text{cm}$ can be expressed as follows:

$$S_T = 0.054X - 3.80$$

where

S_T = overall precision, microsiemens per centimeter, at 25 °C,

and

X = specific conductance, microsiemens per centimeter, at 25 °C.

The correlation coefficient is 0.9005.

9.2 Precision for specific conductance for five of the 36 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean ($\mu\text{S}/\text{cm}$ at 25 °C)	Relative standard deviation (percent)
32	9.0	19
31	112	4
28	557	3
36	1170	5
55	2080	47

9.3 Using automated instrumentation, analysis of two test samples by a single laboratory for 25 replicates of each resulted in mean values of 96.9 and 1,664 $\mu\text{S}/\text{cm}$ and standard deviations of 0.8 and 11 $\mu\text{S}/\text{cm}$, respectively.

References

- Daniels, Farrington, and Alberty, R. A., 1966, *Physical chemistry* (3rd ed.): New York, John Wiley and Sons, 671 p.
- Hughes, L. S., 1966, Use of thermistor-thermometer in determination of specific conductance: U.S. Geological Survey Water-Supply Paper 1822, p. 66.
- Scofield, C. S., 1932, Measuring the salinity of irrigation waters and of soil solutions with the Wheatstone bridge: U.S. Department of Agriculture Circular 232.