Chemistry and Methods

Method-Specific, Applications & Limitations

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AL GHUBRAH INDEPENDENT WATER PROJECT 42 MIGD SWRO

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WHO Definition

* Defines safe drinking water as water that "*does not represent any significant risk to health over the lifetime of consumption, including different sensitivities that may occur between life stages.*"

World Health Organization

Guidelines vs. Standards

- Guideline: a recommended limit that <u>should</u> not be exceeded
- Standard: a mandatory limit that <u>must</u> not be exceeded (often reflects legal duty or obligation)

- WHO Guidelines for Drinking Water Quality (2006)
  - Guideline values to ensure safety of drinking water
- Standards vary among countries and regions

Why Do We Do Water Quality Testing?

* Ensure safe drinking water
* Identify problems
* Adopt precautionary measures
* Raise awareness
* Determine the effectiveness of water treatment technologies
* Select an appropriate water source
* Influence policies to supply safe water

Water Sampling

-**Microbiological sampling**

-Indicator organisms for pathogen presence

Physical sampling

-turbidity, conductivity, total dissolved solids etc

Chemical sampling

- pH, dissolved oxygen, phosphates, chemical oxygen demand, biological oxygen demand, mineral impurities (iron, manganese, chloride, lead, sodium etc)

Types of Testing

* Mobile laboratories
  * <u>Advantages</u>:
    * Controlled environment,
    * High level of precision and accuracy
  * <u>Limitations</u>:
    * Relatively expensive
    * Requires skilled laboratory technicians
* Laboratory testing
  * <u>Advantages</u>:
    * Controlled environment,
    * High level of precision and accuracy
  * <u>Limitations</u>:
    * Expensive
    * Lack of flexibility to conduct own testing

Selecting Test Methods

Depends on:

* Objectives
* Range of concentration
* Required accuracy and precision
* Time period between sampling and analysis
* Technical skills and equipment required
* Familiarity with the method
* Availability of resources

WHAT WE'LL COVER TODAY

* Analytical Test Methods
  * Physical Properties
  * Inorganic Non-Metallic Constituents
    * Halogens & Cyanide
    * Nutrients
  * Aggregated Organics
* Method-specific QA/QC issues
* Method Applications & Limitations

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SAMPLE COLLECTION & PRESERVATION

Parameter	Preservation	Container	Hold Time
Alkalinity	**Cool 4 °C**	**P or G**	**14 days**
NH_3-N	**Cool 4 °C; H_2SO_4 to pH<2**	**P or G**	**28 days**
Cl^-, Br^-, F^-	**None**	**P**	**28 days**
CN^-	**NaOH to pH>12; Cool 4 °C ; Ascorbic acid**	**P or G**	**14 days**
Hardness	**H^+ to pH<2**	**P or G**	**180 days**
Kjeldahl or Organo-N	**H_2SO_4 to pH<2**	**P or G**	**28 days**
$(NO_3)^-$	**H_2SO_4 To pH<2**	**P or G**	**14 days**
$(NO_2)^-$	**Cool 4 °C**	**P or G**	**2 days**
o-$(PO_4)^{-3}$	**Filter ASAP; Cool 4 °C**	**P or G**	**2 days**
Sp. Cond.	**Cool 4 °C**	**P or G**	**28 days**
$(SO_4)^{-2}$	**Cool 4 °C**	**P or G**	**28 days**
TDS, TSS	**Cool 4 °C**	**P or G**	**7 days**
		P or G	**2 days**

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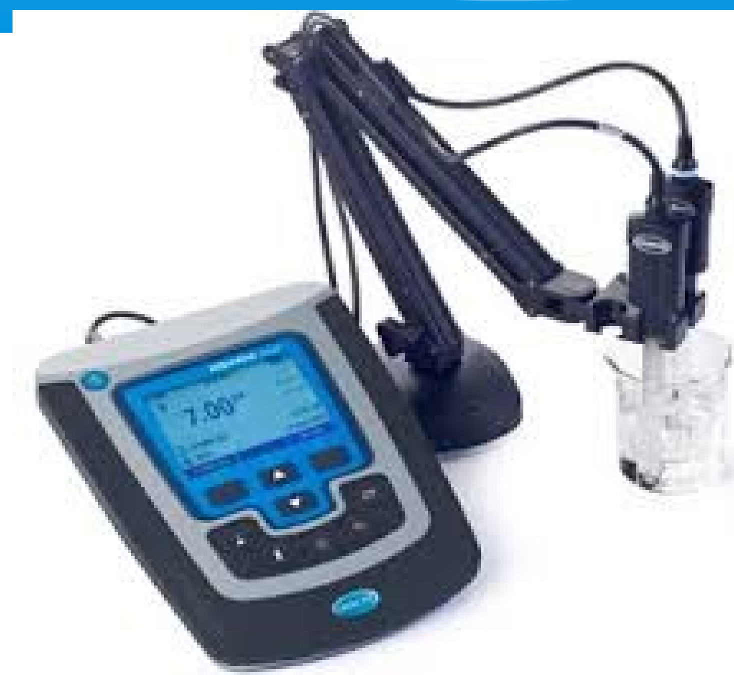
pH

* **pH** is really a measure of the relative amount of free hydrogen and hydroxyl ions in the water.
* **pH** is a measure of how acidic/basic water is.
* The range goes from 0 - 14, with 7 being neutral.
* pHs of less than 7 indicate acidity, whereas a **pH** of greater than 7 indicates a base.



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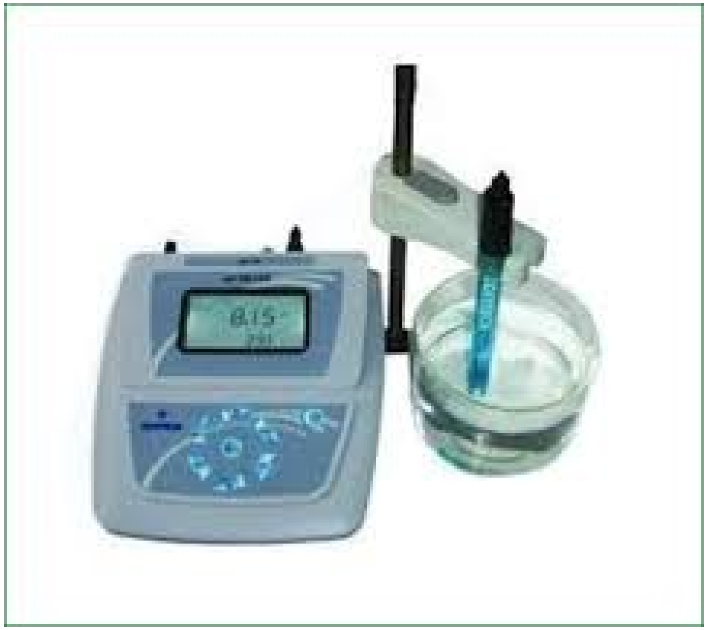
pH

* References
  * HACH-Dig Ph Meter
  * APHA,
* Applies to DW , SW & WW

* *Calibration*
* Place the electrode in the solution of **pH** 7 buffer, allow the display to stabilize and, then, set the display to read 7 by adjusting cal 1. Remove the electrode from the buffer. 4. Rinse the electrode with deionized water and blot dry using a piece of tissue



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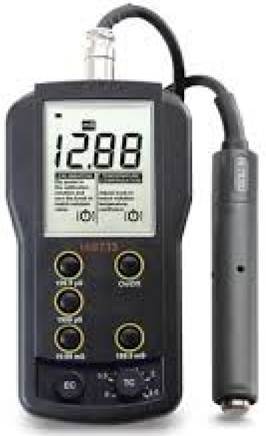
CONDUCTIVITY

* References
  * HANNA-
  * USEPA 120.1
  * APHA-

* Applies to DW & SW

* Measures the ability to an aqueous solution to carry an electrical current

* CO_2 in air can cause problems @ low levels



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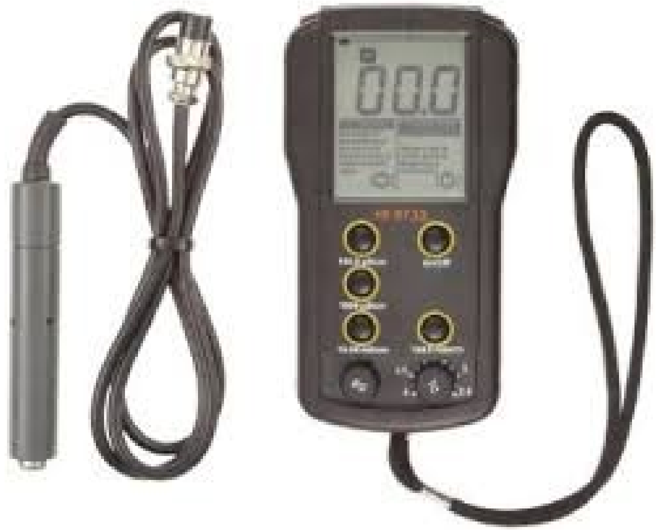
CONDUCTIVITY

* Units of measure: µS/cm (µmhos)
* Use KCl solutions as stds; read @ 25 °C
* Distilled water 0.5-3.0 µmhos; most potable waters range from 50-1500 µmhos
* Cell Constant
  * Determine annually
  * Verify w/each use w/known [KCl]



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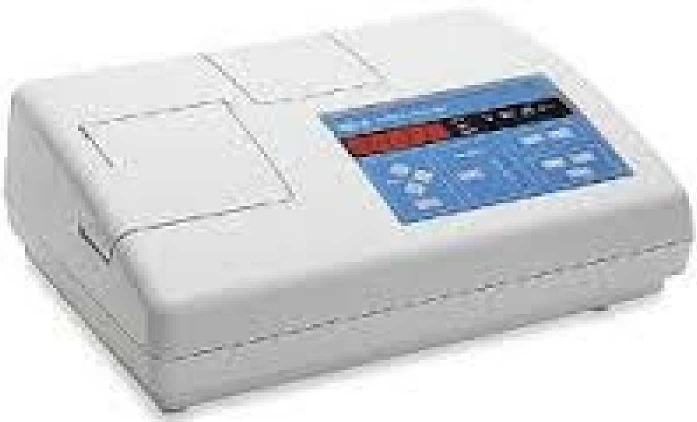
TURBIDITY

- References
  - HACH-2100
  - USEPA 180.1
  - APHA,
- Applies to DW & SW



- Caused by fine suspended matter; measure of the clarity of water

- Units are NTU's;
  - <1 required for DW analyses of metals

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Free Residual Chlorine (FRC) Total Chlorine

* Free chlorine refers to both hypochlorous acid (HOCl) and the hypochlorite (OCl^-) ion or bleach, and is commonly added to water systems for disinfection. When ammonia or organic nitrogen is also present, chloramines known as monochloramine, dichloramine, and trichloramine will quickly form. Chloramines are also known as combined chlorine.
* Total chlorine is the sum of free chlorine and combined chlorine. The level of total chlorine will always be higher than or equal to the level of free chlorine.

TURBIDITY - NEPHELOMETROMETRY

* Compares intensity of scattered light

* Instrument sensitivity must be able to detect turbidity differences of ±0.02 NTU

* Lab. reagent water may have to be filtered prior to use

* Anything blocking light path NG: scratches, smudges, air bubbles, …

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Free Residual Chlorine (FRC) Total Chlorine

* Free chlorine is typically measured in drinking water disinfection systems using chlorine gas or sodium hypochlorite to find whether the water system contains enough disinfectant. Typical levels of free chlorine in drinking water are 0.2 - 2.0 mg/L Cl_2, although regulatory limits allow levels as high as 4.0 mg/L.
* Total chlorine is measured in drinking water and is also typically measured to determine the total chlorine content of treated wastewater. If you are required to measure and report chlorine levels to a regulatory agency, we advise that you check with your regulator to find whether you are required to measure free chlorine or total chlorine.

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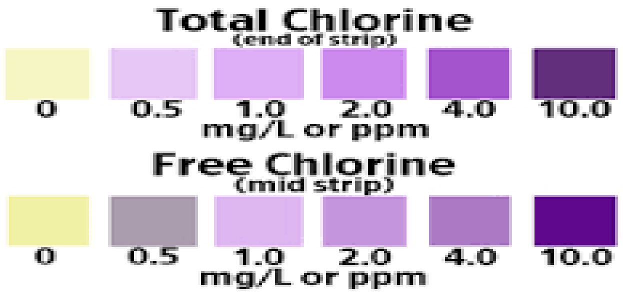
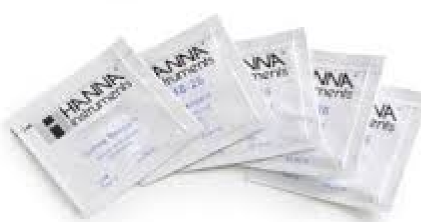
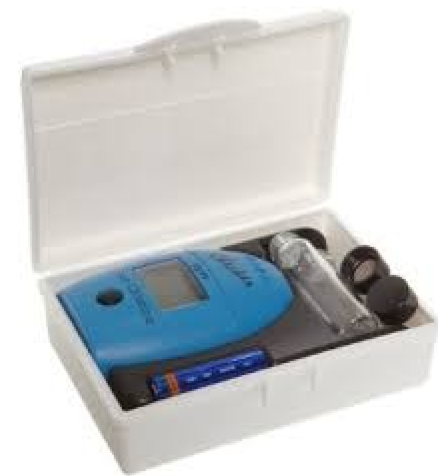


Free Residual Chlorine (FRC)
Total Chlorine

- References
  - HANNA- free chlorine checker
  - iodometric method
- Applies to DW & SW





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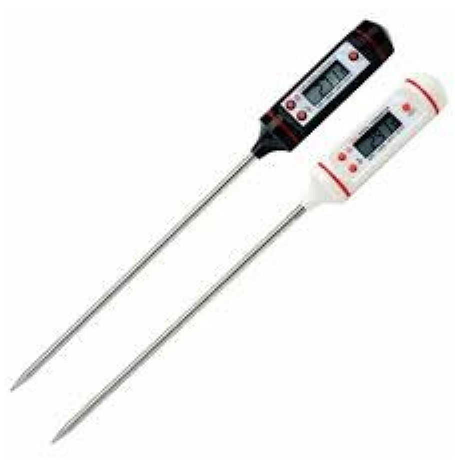
Temperature

- Water temperature is a physical property expressing how hot or cold water is. As hot and cold are both arbitrary terms, temperature can further be defined as a measurement of the average thermal energy of a substance .
- This energy can be transferred between substances as the flow of heat. Heat transfer, whether from the air, sunlight, another water source or thermal pollution can change the temperature of water.



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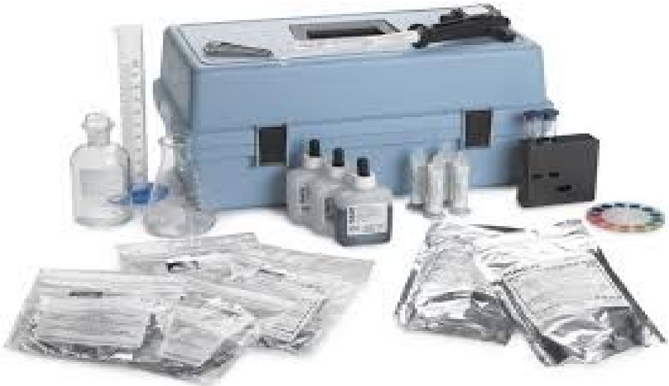
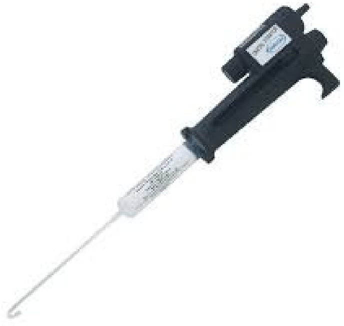
ALKALINITY

- References
  - HACH- Digital Titrator
  - USEPA 310.1
  - APHA,



- Applies to DW & SW

- Measures acid-neutralizing capacity (ANC)



- Mostly measures $(CO_3)^{-2}$, $(HCO_3)^{-}$ & OH^{-}

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ALKALINITY

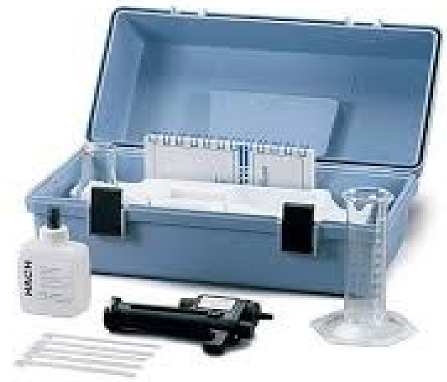
* Oily matter, ppcts. may interfere but cannot be removed since they contribute to ANC
* Analysis by HCl (or H_2SO_4) titration (end-pt. or potentiometric (most accurate)
* For low alkalinity samples (<20), equivalence pt. determined by extrapolation
* RSD's [illegible]5% can be commonly achieved

HARDNESS

- References
  - HACH- Digital Titrator
  - APHA: Sum separate calculations of Ca & Mg
  - APHA: EDTA Titration

- Defined as the sum of [Ca] & [Mg], expressed as $CaCO_3$

- Applies to DW & SW



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HARDNESS

- Ca^{+2} / Mg^{+2} sequestered by NaEDTA
- Titration to dark bluer; forms starch-I complex
- Transition metals can interfere
  - Inhibitors are added to complex metals prior to analysis
- LOD ~ 0.5 mg/L as $CaCO_3$; RSD's of <3% common

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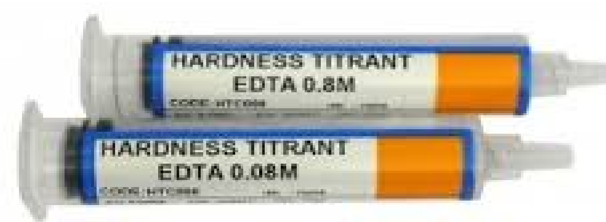
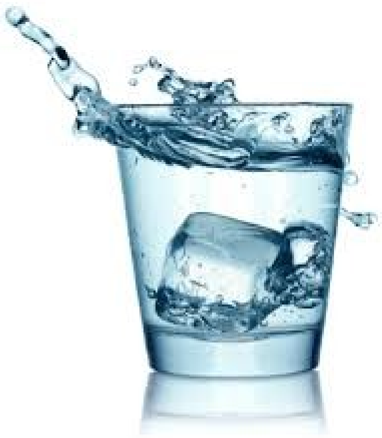


SOLIDS

* Total Solids (TS): residue left after heating sample @ a defined T

* Total Suspended Solids (TSS): portion of solids retained by a filter

* Total Dissolved Solids (TDS): portion of solid passes through a filter



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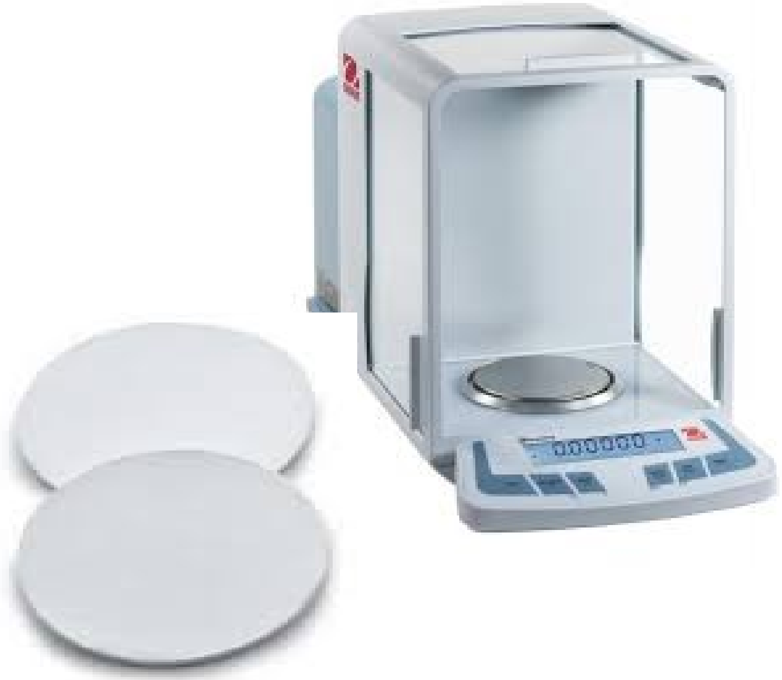
SOLIDS

* Sources of Error
  * Accurate analytical balance
  * Sample homogeneity
  * Accuracy of T in oven
  * Clean glassware between analyses
  * Simple to do; easy to mess up



* TS + TSS: Dry to 104 ± 1 °C

* TDS: Dry to 180 ± 2 °C

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DISSOLVED OXYGEN (DO)

- Electrometric (Electrode)
  - More common
  - Rate of diffusion of molecular O_2 across membrane

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DISSOLVED OXYGEN (DO)

- Winkler
  - More precise & reliable
  - Add Mn^{+2} + strong base, DO oxidizes Mn^{+2} to higher ordered $Mn(OH)_{X+2}$. Add I^{-}/H^{+}; Mn goes back to Mn^{+2} & equivalent I^{-} is liberated. Titrate with $(S_2O_3)^{-2}$ w/starch indicator. $(S_2O_3)^{-2}$ must be standardized at least quarterly. I^{-} takes the place of O^{-2}
  - Interferents include oxid.(+) & red. (-) agents; options include adding azide $[(NO2)^{-}]$, & permanganate $[Fe^{+2}]$
  - Fix on-site & run w/i 8 hrs.

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BY VIS Spectrophotometer

- HACH 3900
- Multi-element capability @ µg/l and mg/l sensitivity
- Anions: F^{-}, Cl^{-}, Br^{-}, $(NO2)^{-}$, $(NO3)^{-}$, $(SO4)^{-2}$, $(PO4)^{-3}$ and others
- Works well for DW, SW and WW

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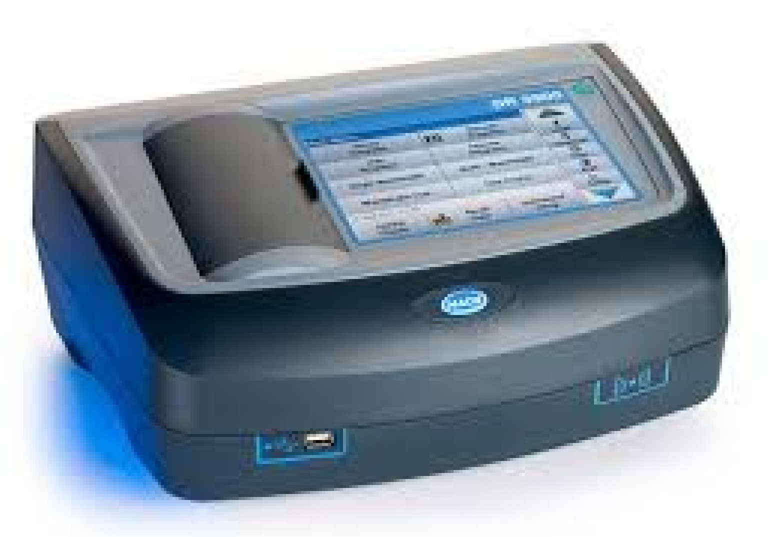
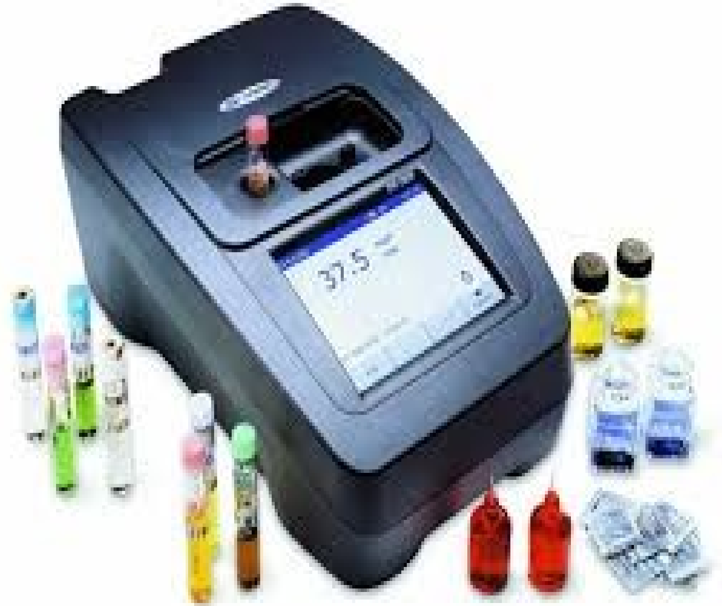
HACH-3900 VIS Spectrophotometer





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Total Iron

- FerroVer® Method1
- Method 10249 Powder Pillows
- Range: 0.1 to 3.0, mg/L Fe
- Scope and application: For water and wastewater.

- USEPA approved for reporting wastewater analysis, Feder
  Register, June 27, 1980; 45 (126:43459).

- Adapted from Standard Methods for the Examination of
  Water and Wastewater.

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Boron

- Carmine Method1
- Method 8015 Powder Pillows
- Range:0.2 to 14.0 mg/L B
- Scope and application: For water and wastewater.

- Adapted from Standard Methods for the Examination of Water and Wastewater.

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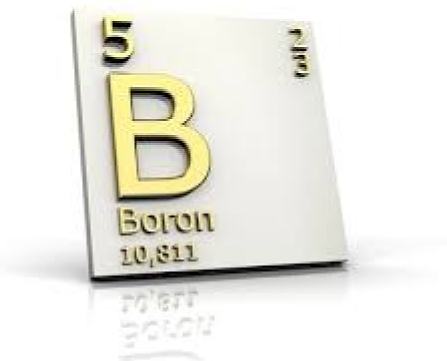
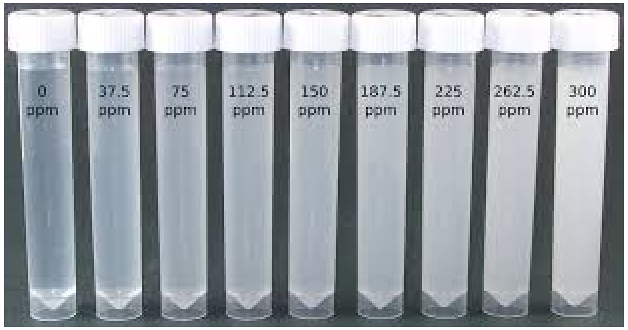


Sulfate

- SulfaVer 4 Method1
- Method 10248 Powder Pillows
- Range: 2 to 70, 20 to 700, 200 to 7000 mg/L SO_4^{2-} Scope and application: For water and wastewater.

- Adapted from Standard Methods for the Examination of Water and Wastewater.



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Nitrate

- Cadmium Reduction Method
- Method 8192 Powder Pillows
- Range:0.01 to 0.50 mg/L NO_3 ––N (LR)
- Scope and application: For water, wastewater and seawater

HALOGEN IONS (F^-, Cl^-, Br^-, I^-)

- Analytical Options
  - Colorimetric
  - Titrimetric
  - IC
  - Ion-Selective Electrodes (ISE) (SM Method 4500)
    - DW only

ION SELECTIVE ELECTRODES

- Measure the activity of free ions in solution
- Interferences known & controllable
- Must control T & ionic strength
- Can measure halides, S^{-2}, NH_3 and $(CN)^-$
- Electrode types:
  - Crystalline
  - Gas Sensing

CYANIDE (CN^-)

- All CN groups that can be determined as CN^-
- Total Cyanide measures all free & bound CN^-
- Cyanide Amenable to Chlorination includes free CN^- & all CN^- complexes that are dissociable such as metal-CN complexes. This requires a much more rigorous digestion.
  - Oxidation of organo-CN complexes can cause problems; keep chlorinated fraction in the dark

CYANIDE (CN^-)

- Both require sample distillation; collect as HCN
- For CN^- amenable to chlorination, divide sample in 2, and subtract CN^- found in dechlorinated & chlorinated fractions
- Measurement Options
  - Titration
  - Colorimetry
  - ISE

NITROGEN SPECIES

- Forms of N to be measured:
  - $(NO_3)^-$
  - $(NO_2)^-$
  - NH_3
  - Organic N

- Organic N = $(NO_3)^- + (NO_2)^-$

- NH_3: generally low in GW because of particle absorption

AMMONIA (NH_3)

* As per Federal regulations,a preliminary distillation step MUST be performed unless you can demonstrate the absence of interferences for YOUR effluent

* Measurement Options
  * Titration
  * ISE
  * Phenate w/ or w/o automation

AMMONIA (NH_3)

- Titration
  - Only used after distillation
  - H_3BO_3 added to decrease hydrolysis of organo-N species
  - Titrate w/std. H_2SO_4; end-pt. either w/indicator or electrometrically
  - Useful below 5 mg/L
- ISE
  - Gas-permeable membrane to measure $NH_{3(aq)}$ & $(NH_4)^+$ converted to $NH_{3(aq)}$ by pH adjust. to 10-11

AMMONIA (NH_3)

- Phenate
  - Indophenol (VERY blue) is made from reaction between NH_3, $(ClO3)^-$ & phenol catalyzed by nitroprusside
  - Measure spectrophotometrically @ 640 nm
  - Interfering Ca & Mg can be complexed
  - Can be easily automated
  - RSD's much better than titrimetry or ISE

$(NO_2)^-$ & $(NO_3)^-$

- Both can be done by IC
- $(NO_2)^-$ can also be done by spectrophotometry
- $(NO3)^-$
  - UV-Spec.
  - ISE
  - Cd Reduction

ORGANIC (KJELDAHL) N

- Measures N as N^{-3}; Kjeldahl N is the same as organic N. Digest sample, convert to NH_3, and measure as per NH_3 options.

- Does not measure e.g., azide, azo, nitro, nitoso, nitrite or nitrate N species

- Macro: low [NH_3], requires larger sample volume (500 ml.)
  Micro: higher [NH_3]

PHOSPHOROUS SPECIES

- P analyses consist of 2 steps
  - Digestion converts phosphorous to orthophosphate
  - Colorimetric determination

- Reactive P (Orthophosphate): respond to colorimetry w/o hydrolysis or oxidation

- Organic P: Fraction convertible to orthophosphate by destruction of organic matter

SULFITE $(SO_3)^{-2}$

- Occurs in boilers & feedwaters & treatment plant effluents

- Method Options
  - Iodometric: KI titration w/starch indicator
  - Colorimetric: (easier) Reaction w/1,10-phenanthroline & vis. detection @ 510 nm.

SULFATE $(SO_4)^{-2}$

- Method Options
  - IC (BEST CHOICE)
  - Turbidimetry: $BaSO_4$ ppct. light scattering is measured (MOST COMMON)
  - Gravimetry: (Ppct. as $BaSO_4$)
  - Titrimetry: xs. Ba is complexed w/methylthymol blue to yield blue color

SULFIDE (S^{-2})

- "Total S^{-2}" includes both H_2S & HS^- as well as acid-soluble metallic sulfides; [S^{-2}] very low

- There are several qualitative tests

- Quantitative Methods: I^- oxidizes S^{-2} / H^+
  - Titration: OK if [S^{-2}] > 1 ppm
  - Iodimetric
  - ISE

[illegible]

BOD

- Measures molecular O_2 used during the biochemical degradation of organic matter (C) in water

- Usually applied to determine waste loadings to treatment plants & efficiency of control measures

- w/o inhibitor is added, can also measure O_2's ability to oxidize N species

- 5 day test: BOD_5
- 20 day test: BOD_{20}
- 60-90 day test: UBOD

BOD

- Fill sample to overflow & seal airtight
- Incubate for fixed time
- Measure DO initially & @ end
- BOD = $\text{Final}_{[DO]}$ - $\text{Initial}_{[DO]}$
- See SM for working ranges & DLs

BOD

- Do a series of dilutions for sample analyses
- Some samples may need to be seeded with microorganisms
  - high pH, chlorination, high T
- CBOD (carbanaceous demand0 is used where nitrification inhibitor is employed
- Holding time is 48 hrs.

COD

* Amt. of O_2 that certain organisms & chemicals will consume

* Interferences
  * $[Cl^-] > 1000$ mg/l
  * VOCs might be lost prior to oxidation

* Method Summary
  * Most organics & oxidative inorganics are oxidized by addition of $K_2Cr_2O_7$ / H_2SO_4
  * xs. $(Cr_2O_7)^{-2}$ is titrated w/$Fe(NH_4)_2(SO_4)_2.6H_2O$

TOTAL ORGANIC CARBON (TOC)

- Better expression of organic content than BOD or COD
- TOC is independent of the ox. state of the organic matter and does not measure H or N
- Organic molecules $\Rightarrow$ C $\Rightarrow$ CO_2

TOTAL ORGANIC CARBON (TOC)

- Measurement Options
  - Non-Dispersive IR (5310B)
    - Sample is combusted
    - Measures total C; inorganic C must be subtracted to give TOC
  - Reduce to Methane (5310C)
    - Measure by dedicated FID analyzer
  - Wet-Oxidative (5310D)
    - Oxidized with $KHSO_4$ in autoclave
    - Resulting CO_2 measured by non-dispersive IR
  - UV-Persulfate

GENERAL RULE

- COD > BOD > TOC

TOX (DOX)

- Measures total dissolved organic matter in H_2O
- Contributing compounds include: THMs, org. solvents (TCE), halogenated alkanes, alkenes, & pesticides, PCBs, chlorinated aromatics ($C_6H_4Cl_2$), chlorinated humics
- Does not tell you ANYTHING about the structure or nature of the chlorinated organic(s); does not detect organo-F species

TOX (DOX)

* Measurement consist of 4 steps
  * Dissolved organic matter is separated from inorganic halides by adsorption onto activated C
  * Inorganic halides are removed by $(NO3)^-$ displacement
  * Pyrolyze activated C
    * $C \Rightarrow CO_2$
    * Bound halogens $\Rightarrow$ HX
  * HX species by Ag^+ titration

METHOD REFERENCES

* Standard Methods for the Examination of Water and Wastewater, 19th Edition
* Code of Federal Regulations
  * Part 136: DW
  * Part 141: WP
* American Society for Testing and Materials, Section 11, Volumes 11.01 & 11.02

Thanks You

Gracias

Merci