الشركة القابضة
لمياه الشرب والصرف الصحى

برنامج المسار الوظيفي
للعاملين بقطاع مياه الشرب والصرف الصحي

دليل المتدرب

برنامج
التحاليل الفيزيائية والكيميائية
Physical and Chemical analysis
Part II

كيميائي مياه- الدرجة الثالثة

تم إعداد المادة بواسطة الشركة القابضة لمياه الشرب والصرف الصحي
قطاع تنمية الموارد البشرية - الادارة العامة لتخطيط المسار الوظيفي
الإصدار الثانى - 2019.

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مقدمة الإصدار الثانى

تهدف مجموعة البرامج التدريبية المعدة من إدارة المسار الوظيفى بالشركة القابضة لمياه الشرب والصرف الصحى إلى رفع كفاءة الكيميائين العاملين بالشركة القابضة لمياه الشرب والصرف الصحى والشركات التابعة لها وتنمية مهاراتهم ومعارفهم بالشكل الذى يضمن الوصول إلى كوب مياه نظيف وبيئة آمنة يرضى متطلبات وإحتياجات العملاء الكرام.

ويعتبر الإصدار الثانى من برامج المسار الوظيفى لوظيفة كيميائى مياه الشرب هو ثمرة جهود الكيميائيين العاملين بمعامل الشركات التابعة والمعمل المرجعى لمياه الشرب بالشركة القابضة بما تحمله من مزيج متجانس من الخبرات والكفاءات الذين لم يدخروا جهدا حتى يخرج هذا العمل بالطريقة اللائقة.

وجدير بالذكر أن هذا الإصدار يعتبر مكتبة مرجعية وافية وشاملة لجميع الجدارات المتضمنة المهارات والمعارف التي تجعل الكيميائى كفؤا لوظيفته.

ومما تجدر الإشارة إليه بأنه تم الاعتماد على منهجية للمسار التدريبى بحيث يكون المتدرب قد تلقى الدورات الحقلية بداية من التعرف على مراحل التنقية والمعالجة ثم الانتقال إلى الدورات المعملية داخل معمله طبقا للإطار الزمنى المحدد للمدد البينية لكل درجة وظيفية.

ولقد اعتمدنا على وضع معايير لكل مرحلة فى إعداد هذا الاصدار وكان من أهم هذه المعايير:

- المشاركة الفعالة للخبرات والكفاءات التدريبية بالشركات التابعة فى وضع المناهج بما يناسب عموم الكيميائيين على مستوى الجمهورية.
- عقد ورشة عمل متخصصة لكل مادة تدريبية يشارك بها جميع المدربين ذوى التخصص والخبرات سواء من المعمل المرجعى أو معامل الشركات فضلا عن أن يكون المدرب قد قام بتدريس هذه المادة مرات عديدة.
- استخدام وسيلة اتصال غير تزامنى بين جميع المدربين المعتمدين لكل مادة على حدة من خلال انشاء جروب على الفيس بوك لكل مادة على حده (مذكور فى دليل المدرب).
- وضع حقيبة تدريبية كاملة لكل برنامج معدة طبقا لأحدث النظم والمعايير العالمية تحتوى على (دليل المتدرب- شرائح العرض- ملحقات مقروءة ومرئية- دليل المدرب- بنك الأسئلة).
- بناء المحتوى لكل برنامج تدريبى طبقاً لأحدث المراجع العالمية ومن أهمها كتاب الطرق القياسية لتحليل مياه الشرب والصرف الصحى (الإصدار رقم 23) وبما يتوافق مع متطلبات آخر إصدارات الايزو(17025)، مع مراعاة التحديثات الخاصة بالتشريعات والقوانين ذات الصلة.

وجدير بالذكر أن الإصدار الثانى من البرامج التدريبية اعتمد فى تصميمه على عرض مبسط للمعلومات قدر الامكان طبقاً للأسس العلمية وطبقاً للجدارات المعتمدة على تحديد أهداف واضحة وصريحة لتدريب المتدربين، وتشتق تلك الجدارات من الفهم الواضح لدور المتدرب طبقا لبطاقة الوصف الوظيفى، وتتضمن معارف ومهارات وسلوك. مما يضمن إكساب المتدرب مهارات سلوكية بالإضافة إلى المواد التخصصية.

كما تم تصميم العديد من ورش العمل على أساس تسهيل و تسريع عمليتي التعلم و كسب المهارات بما يسمح بتعظيم الفائدة من العملية التدريبية.

كذلك تم استخدام أساليب التدريب الحديثة والاعتماد على التدريب التفاعلى والتركيز على الجوانب التطبيقية في استخدام الوسائل والأساليب المختلفة ، كما تم استخدام الطرق الحديثة للتعليم التفاعلي والغير تزامني كمصادر مساندة للتعلم من خلال انشاء جروب على الفيس بوك للمدربين المعتمدين **(HCWW Trainers)** .

وفى الختام نرجوا من الله أن يتقبل منا هذا العمل كما نأمل أن يكون هذا العمل علما نافعا للعاملين بقطاع المعامل بالشركة القابضة والشركات التابعة لما يشمله من معلومات فنية قيمة وأن يفيد العاملين الجدد بها ليصبحوا قادرين على تنفيذ مهامهم الوظيفية بالشكل الأمثل .

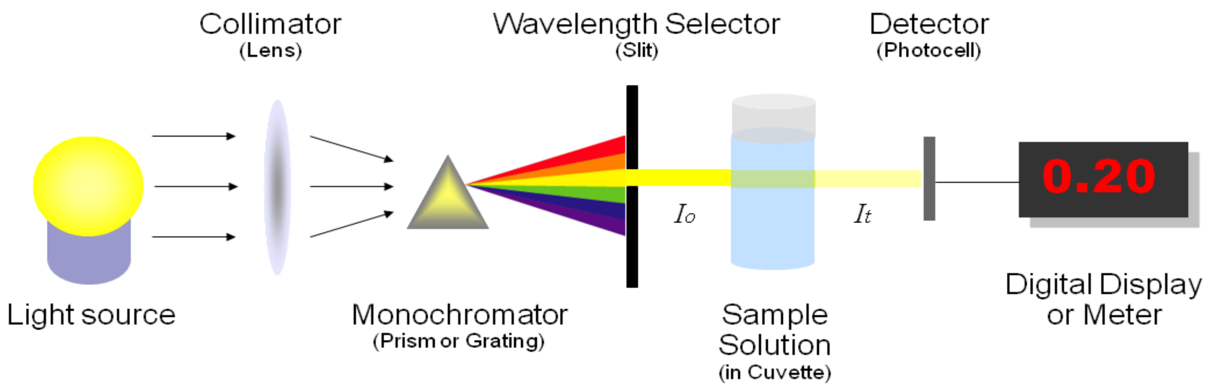
والله ولي التوفيق.

Spectrophotometry

1.1. Introduction

- Spectrophotometry is a method to measure how much a chemical substance absorbs light by measuring the intensity of light as a beam of light passes through sample solution.
- A spectrophotometer is an instrument that can pass light of a single wavelength through a solution and measure the amount that passes through. First, the spectrophotometer must be zeroed by passing light of the chosen wavelength (500 nm for example) through a blank containing only the solvent. Then, the same wavelength of light is passed through the solution.
- The percentage of light that passed through the solution relative to
- The amount that passed through the solvent alone is called:
- the percent transmittance (نسبة النفاذيه) at 500 nm.
- For example, if half as much light passes through a solution as passes through the solvent alone, we would record this as 50% T:
  - $\textbf{\textit{Percent Transmittance}}(\%\boldsymbol{T}) = \frac{(\textbf{\textit{amount of light transmitted through the solution}}}{\textbf{\textit{amount of light transmitted through the solvent}})\ \boldsymbol{x}\ \mathbf{100}}$
- On the other hand, the amount of light at 500 nm that is absorbed by the solution is called the absorbance at 500 nm.
- ***Absorbance:*** is the negative logarithm of the percent transmittance divided by 100. ***Because logarithms have no units, absorbance has no units:***
- $Absorbance\ (A) = -\log\ (\%\ transmittance\ /\ 100)$
- ***Absorbance :*** amount of light absorbed by a sample (the amount of light that doesn't pass through or reflect off a sample)
- ***Transmittance :*** The passing of light through a sample.
- ***A spectrophotometer*** is an instrument that measures the amount of photons (the intensity of light -) absorbed after it passes through sample solution. With the spectrophotometer, the amount of a known chemical substance (concentrations) can also be determined by measuring the intensity of light detected.
  - Depending on the range of wavelength of light source, it can be classified into two different types:
    - UV range: uses light over the ultraviolet range (185 - 400 nm) and;
    - Visible range (400 - 700 nm) of electromagnetic radiation spectrum.

1.2. Components of spectrophotometer:

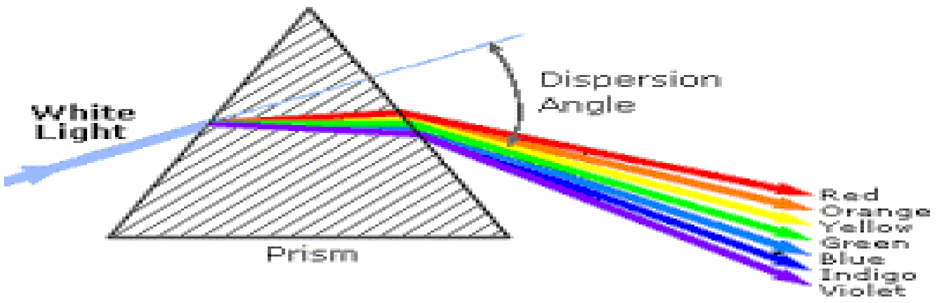


1.2.1.Light Source:

- To provide a Sufficient of light which is: suitable for marking a measurement. Light source is as following:
  - Tungsten Lamp.
  - Hydrogen (Deuterium Lamps).
  - Xenon Lamp.

1.2.2. Monochromator:

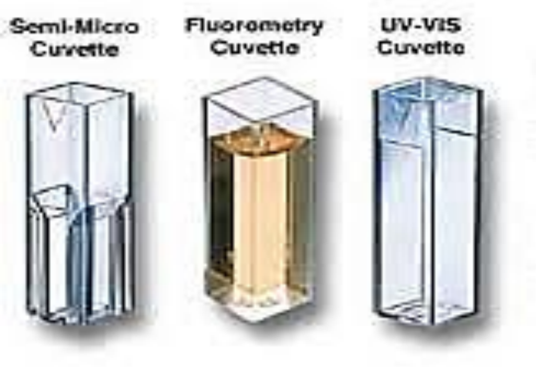
The main function of monochromator is to select λ_{max} from the light. The dispersion of the light is taken place prior to the sample. Monochromatic light is therefore passed through the sample to give very precise and accurate result even at very low absorbance. The examples of monochromators are prism, grating.



1.2.3.Cuvettes:(sample cell)

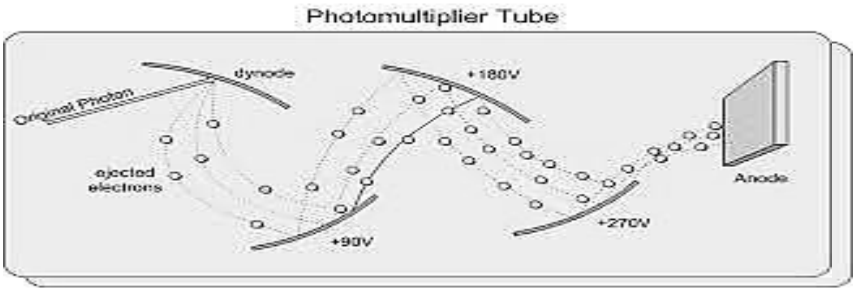
- A small square tube, made of: Plastic, glass, or quartz.
- Should be as (Clear) as possible, without impurities.

- That might affect a Spectroscopic reading.



1.2.4. Detector:(الكاشف)

- The detector is a photo cell (خليه ضوئيه) that: play arole in changing the light transmitted from a sample into an electric signal that can be detected easily.
- Convert a radiant energy (photons)الفوتونات الضوئيه into an electric signal.
- Photomultipliers and silicon photodiodes are typical detectors used with spectrophotometers for the ultraviolet and visible regions.
  - Photomultipliers and silicon photodiodes are described below.



1.2.5.Recorder: (output display device)

- It is the screen that displays the final reading from the detector.
- In addition, the output may be sent to a printer, or computer.

Note:

- Transmittance is the fraction of light that passes through the sample. This can be calculated using the equation:

$$\textit{Transmittance}\ (T) = \frac{\mathbf{It}}{\mathbf{Io}}$$

- Where:
  - It is the light intensity after the beam of light passes through the cuvette
  - Io is the light intensity before the beam of light passes through the cuvette.

- Transmittance is related to absorption by the expression:

$$\textbf{Absorbance (A)} = -\log(T) = -\log\left(\frac{It}{\quad}\right)$$

- Where: absorbance stands for the amount of photons that is absorbed. With the amount of absorbance known from the above equation, you can determine the unknown concentration of the sample by using Beer-Lambert Law.

- Figure 5 illustrates transmittance of light through a sample. The length l is used for Beer-Lambert Law described below.

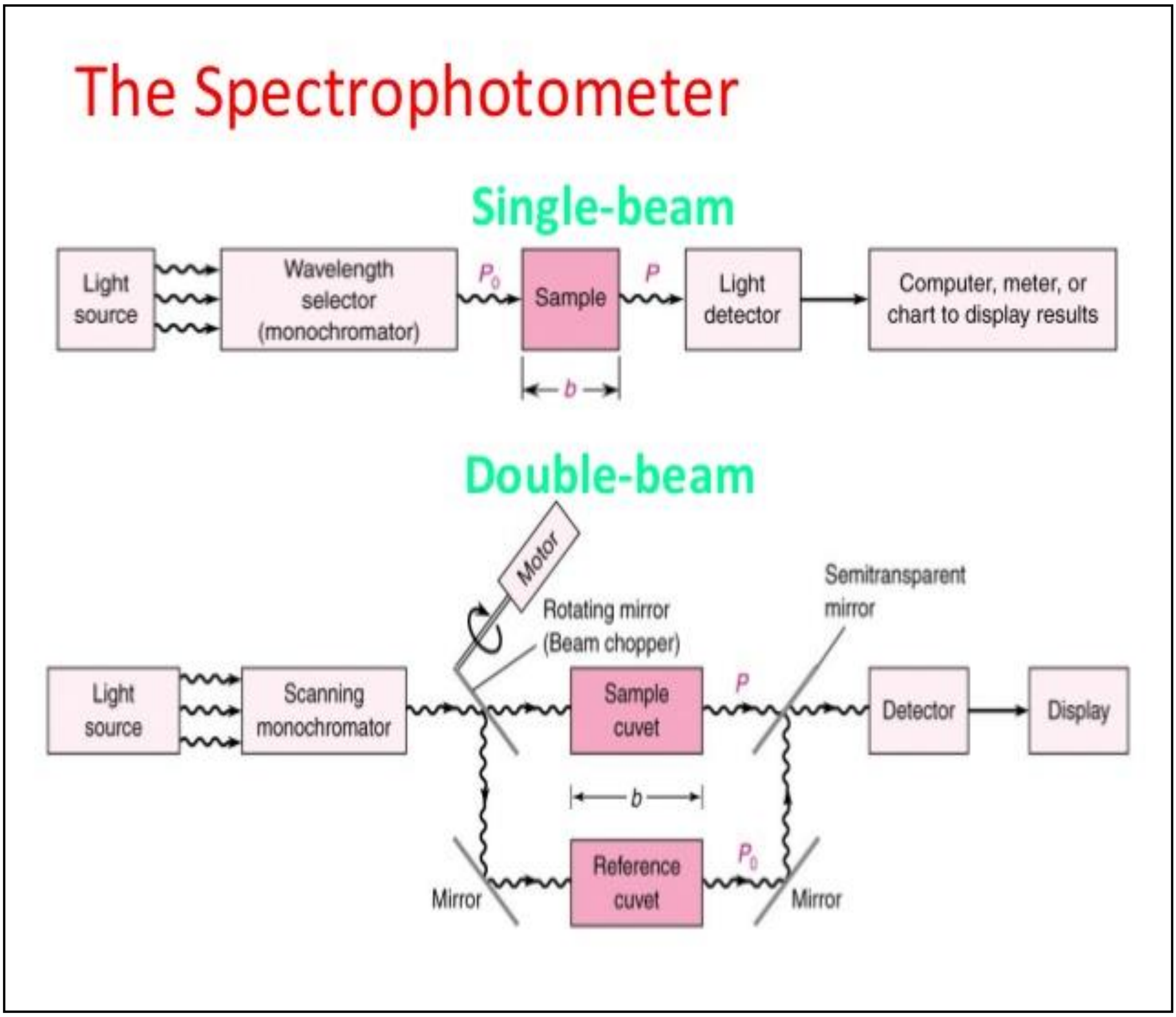
1.3. Types of spectrophotometers:

1.3.1.Single Beam:

- In this type, all the light passes through the sample. To measure the intensity of the incident light the sample must be removed so that all the light can pass through.
  - ***Advantages:*** Less expensive, high energy throughput due to non –splitting of source beam
  - ***Disadvantages:*** Unstable, as there is no compensation for disturbances.

1.3.2. Double Beam:

- In this type the light beam from the source is split into sample beam and reference beam by a mechanical chopper.
  - ***Advantages:*** *Modern optical improvements yielded better detection limits, and discarded instability factors due to lamp drifts, stray light or power fluctuations.*
  - ***Disadvantages:*** *More expensive, require higher accuracy and precision during manipulation.*



1.4. Beer-Lambert Law

Beer-Lambert Law (also known as Beer's Law) states that there is a linear relationship between the absorbance and the concentration of a sample. For this reason, Beer's Law can only be applied when there is a linear relationship. Beer's Law is written as:

$$A = \epsilon l c$$

Where:

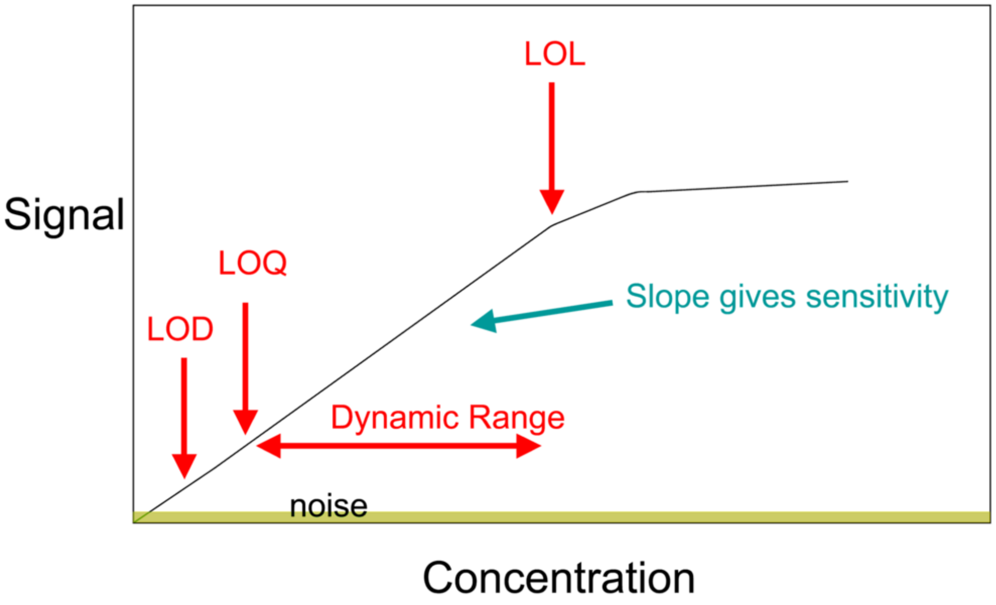
- **A** is the measure of absorbance (no units),
- **ϵ** is the molar extinction coefficient or molar absorptivity (or absorption coefficient),
- **l** is the path length, and

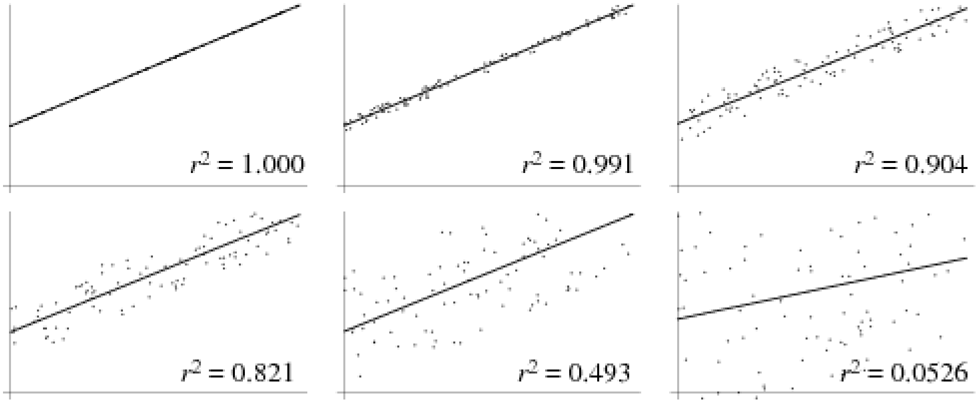
- **C** is the concentration.

- The molar extinction coefficient is given as a constant and varies for each molecule. Since absorbance does not carry any units, the units for ϵ must cancel out the units of length and concentration. As a result, ϵ has the units: $L\cdot mol^{-1}\cdot cm^{-1}$.
- The path length is measured in centimeters. Because a standard spectrometer uses a cuvette that is 1 cm in width, l is always assumed to equal 1 cm. Since absorption, ϵ, and path length are known, we can calculate the concentration c of the sample.
- The light absorption is directly related to the concentration of the compound in the sample
- As concentration increases ↑, light absorption increases ↑

1.5. calibration curve

- a calibration curve, also known as a standard curve, is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration.
- The calibration curve is a plot of how the instrumental response, the so-called analytical signal, changes with the concentration of the analyte (the substance to be measured). The operator prepares a series of standards across a range of concentrations near the expected concentration of analyte in the unknown.





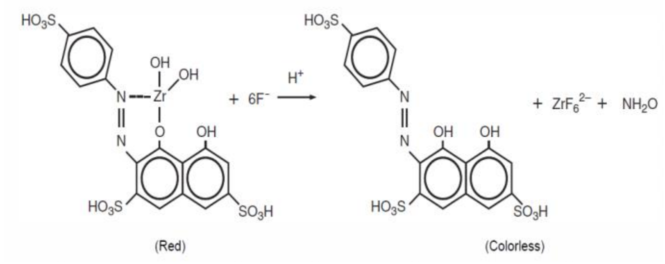
Correlation Coefficient

2.Fluoride

Ref: Standard Methods 23rd Edition, 4500-F Flouride 1997 (Editorial revision, 2017) 4500-F D. SPADNS Method

2.1. Principle:

- The SPADNS colorimetric method is based on the reaction between fluoride and a zirconium-dye lake. Fluoride reacts with the dye lake, dissociating a portion of it into a colorless complex anion (ZrF_6^{2-}); and the dye. As the amount of fluoride increases, the color produced becomes progressively lighter.



- The reaction rate between fluoride and zirconium ions is influenced greatly by the acidity of the reaction mixture. If the proportion of acid in the reagent is increased, the reaction can be made almost instantaneous. Under such conditions, however, the effect of various ions differs from that in the conventional alizarin methods. The selection of dye for this rapid fluoride method is governed largely by the resulting tolerance to these ions.

2.2. Interference:

- The following factors may cause interferences during fluoride measurements.

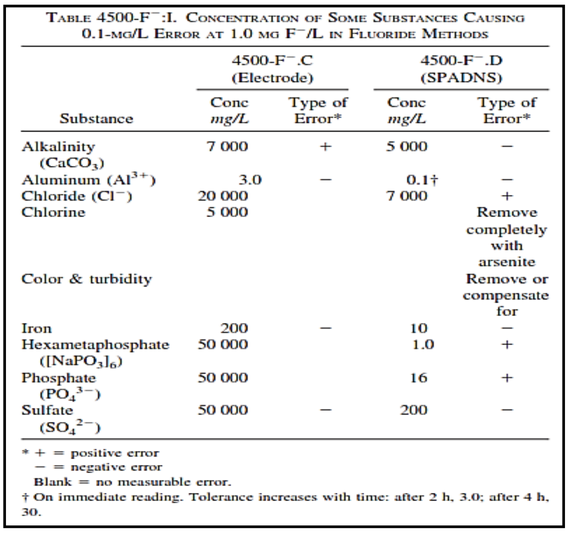


TABLE 4500-F⁻:I. CONCENTRATION OF SOME SUBSTANCES CAUSING 0.1-MG/L ERROR AT 1.0 MG F⁻/L IN FLUORIDE METHODS

	4500-F⁻.C (Electrode)		4500-F⁻.D (SPADNS)	
Substance	Conc *mg/L*	Type of Error*	Conc *mg/L*	Type of Error*
Alkalinity ($CaCO_3$)	7 000	+	5 000	−
Aluminum (Al^{3+})	3.0	−	0.1†	−
Chloride (Cl^-)	20 000		7 000	+
Chlorine	5 000			Remove completely with arsenite
Color & turbidity				Remove or compensate for
Iron	200	−	10	−
Hexametaphosphate ($[NaPO_3]_6$)	50 000		1.0	+
Phosphate (PO_4^{3-})	50 000		16	+
Sulfate (SO_4^{2-})	50 000	−	200	−

* + = positive error
− = negative error
Blank = no measurable error.

† On immediate reading. Tolerance increases with time: after 2 h, 3.0; after 4 h, 30.

2.3. Equipment:

- Spectrophotometer 570 nm.

- Volumetric pipette; 2ml
- volumetric pipette; 10ml
- Two Sample cells, 1-insh. square, 10-ml
- Thermometer, (–10 to 110 °C)

2.4. Chemicals and reagents:

- **Reagent water: Deionized or milli Q water.**
- **Stock fluoride standard (1000 mg F/L)**
- **Standard Fluoride solution (10 mg F/L):**
  - dilute 1 ml of Stock solution up to 100 ml with Deionized water.
- **Standard fluoride solution:**
  - Prepare a series of standards by diluting with distilled water 0.3, 5.0, 10.0, and 20.0 ml of standard fluoride solution to 100 ml with Deionized water. These standards are equivalent to 0.3, .0.5, 1.0, and 2.0 mg F–/l or as the range achieved.
- **SPADNS solution reagent:**
- **Stock fluoride solution:**
  - Dissolve 221.0 mg anhydrous sodium fluoride, NaF, in distilled water and dilute to 1000 mL; 1.00 mL = 100 µgF.
- **Standard fluoride solution:**
  - Dilute 100 mL stock fluoride solution to 1000 mL with distilled water; 1.00 mL = 10.0 µgF.
- **SPADNS solution:**
  - Dissolve 958 mg SPADNS, sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate, also called 4,5-dihydroxy-3-(parasulfophenylazo)-2,7naphthalenedisulfonic acid trisodium salt, in distilled water and dilute to 500 mL. This solution is stable for at least 1 year if protected from direct sunlight.
- **Zirconyl-acid reagent:**
  - Dissolve 133 mg zirconyl chloride octahydrate, $ZrOCl_2 . 8H_2O$, in about 25 mL distilled water. Add 350 mL conc HCl and dilute to 500 mL with distilled water.
- **Acid zirconyl-SPADNS reagent:**

- ➢ Mix equal volumes of SPADNS solution and zirconyl-acid reagent. The combined reagent is stable for at least 2 years.

- **Reference solution:**
  - ➢ Add 10 mL SPADNS solution to 100 mL distilled water. Dilute 7 mL conc HCl to 10 mL and add to the diluted SPADNS solution. The resulting solution, used for setting the instrument reference point (zero), is stable for at least 1 year.
  - ➢ Alternatively, use a prepared standard of 0 mg F /L as a reference.

- **Sodium arsenite solution:**
  - ➢ Dissolve 5.0 g $NaAsO_2$ and diluteto 1 L with distilled water. (CAUTION: Toxic—avoid ingestion.)

2.5. Procedure:

2.5.1.Preparation of standard curve:

- Prepare fluoride standards in the range of 0 to 1.40 mg F-/L by diluting appropriate quantities of standard fluoride solution to 50 mL with distilled water. Pipet 5.00 mL each of SPADNS solution and zirconylacid reagent, or 10.00 mL mixed acid-zirconyl-SPADNS reagent, to each standard and mix well. Avoid contamination. Set photometer to zero absorbance with the reference solution and obtain absorbance readings of standards.

- Plot a curve of the milligrams fluoride-absorbance relationship. Prepare a new standard curve whenever a fresh reagent is made or a different standard temperature is desired. As an alternative to using a reference, set photometer at some convenient point (0.300 or 0.500 absorbance) with the prepared 0 mg F- /L standard.

2.5.2.Sample pretreatment:

- If the sample contains residual chlorine, remove it by adding 1 drop (0.05 mL) NaAsO solution/0.1 mg residual chlorine and mix. (Sodium arsenite concentrations of 1300 mg/L produce an error of 0.1 mg/L at 1.0 mg F/L.)

2.5.3.Color development:

- Use a 50.0-mL sample or a portion diluted to 50 mL with distilled water. Adjust sample temperature to that used for the standard curve. Add 5.00 mL each of SPADNS solution and zirconyl-acid reagent, or 10.00 mL acidzirconyl-SPADNS reagent; mix well and read absorbance, first setting the reference point of the photometer as above. If the absorbance falls beyond the range of the standard curve, repeat using a diluted sample.

2.6. Calculation:

- Results are directly read from the instrument's display.

2.7. Reporting:

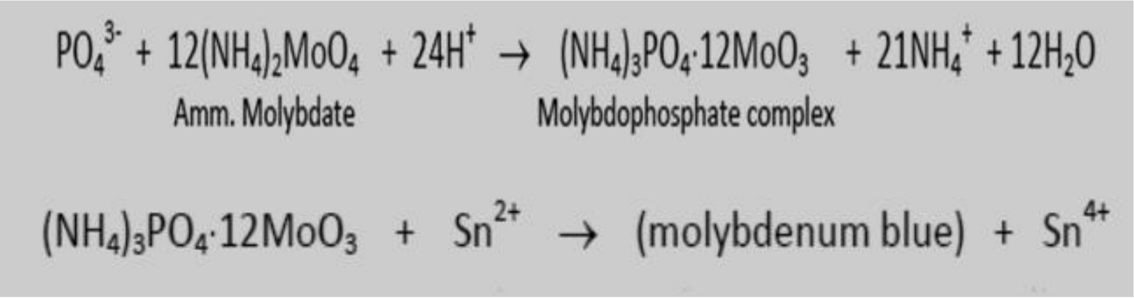
- The results of this method express as mg/l F- for three decimals.

3.Phosphates $(PO_4)^{-3}$

Ref: Standard Methods 23rd Edition, 4500-P PHOSPHORUS 1999 (Editorial revision, 2017) 4500-P D. Stannous Chloride Method

3.1. Principle:

- Molybdophosphoric acid is formed and reduced by stannous chloride to intensely colored molybdenum blue. This method is sensitive and makes feasible measurements down to 7 µg P/l by use of increased light path length.



$$PO_4^{3-} + \underset{\text{Amm. Molybdate}}{12(NH_4)_2MoO_4} + 24H^+ \rightarrow \underset{\text{Molybdophosphate complex}}{(NH_4)_3PO_4{\cdot}12MoO_3} + 21NH_4^+ + 12H_2O$$

$$(NH_4)_3PO_4{\cdot}12MoO_3 + Sn^{2+} \rightarrow (\text{molybdenum blue}) + Sn^{4+}$$

3.2. Interference

- Positive interference is caused by silica and arsenate only if the sample is heated. Negative interferences are caused by arsenate, fluoride, thorium, bismuth, sulfide, thiosulfate, thiocyanate, or excess molybdate.
- Blue color is caused by ferrous iron but this does not affect results if ferrous iron concentration is less than 100 mg/l.
- Sulfide interference may be removed by oxidation with bromine water.
- Ions that do not interfere in concentrations up to 1000.

3.3. Apparatus:

- Colorimetric equipment: Spectrophotometer, for wavelength use at 690 nm.
- Acid-washed glassware:
  - Use acid-washed glassware for determining low concentrations of phosphorus. Phosphate contamination is common because of its absorption on glass surfaces.
  - Avoid using commercial detergents containing phosphate.
  - Clean all glassware with hot dilute HCl and rinse well with distilled water
- Filtration apparatus and filter paper

3.4. Reagents

- **Phenolphthalein indicator aqueous solution.**
- **Strong-acid solution:**
  - ➢ Slowly add 300 ml conc H_2SO_4 to about 600 ml distilled water.
  - ➢ When cool, add 4.0 ml conc HNO_3 and dilute to 1 L.
- **Ammonium molybdate reagent:**
  - ➢ Dissolve 25 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 175 ml distilled water. Cautiously add 280 ml conc H_2SO_4 to 400 ml distilled water. Cool, add molybdate solution, and dilute to 1 L.
- **Stannous chloride reagent:**
  - ➢ Dissolve 2.5 g fresh $SnCl_2\cdot 2H_2O$ in 100 ml glycerol. Heat in a water bath and stir with a glass rod to hasten dissolution. This reagent is stable and requires neither preservatives nor special storage.
- **Standard phosphate solution:**
  - ➢ Dissolve in distilled water 673.11 mg anhydrous KH_2PO_4 and dilute to 1000 ml; 1.00 ml = 50.0 µg PO_4^{3-}.

3.5. Procedure:

3.5.1.Preliminary sample treatment:

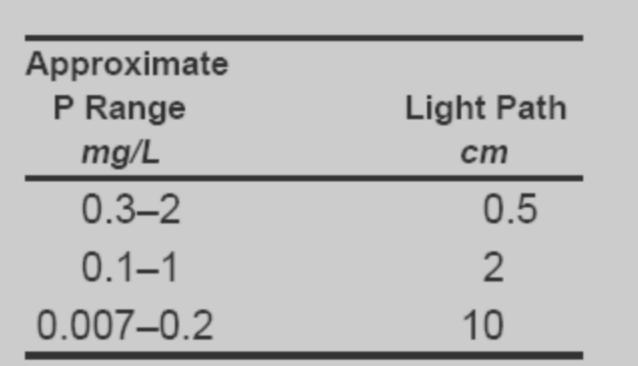
- To 100 ml sample containing not more than 200 µg P and free from color and turbidity, add 0.05 ml (1 drop) phenolphthalein indicator. If sample turns pink, add strong acid solution drop wise to discharge the color. If more than 0.25 ml (5 drops) is required, take a smaller sample and dilute to 100 ml with distilled water after first discharging the pink color with acid.

3.5.2.Color development:

- Add, with thorough mixing after each addition, 4.0 ml molybdate reagent and 0.5 ml (10 drops) stannous chloride reagent. Rate of color development and intensity of color depend on temperature of the final solution, each 1°C increase producing about 1% increase in color. Hence, hold samples, standards, and reagents within 2°C of one another and in the temperature range between 20 and 30°C.

3.5.3.Color measurement:

- After 10 min, but before 12 min, using the same specific interval for all determinations, measure color photometrically at 690 nm and compare with a calibration curve, using distilled water blank. Light path lengths suitable for various concentration ranges are as follows:



Approximate P Range *mg/L*	Light Path *cm*
0.3–2	0.5
0.1–1	2
0.007–0.2	10

3.6. Calculation:

- Record sample concentration directly from instrument read out according to standard curve.

3.7. Reporting:

- Results are reported as mg/l PO_4 with two digits.

4. AMMONIA

Ref: Standard Methods 17th Edition, 4500- NH_3 Nesslerization Method

4.1. Scope and Application

- Ammonia nitrogen is present naturally in surface water and wastewaters. Its concentration is generally low in ground water. A sudden increase in ammonia concentration of the raw water generally indicates pollution from organic wastes. The presence of ammonia in drinking water at levels above 1.5 mg/L can cause taste and odor problems.

- The level of ammonia in water determines to a great extent the chlorine needed to obtain a free chlorine residual. Ammonia exerts a demand for chlorine equal to about 10 times on a weight by weight basis. For example, 0.2 mg/L of ammonia will consume about 2.0 mg/L of chlorine before a free chlorine residual is obtained.

4.2. Principle

- This test describes the procedures for measuring ammonia in various types of water samples. Treatment with Nessler reagent, a strong alkaline solution of potassium mercuric iodide (K_2HgI_4), is used to measure the amount of ammonia nitrogen present in water. Nessler reagent combines with ammonia (NH_3) in alkaline solution to form a yellowish-brown colloidal dispersion whose intensity of color is directly proportional to the amount of ammonia present.

4.3. Interferences

- This procedure is affected by color and turbidity. Glycine, hydrazine, and some amines can react with Nessler reagent to give the characteristic yellow color.

- Addition of EDTA or Rochelle salt soln. inhibit precipitate of residual Ca^{+2}, Mg^{+2} ions in the presence of the alkaline Nessler reagent.

4.4. Equipment

- The equipment required include: glassware, pipettes, and Nessler tubes.

4.5. Reagents and Standards

- Use ammonia-free water for preparing all reagents rinsing, and making dilutions.

Four chemical reagents are required as follows:

- **Rochelle Salt Solution**

- ➢ Dissolve 50 g potassium sodium tartrate tetrahydrate ($K\sim NaC_4H_4O_6\text{-}4H_2O$) in 100 mL of distilled water. Remove ammonia usually present in the salt by boiling off 30 mL of solution. After cooling, dilute to 100 mL with distilled water.

- **Nessler Reagent**
  - ➢ Dissolve 100 g of mercuric iodide Hgl2 and 70 g potassium iodide (KI) in a small quantity of distilled water and add this mixture slowly, with stirring, to a cool solution of 160 g sodium hydroxide (NaOH) dissolved in 500 mL of distilled water. Dilute to l liter. Store in rubber - stoppered borosilicate glassware and out of sunlight to maintain reagent stability for up to one year under normal laboratory conditions. Check reagent to make sure that it yields the characteristic color with 0.1 mg ammonia nitrogen per liter within 10 minutes after addition and does not produce a precipitate with small amounts of ammonia within 2 hours. (CAUTION: Toxic, avoid ingestion.)

- **Stock Ammonium Chloride Solution**
  - ➢ (1.00 mL = 1.00 mg N = 1.22 mg NH_3)

  - ➢ NH_4Cl ----------------- NH_3-------------N
  - ➢ 53.49 17.03 14 gm
  - ➢ ????????? 1220mg/L 1000mg/L
  - ➢ ?????????= 1000(mg/L)* 53.49~~gm~~/14~~gm~~
  - ➢ ?????????= ?????????= 1000(mg/L)* 53.49~~gm~~/14~~gm~~ = 3819 mg = 3.819 g

- Dissolve 3.819 g anhydrous ammonium chloride (NH_4Cl), dried at 100 ^{0}C, in distilled water and dilute to 100 mL.

- **Standard Ammonium Chloride Solution**
  - (1.00 mL = 0.0100 mg N = 0.0122 mg NH_3)
  - ➢ Dilute 10.00 mL stock ammonium chloride solution to l liter with distilled water.

4.6. Procedure

- Prepare a series of visual standards (0, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 mg/L N) or as achieved in Nessler tubes by adding the following volumes of standards ammonium chloride solution and dilute to 100 mL with distilled water: 0, 1, 2, 3, 4, 5, and 6 mL or calculate other.

- Add l drop of Rochelle salt solution and 2.0 mL Nessler reagent to samples and standards and mix thoroughly.
- Let treated samples and standards stand for 10 to 15 minutes and compare color produced in samples against that of the standards.

4.7. Calculation:

- Record sample concentration directly from instrument read out according to standard curve.

4.8. Reporting

- Results should be reported to the nearest five hundredth (for example, 0.15 mg/L).

5.Nitrite (NO_2^-)

Ref: Standard Methods 23rd Edition, 4500-NO_2 NITORGEN (NITRITE) 2000 (Editorial revision, 2011)

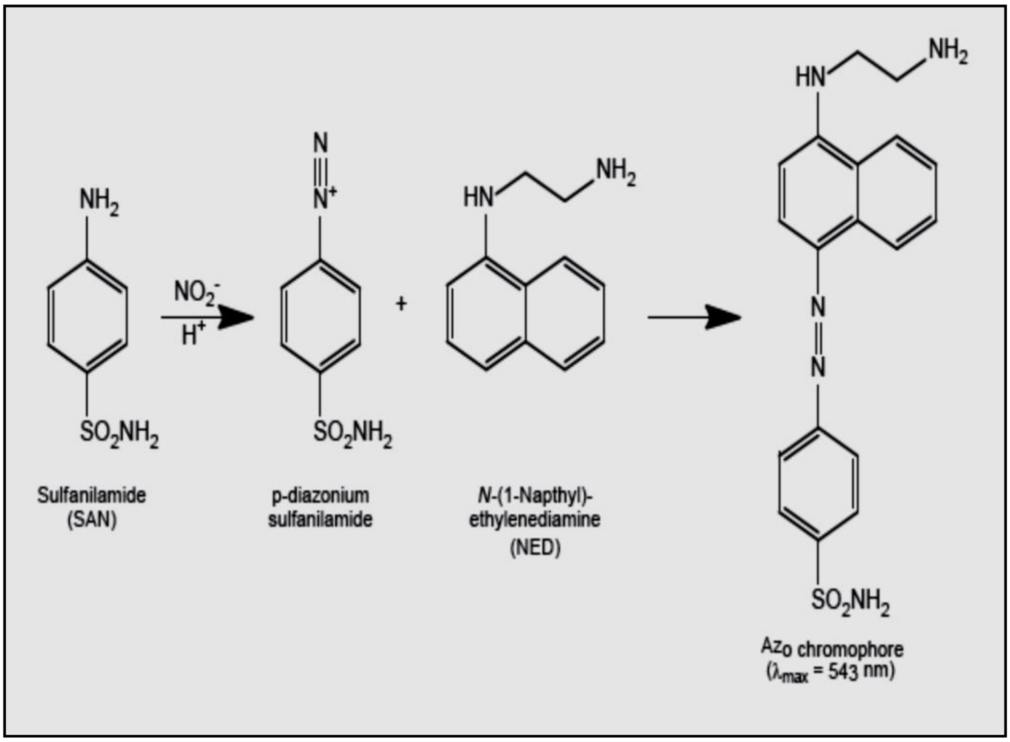
4500-NO_2B. Colorimetric Method

5.1. Principle:

- Nitrite is an intermediate oxidation state of nitrogen, both in the oxidation of ammonia to nitrate and in the reduction of nitrate. Such oxidation and reduction may occur in wastewater treatment plants, water distribution systems, and natural waters. Nitrite can enter a water supply system through its use as a corrosion inhibitor in industrial process water.

- Nitrite is the actual etiologic agent of methemoglobinemia. Nitrous acid, which is formed from nitrite in acidic solution, can react with secondary amines (RR'NH) to form nitrosamines (RR'N-NO), many of which are known to be carcinogens.

- Nitrite (NO_2^-) is determined through formation of a reddish purple azo dye produced at pH 2.0 to 2.5 by coupling diazotized sulfanilamide with N-(1-naphthyl) ethylenediamine dihydrochloride (NED dihydrochloride).



5.2. Interference:

- Chemical incompatibility makes it unlikely that NO_2^-, free chlorine and nitrogen trichloride (NCl3) will coexist. NCl3 imparts a false red color when color reagent is added. -).
- Cupric ion may cause low results by catalyzing decomposition of the diazonium salt. Colored ions that alter the color system also should be absent. Remove suspended solids by filtration.

5.3. Equipment:

- Colorimetric equipment: Spectrophotometer for use at 543nm, providing a light path of 1 cm or longer

5.4. Reagent:

- For the all standards and reagents use water is free from NO_2^-.
- N.B: Use nitrite-free water in making all reagents and dilutions.
- **Color Reagent:**
  - To 800 ml water add 100 ml 85% phosphoric acid and 10 g sulfanilamide. After dissolving sulfanilamide completely, add 1 g N-(1-naphthyl)-ethylenediamine dihydrochloride. Mix to dissolve, then dilute to 1 L with distilled water. (Solution is stable for about a month when stored in a dark bottle in refrigerator).
- **Intermediate nitrite solution:**
  - From stock standard 1000 mg/L Prepare intermediate 10 mg/L (1ml from stock in 100 ml D.W.) stable for about 15 days when stored in refrigerator
  - From intermediate solution prepare series of standards for calibration curve depend on the range needed for analysis
  - Example for series of standards for calibration curve: 0.006, 0.008, 0.01, 0.03, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3 mg/L.

5.5. Procedure

- Removal of suspended solids: If sample contains suspended solids, filter through a 0.45µm-pore-diameter membrane filter.
- Color development: If sample pH is not between 5 and 9, adjust to that range with 1N HCl or NH_4OH as required. To 50.0 ml sample, or to a portion diluted to 50.0 ml, add 2ml color reagent and mix.

- Photometric measurement: Between 10 min and 2 h after adding color reagent to samples and standards, measure absorbance at 543 nm.

5.6. Calculation:

- Record sample concentration directly from instrument read out according to standard curve

5.7. Reporting:

- Results are reported as mg/l NO_2 with two digits.

6.Nitrate (NO_3^-)

Ref: Standard Methods 23nd Edition, 4500-NO3 NITROGEN (NITRATE) 2000 (Editorial revision, 2011) 4500-NO3- B. Ultraviolet Spectrophotometric Screening Method

6.1. Principle:

- Use this technique only for screening samples that have low organic matter contents, i.e., uncontaminated natural waters and potable water supplies.
- The NO_3^- calibration curve follows Beer's law up to 44 mg NO_3^- /l ppm.
- Range for this method is (0.8-44) mg (NO_3^-)/l.
- Measurement of UV absorption at 220 nm enables rapid determination of NO_3^-.
- Because dissolved organic matter also may absorb at 220 nm and NO_3^- does not absorb at 275 nm, a second measurement made at 275 nm may be used to correct the NO_3^- value.
- The extent of this empirical correction is related to the nature and concentration of organic matter and may vary from water to another.
- Consequently, this method is not recommended if a significant correction for organic matter absorbance is required, although it may be useful in monitoring NO_3^- levels within a water body with a constant type of organic matter.
- Correction factors for organic matter absorbance can be established by the method of additions in combination with analysis of the original NO_3^- content by another method.
- Sample filtration is intended to remove possible interference from suspended particles.
- Acidification with 1N HCl is designed to prevent interference from hydroxide or carbonate concentrations up to 1000 mg $CaCO_3$/L.
- Chloride has no effect on the determination.

6.2. Interference

- Dissolved organic matter, surfactant, NO_2^- , Cr6+interfere.
- Inorganic ions such as chlorite and chlorate may interfere.
- Filter a turbid sample through 0.45 µm membrane filter.

6.3. Apparatus

- Spectrophotometer, for use at 220 nm and 275 nm with matched silica cells of 1-cm or longer light path.

6.4. Reagent:

- Nitrate-free water:
- Use redistilled or distilled deionized water of highest purity to prepare all solutions and dilutions.
- **Stock nitrate solution (500ppm as NO_3^-):**
  - Dry potassium nitrate (KNO_3) in an oven at (103-105)°C for 24 h. Dissolve 0.8145 gm in water and dilute to 1000 mL; 1.00 mL = 500 µg NO_3^-. Preserve with 2 mL, $CHCl_3$/L. This solution is stable for at least 6 months.
- **Hydrochloric acid solution, HCl, 1N.**
  - Dilute 83 ml of conc.HCl to 1L with distilled water.store in glass bottle and stable for 1 year if kept close.

6.5. Procedure:

6.5.1. Treatment of sample:

- To 50 ml clear sample, filtered if necessary, add 1 ml (1N) HCl & mix thoroughly.

- **Example for preparation of standard curve:**

- ➢ Prepare NO_3^- calibration standards in the range 0 to 50 ppm as NO_3^- by diluting to 100 mL the following volumes of the 500 ppm stock nitrate solution: 0, 1, 2, 3, 4 … 10 mL as per the following table:

NO_3											
500											**ppm**
Blank	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**Series**
0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**ml taken from 500 ppm**
0	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**ppm**
100											**Total Volume (ml)**

- ➢ Treat NO^{3-} standards in same manner as samples by adding 2 ml (1N) HCl & mixing thoroughly for each.

6.5.2. Spectrophotometric measurement:

- Read absorbance against redistilled water set at zero absorbance.
- Use a wavelength of 220 nm to obtain NO_3^- reading and a wavelength of 275 nm to determine interference due to dissolved organic matter.

6.6. Calculation

- For samples and standards, subtract two times the absorbance reading at 275 nm from the reading at 220 nm to obtain absorbance due to NO_3^-
- Construct a standard curve by plotting absorbance due to NO_3^- against the theoretical NO_3^- concentration values of standard.
- Using corrected sample absorbances, obtain sample concentrations directly from standard curve.
- NOTE: If correction value is more than 10% of the reading at 220 nm, do not use this method.

6.7. Reporting:

- Results are reported as mg/l NO_3 with two digits.

7.Aluminum (Al)

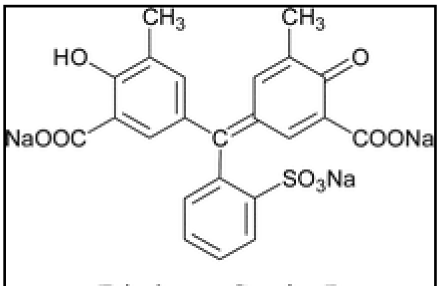
Ref: Standard Methods 23nd Edition, 3500-Al ALUMINUM 2001(Editorial revisions, 2011) 3500-Al B. Eriochrome Cyanine R Method

7.1. Aim:

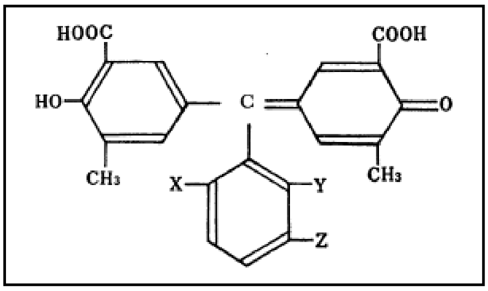
- Aluminum potassium sulfate (alum) is used in water treatment processes to flocculate suspended particles and it will leave residue in water as residual aluminum in the drinking water for this it is important to be measured.

7.2. Principle:

- With Eriochrome cyanine R dye, dilute aluminum solutions buffered to a pH of 6.0 produce a red to pink complex that exhibits maximum absorption at 535 nm.



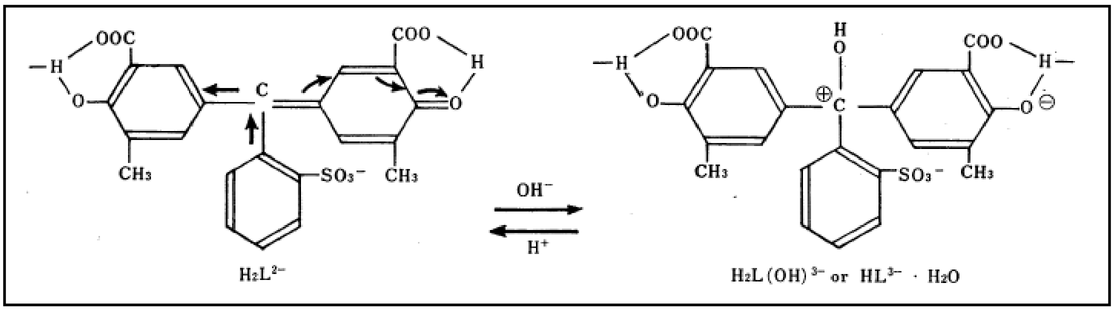
Eriochrome Cyanine R.



Structural formula of reagents

ECR (X : H, Y : SO_3^-, Z : H)

CAS (X : Cl, Y : Cl, Z : SO_3^-)



The reaction expected for the fading of ECR aqueous solution

- The intensity of the developed color is influenced by:
  - The aluminum concentration,
  - Reaction time,
  - Temperature,
  - pH,
  - Alkalinity,
  - Concentration of other ions in the sample.
  - Color
  - Turbidity.
- To compensate for color and turbidity, the aluminum in one portion of sample is complexes with EDTA to provide a blank.
- The optimum aluminum range lies between 20 and 300 µg/L but can be extended upward by sample dilution.

7.3. Interference:

- Negative errors are caused by both fluoride and polyphosphates. When the fluoride concentration is constant, the percentage error decreases with increasing amounts of aluminum. Because the fluoride concentration often is known or can be determined readily, fairly accurate results can be obtained by adding the known amount of fluoride to a set of standards. A simpler correction can be determined from the family of curves in Figure (1).
- The interference of iron and manganese is eliminated by adding ascorbic acid.
- A procedure is given for the removal of complex phosphate interference.

- Orthophosphate in concentrations under 10 mg/L does not interfere. The interference caused by even small amounts of alkalinity is removed by acidifying the sample just beyond the neutralization point of methyl orange.

7.4. Minimum detectable concentration

- The minimum aluminum concentration detectable by this method in the absence of fluorides and complex phosphates is approximately 6 µg/L.

7.5. Sample handling:

- Collect samples in clean, acid-rinsed bottles, preferably plastic, and examine them as soon as possible after collection.
- If only soluble aluminum is to be determined, filter a portion of sample through a 0.45-µm membrane filter, discard first 50 ml of filtrate and use succeeding filtrate for the determination.
- Do not use filter paper, absorbent cotton, or glass wool for filtering any solution that is to be tested for aluminum, because they will remove most of the soluble aluminum.

7.6. Apparatus:

- Colorimetric equipment: Spectrophotometer, for use at 535 nm, with a light path of 1 cm or longer.
- Nessler tubes, 50ml, tall form, matched.
- Glassware: Treat all glassware with warm 1+1 HCl and rinse with aluminum-free distilled water to avoid errors due to materials absorbed on the glass. Rinse sufficiently to remove all acid.

7.7. Reagent:

- Use reagents low in aluminum, and aluminum-free distilled water.
- **Stock aluminum solution:**
  - Use either the metal (1) or the salt (2) for preparing stock solution 500ppm; 1.00 ml = 500 µg Al:
  - Dissolve 500.0 mg aluminum metal in 10 ml conc HCl by heating gently. Dilute to 1000 ml with water, or
  - To prepare 500 ppm Al:

$AlK(SO_4)_2.12H_2O$ ----------------- Al

M.wt	474.3884	26.98	gm

Wt. ????????? 500mg/L

?????????= 500(mg/L)* 474.3884~~gm~~/26.98~~gm~~

?????????= 500(mg/L)* 474.3884~~gm~~/26.98~~gm~~ =8790.98 mg = 8.791 g

- ➢ Dissolve 8.791 g aluminum potassium sulfate (also called potassium alum), $AlK(SO_4)_2.12H_2O$, in water and dilute to 1000 ml. Correct this weight by dividing by the decimal fraction of assayed $AlK(SO_4)_2.12H_2O$ in the reagent used.

- **Standard aluminum solution (5ppm):**
  - ➢ Dilute 10.00 ml stock aluminum solution to 1000 ml with water; 1.00 ml = 5.00 µg Al. Prepare daily.
- **Sulfuric acid, H_2SO_4, 0.02N and 6N.**
  - ➢ We can use the following relation:

$$V_{1\ \text{before dilution}} = \text{Eq.Wt} * (N_2 * V_2)_{\text{after dilution}}/(P*d*10)$$

P=% of stock solution, d=density of stock solution

- **Ascorbic acid solution:**
  - ➢ Dissolve 0.1 g ascorbic acid in water and make up to 100 ml in a volumetric flask. Prepare fresh daily.
- **Buffer reagent:**
  - ➢ Dissolve 136 g sodium acetate, $NaC_2H_3O_2.3H_2O$, in water, add 40 ml 1N acetic acid, and dilute to 1 L.
- **Stock dye solution:**
  - ➢ Use any of the following products:
    - Solochrome cyanine R-200 or Eriochrome cyanine: Dissolve 100 mg in water and dilute to 100 ml in a volumetric flask. This solution should have a pH of about 2.9.
    - Eriochrome cyanine R: Dissolve 300 mg dye in about 50 ml water. Adjust pH from about 9 to about 2.9 with 1+1 acetic acid (approximately 3 ml will be required). Dilute with water to 100 ml.

      OR

- Eriochrome cyanine R: Dissolve 150 mg in about 50 ml water. Adjust pH from about 9 to about 2.9 with 1 + 1 acetic acid (approximately 2 ml will be required). Dilute with water to 100 ml.

➢ Stock solutions have excellent stability and can be kept for at least a year.

- **Working dye solution:**

➢ Dilute 10.0 ml of selected stock dye solution to 100 ml in a volumetric flask with water. Working solutions are stable for at least 6 months.

- **Methyl orange indicator solution** or **Bromcresol green indicator solution** specified in the total alkalinity determination.

➢ EDTA (sodium salt of Ethylene Diamine Tetra Acetic acid dihydrate), 0.01M: Dissolve 3.7 g in water, and dilute to 1 L.

- **Sodium hydroxide, NaOH, 1N and 0.1N.**

7.8. <u>Procedure:</u>

7.8.1.Preparation of calibration curve:

- Prepare a series of aluminum standards
- ***Example:*** Prepare a series of aluminum standards from 0 to 7 µg (0 to 280 µg/l based on a 25-ml sample) by accurately measuring the calculated volumes of standard aluminum solution into 50-ml volumetric flasks or Nessler tubes. Add water to a total volume of approximately 25 ml.

Al								
5								ppm
Blank	1	2	3	4	5	6	7	Series
0	0.2	0.4	0.6	0.8	1	1.2	1.4	ml taken from 5 ppm
0	40	80	120	160	200	240	280	ppb
0	1	2	3	4	5	6	7	µg/25ml
25								Total Volume (ml)

- **Follow the following steps:**

➢ Add 1 ml 0.02N H_2SO_4 to each standard and mix.

➢ Add 1 ml ascorbic acid solution and mix.

- Add 10 ml buffer solution and mix.
- With a volumetric Pipette, add 5.00 ml working dye reagent and mix.
- Immediately make up to 50 ml with distilled water. Mix and let stand for 5 to 10 min.
- The color begins to fade after 15 min.

- **Read transmittance or absorbance on a spectrophotometer**,
  - using a wavelength of 535 nm. Adjust instrument to zero absorbance with the standard containing no aluminum. Plot concentration of Al (mg/l) against absorbance.

- **Sample treatment in absence of fluoride and complex phosphates:**
  - Place 25.0 ml sample, or a portion diluted to 25 ml, in a porcelain dish or flask,
  - add a few drops of methyl orange indicator,
  - Titrate with 0.02N H_2SO_4 to a faint pink color.
  - Record reading and discard sample.
  - To two similar samples at room temperature add the same amount of 0.02N H_2SO_4 used in the titration and 1 ml in excess.
  - To one sample add 1 ml EDTA solution. This will serve as a blank by complexing any aluminum present and compensating for color and turbidity.
  - To both samples add 1 ml ascorbic acid, 10 ml buffer reagent, and 5.00 ml working dye.
  - Set instrument to zero absorbance or 100% transmittance using the EDTA blank.
  - After 5 to 10 min contact time, read transmittance or absorbance and determine aluminum concentration from the calibration curve previously prepared.

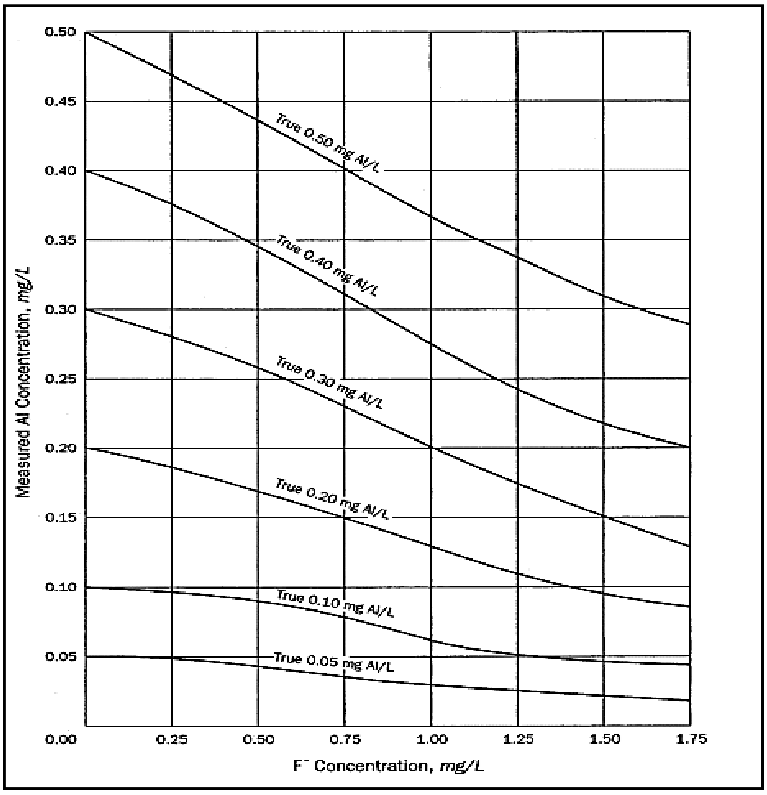
7.8.2.Removal of phosphate interference:

- Add 1.7 ml 6N H_2SO_4 to 100 ml sample in a 200-ml Erlenmeyer flask.
- Heat on a hot plate for at least 90 min, keeping solution temperature just below the boiling point.
- At the end of the heating period solution volume should be about 25 ml.
- Add water if necessary to keep it at or above that volume.
- After cooling, neutralize to a pH of 4.3 to 4.5 with NaOH, using 1N NaOH at the start and 0.1N for the final fine adjustment. Monitor with a pH meter. Make up to 100 ml with water, mix, and use a 25-ml portion for the aluminum test.
- Run a blank in the same manner, using 100 ml distilled water and 1.7 ml 6N H_2SO_4.

- Subtract blank reading from sample reading or use it to set instrument to zero absorbance before reading the sample.

7.8.3.Correction for samples containing fluoride more than 3 ppm:

- Measure sample fluoride concentration by the SPADNS or electrode method.
- Either: Add the same amount of fluoride as in the sample to each aluminum standard, or
- Determine fluoride correction from the set of curves in Figure 1.



7.9. Calculation:

- Take the reading directly from the curve in mg Al/l if you use 25 ml sample, else multiply the reading by the dilution to 25ml.

7.10. Reporting:

- Results are reported as mg/l with two digits.

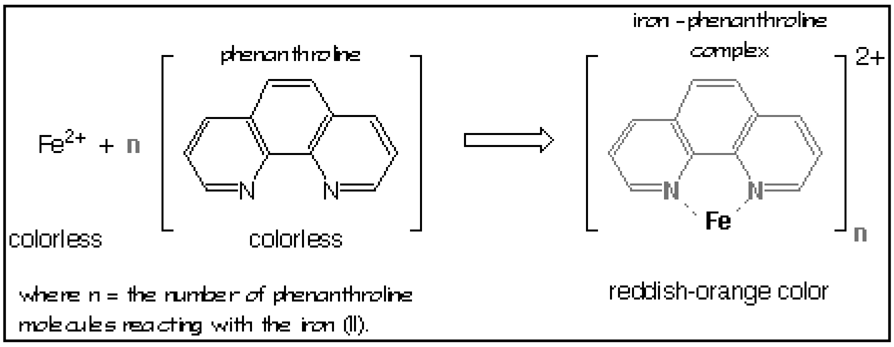
8. Iron (Fe)

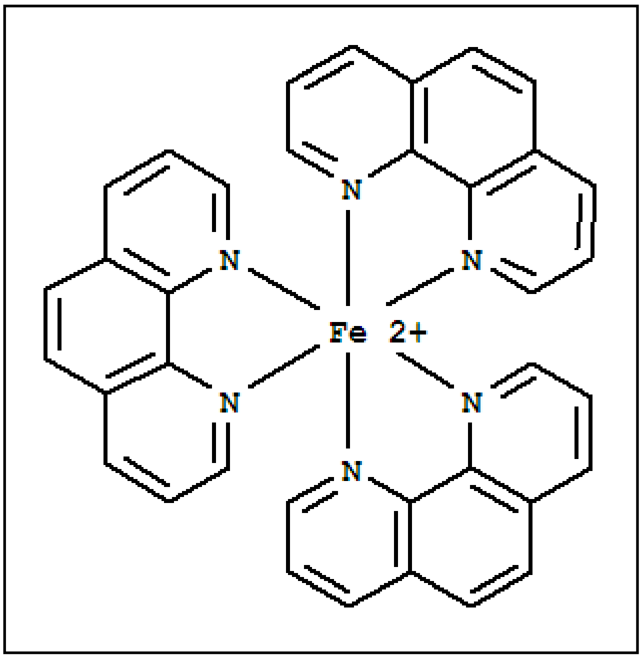
Ref: Standard Methods 23nd Edition, 3500-Fe IRON 1997 (Editorial revisions, 2011);3500-Fe B. Phenanthroline Method

8.1. Principle:

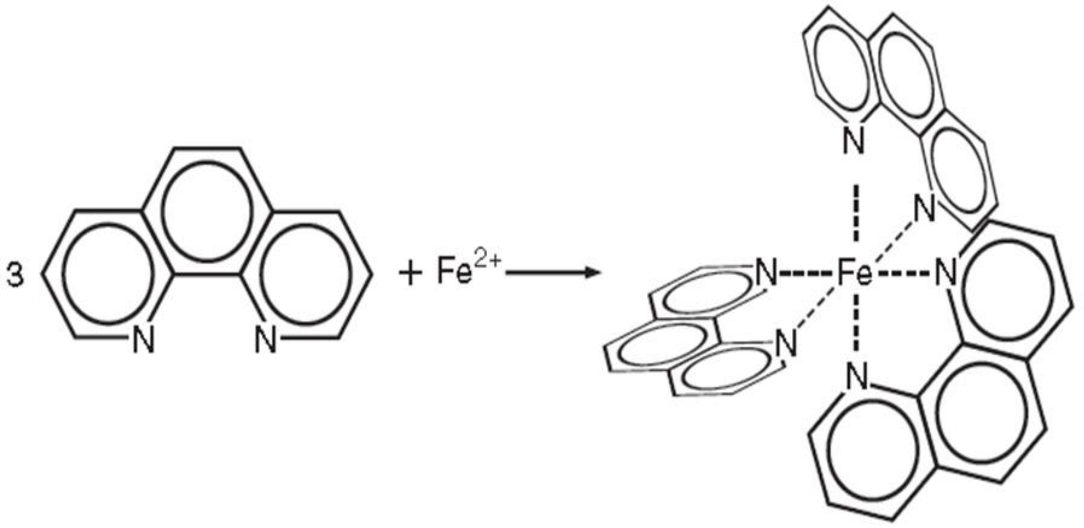
- Iron is brought into solution soluble or in soluble, reduced to the soluble ferrous state by boiling with acid and hydroxylamine, and treated with 1,10-phenanthroline at pH 3.2 to 3.3.
- Hydroxylamine reduces iron (III) according to the equation:

$$2NH_2OH + 4\,Fe^{3+} \rightarrow N_2O(g)\uparrow + H_2O + 4\,Fe^{2+} + 4H^+$$





- Three molecules of phenanthroline chelate each atom of ferrous iron to form an orange-red complex. The colored solution obeys Beer’s law; its intensity is independent of pH from 3 to 9. A pH between 2.9 and 3.5 insures rapid color development in the presence of an excess of phenanthroline. Color standards are stable for at least 6 months.



Chemical reaction for 1,10-Phenanthroline method

8.2. Interference:

- Among the interfering substances are strong oxidizing agents, cyanide, nitrite, and phosphates (polyphosphates more so than orthophosphate), chromium, zinc in concentrations exceeding 10 times that of iron, cobalt and copper in excess of 5 mg/l, and nickel in excess of 2 mg/l.
- Bismuth, cadmium, mercury, molybdate, and silver precipitate phenanthroline.
- The initial boiling with acid converts polyphosphates to orthophosphate and removes cyanide and nitrite that otherwise would interfere.
- Adding excess hydroxylamine eliminates errors caused by excessive concentrations of strong oxidizing reagents.
- In the presence of interfering metal ions, use a larger excess of phenanthroline to replace that complexes by the interfering metals. Where excessive concentrations of interfering metal ions are present, the extraction method may be used.
- If noticeable amounts of color or organic matter are present, it may be necessary to evaporate the sample, gently ash the residue, and re-dissolved in acid. The ashing may be carried out in silica, porcelain, or platinum crucibles that have been boiled for several hours in 6N HCl.
- The presence of excessive amounts of organic matter may necessitate digestion before use of the extraction procedure.

8.3. Minimum detectable concentration:

- Dissolved or total concentrations of iron as low as 10 µg/l can be determined with a spectrophotometer using cells with a 5 cm or longer light path. Carry a blank through the entire procedure to allow for correction.

8.4. Apparatus:

- Colorimetric equipment: Spectrophotometer, for use at 510 nm, providing a light path of 1 cm or longer.
- Acid-washed glassware: Wash all glassware with conc hydrochloric acid (HCl) and rinse with reagent water before use to remove deposits of iron oxide.
- Separatory funnels: 125ml, Squibb form, with ground-glass or TFE stopcocks and stoppers.

8.5. Reagent:

- Use reagents low in iron in preparing standards and reagent solutions and in procedure. Store the reagents in glass-stopper bottles. The HCl and ammonium acetate solutions are stable indefinitely if tightly stoppered.
- The hydroxylamine, phenanthroline, and stock iron solutions are stable for several months. The standard iron solutions are not stable; prepare daily as needed by diluting the stock solution. Visual standards in Nessler tubes are stable for several months if sealed and protected from light.
- **Hydrochloric acid, HCl, conc, containing less than 0.5 ppm iron.**
- **Hydroxylamine solution:**
  - ➢ Dissolve 10 g $NH_2OH.HCl$ in 100 ml water.
- **Ammonium acetate buffer solution:**
  - ➢ Dissolve 250 g $NH_4C_2H_3O_2$ in 150 ml water. Add 700 ml conc (glacial) acetic acid. Because even a good grade of $NH_4C_2H_3O_2$ contains a significant amount of iron, prepare new reference standards with each buffer preparation.
- **Sodium acetate solution:**
  - ➢ Dissolve 200 g $NaC_2H_3O_2.3H_2O$ in 800 ml water.
- **Phenanthroline solution:**

  - Dissolve 100 mg 1,10-phenanthroline monohydrate, $C_{12}H_8N_2.H_2O$, in 100ml water by stirring and heating to 80°C. Do not boil. Discard the solution if it darkens. Heating is unnecessary if 2 drops conc HCl are added to the water.

- (NOTE: One milliliter of this reagent is sufficient for no more than 100 µg Fe.)

- **Potassium permanganate, 0.02 M:**

  - Dissolve 0.316 gm $KMnO_4$ in reagent water and dilute to100 ml.

- **<u>Stock iron solution: Use salt for preparing the stock solution.</u>**

  - **To prepare *<u>(200 ppm)</u>* Fe:**

$Fe(NH_4)_2(SO_4)_2.6H_2O$ ----------------- Fe

474.3884 26.98 gm

????????? 200mg/L

?????????= 200(mg/L)* 392.14 ~~gm~~/ 55.84 ~~gm~~

?????????= 200(mg/L)* 392.14 ~~gm~~/ 55.84 ~~gm~~ =1404.mg = 1.404 g

  - If ferrous ammonium sulfate is preferred, slowly add 20 ml conc H_2SO_4 to 50 ml water and dissolve 1.404 g $Fe(NH_4)_2(SO_4)_2.6H_2O$. Add 0.02 M potassium permanganate ($KMnO_4$) drop wise until a faint pink color persists. Dilute to 1000 ml with water and mix; 1.00 ml = 200 µg Fe.

- **<u>Standard iron solutions: Prepare daily for use.</u>**

  - Pipette 50.00 ml stock solution into a 1000-ml volumetric flask and dilute to mark with water; 1.00 ml = 10.0 µg Fe. (10 ppm)
  - Pipette 5.00 ml stock solution into a 1000-ml volumetric flask and dilute to mark with water; 1.00 ml = 1.00 µg Fe. (1 ppm)

8.6. <u>Procedure:</u>

8.6.1. Total iron:

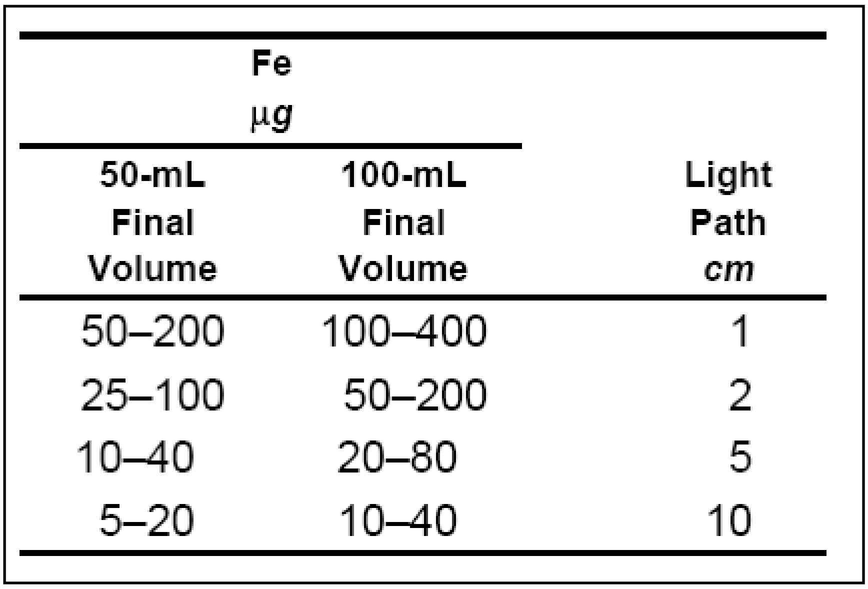
- Mix sample thoroughly

- Measure 50.0 ml into a 125ml Erlenmeyer flask. If this sample volume contains more than 200 µg iron use a smaller accurately measured portion and dilute to 50.0 ml.
- Add 2 ml conc HCl
- Add 1 ml NH2OH.HCl solution.
- Add a few glass beads and heat to boiling. To insure dissolution of all the iron, continue boiling until volume is reduced to 15 to 20 ml.
- (If the sample is ashed, take up residue in 2 ml conc HCl and 5 ml water.) Cool to room temperature and transfer to a 50- or 100-ml volumetric flask or Nessler tube.
- Add 10 ml $NH_4C_2H_3O_2$ buffer solution
- Add 4 ml phenanthroline solution, and dilute to mark with water. Mix thoroughly and allow a minimum of 10 min for maximum color development.

8.6.2. Dissolved iron:

- Immediately after collection filter sample through a 0.45-µm membrane filter into a vacuum flask containing 1 ml conc HCl/100 ml sample.
- Analyze filtrate for total dissolved iron and/or dissolved ferrous iron. (This procedure also can be used in the laboratory if it is understood that normal sample exposure to air during shipment may result in precipitation of iron.)

- **Calculate suspended iron by subtracting dissolved from total iron.**
- **For photometric measurement,**
  - use Table as a rough guide for selecting proper light path at 510 nm. Read standards against water set at zero absorbance and plot a calibration curve, including a blank.
  - If samples are colored or turbid, carry a second set of samples through all steps of the procedure without adding phenanthroline. Instead of water, use the prepared blanks to set photometer to zero absorbance and read each sample developed with phenanthroline against the corresponding blank without phenanthroline. Translate observed photometer readings into iron values by means of the calibration curve. This procedure does not compensate for interfering ions.



Fe µg		
50-mL Final Volume	100-mL Final Volume	Light Path *cm*
50–200	100–400	1
25–100	50–200	2
10–40	20–80	5
5–20	10–40	10

SELECTION OF LIGHT PATH LENGTH FOR VARIOUS IRON CONCENTRATIONS

8.7. Calculation

- Take the reading directly from the curve in mg Fe/l if you use 50 ml sample, else multiply the reading by the dilution to 50ml.

8.8. Reporting:

- Results are reported as mg/l with two digits.

9. Manganese (Persulfate Method)

(3500-Mn B.)

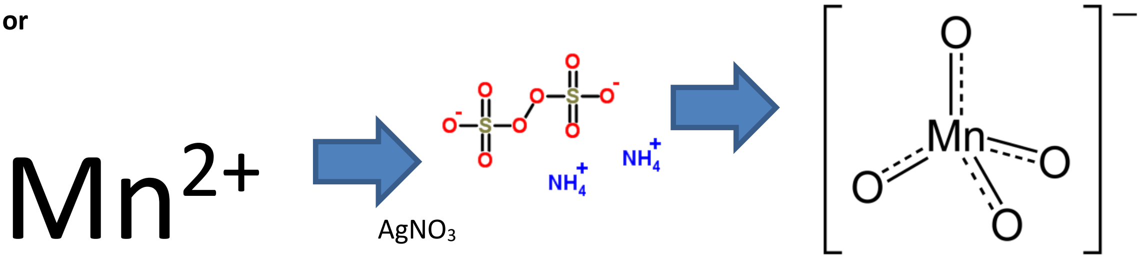
Ref: Standard Methods 23nd Edition, 3500-Mn MANGANESE 1999 (Editorial revisions, 2011)

3500-Mn B. Persulfate Method

9.1. Principle:

- Persulfate oxidation of soluble manganous compounds to form permanganate is carried out in the presence of silver nitrate$_3$

or



- The resulting color is stable for at least 24 h if excess persulfate is present and organic matter is absent.

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+.$$

$$2\,Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \xrightarrow{AgNO_3} \underset{\text{purple color}}{2\,MnO_4^-} + 10SO_4^{2-} + 16H^+$$

9.2. Interference:

- As much as 0.1 g chloride **(Cl^-)** in a 50-ml sample can be prevented from interfering by adding 1 g mercuric sulfate ($HgSO_4$) to form slightly dissociated complexes.
- **Bromide and iodide** still will interfere and only trace amounts may be present.
- The persulfate procedure can be used for potable water with trace to small amounts of organic matter if the period of heating is increased after more persulfate has been added.

- For wastewaters containing organic matter, use preliminary digestion with nitric and sulfuric acids (HNO_3 and H_2SO_4) (see the method).
- If large amounts of Cl^- also are present, boiling with HNO_3 helps remove it. Interfering traces of Cl^- are eliminated by $HgSO_4$ in the special reagent.
- Colored solutions from other inorganic ions are compensated for in the final colorimetric step.
- Samples that have been exposed to air may give low results due to precipitation of manganese dioxide (MnO_2). Add 1 drop 30% hydrogen peroxide (H_2O_2) to the sample, after adding the special reagent, to re-dissolve precipitated manganese.

9.3. Minimum detectable concentration:

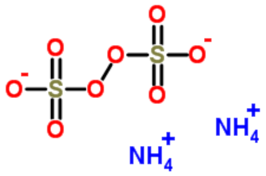
- a minimum detectable concentration (98% transmittance) of 210 µg Mn/L when a 1-cm cell is used or 42 µg Mn/L when a 5-cm cell is used.

9.4. Apparatus:

- Colorimetric equipment: Spectrophotometer, for use at 525nm, providing a light path of 1 cm or longer.

9.5. Reagents:

- **Special reagent:**
  - Dissolve 75 g $HgSO_4$ in 400 ml conc HNO_3 and 200 ml distilled water. Add 200ml 85% phosphoric acid (H_3PO_4), and 35 mg silver nitrate ($AgNO_3$). Dilute the cooled solution to 1 L.
- **Ammonium persulfate, $(NH_4)_2S_2O_8$, solid.**



- **Standard manganese solution 0.1N (KMnO4):**
  - KMnO4 M.Wt = 158. The Mn in $KMnO_4$ exists in +7 state. In Acidic medium, This Mn^{+7} goes to Mn^{+2} state and hence there is a net gain of 5 electrons.
  - Therefore, the Equivalent Weight = 158/5 = 31.6 grams.
    - Wt(gm)=N*Eq.Wt*V(ml)/1000
    - Wt(gm)=0.1*31.6*1000/1000
    - Wt(gm)= 3.2

- So, we can prepare a 0.1N potassium permanganate ($KMnO_4$) solution by dissolving 3.2 g $KMnO_4$ in distilled water and making up to 1 L. Age for several weeks in sunlight or heat for several hours near the boiling point, then filter through a fine fritted-glass filter crucible and standardize against sodium oxalate as follows:
    - Weigh several 100- to 200-mg samples of $Na_2C_2O_4$ to 0.1 mg and transfer to 400-ml conical flasks.
    - To each beaker, add 100 ml distilled water and stir to dissolve.
    - Add 10 ml 1+1 H_2SO_4
    - Heat rapidly to 90 to 95°C.
    - Titrate rapidly with the $KMnO_4$ solution to be standardized, while stirring, to a slight pink end-point color that persists for at least 1 min. Do not let temperature fall below 85°C. If necessary, warm beaker contents during titration; 100 mg $Na_2C_2O_4$ will consume about 15 ml permanganate solutions.
    - Run a blank on distilled water and H_2SO_4.
    - **$(N_1*V_1)_{KMnO4} = (N_2*V_2)_{Na2C2O4}$ --------1**
- But we know that $Na_2C_2O_4$ Wt(gm)=N*Eq.Wt*V(ml)/1000
    - **$Na_2C_2O_4$ Wt(gm)*1000 / Eq.Wt =N* V(ml) --------2**
- **From 1 & 2**
    - (N1*V1) $KMnO_4$ = (Wt (gm)*1000 / Eq.Wt) $Na_2C_2O_4$
    - (N1)$KMnO_4$ = (Wt(gm) $Na_2C_2O_4$*1000 / Eq.Wt $Na_2C_2O_4$ *V1 $KMnO_4$)
    - $Na_2C_2O_4$ M.Wt= 134, Eq.Wt = M.Wt/2 = 134/2 = 67
    - $(N_1)_{KMnO4} = (Wt(gm)_{Na2C2O4}*1000 / 67 *V_{1\ KMnO4})$
    - $(N_1)_{KMnO4} = (Wt(gm)_{Na2C2O4} / V_{1\ KMnO4}*0.067)$
- Or

$$\text{Normality of } KMnO_4 = \frac{g\ Na_2C_2O_4}{(A - B) \times 0.067\ 01}$$

- Where: A = ml titrant for sample and B = ml titrant for blank.

- Average results of several titrations. Calculate volume of this solution necessary to prepare 1 L of solution so that 1.00 ml = 50.0 µg Mn, as follows:
    - $KMnO_4$ ----------------- Mn
    - 158 54.94 gm
    - ????????? 50 mg/L
    - ?????????= 50(mg/L)* 158 gm/ 54.94 gm
    - ?????????= 143.793 (mg/L)
    - ?????????= 0.143793 (g/L)
- And we know that to prepare diluted concentration (C_2) of volume (V_2), we take Volume (V_1) from original concentration (C_1), as per the following relation:
    - $(C_1 * V_1)_{\text{before dilution}} = (C_2 * V_2)_{\text{after dilution}}$
- So
    - (C1 (g/L) * V1) before dilution = (C2 (g/L)* V2) after dilution
    - (V1) before dilution = (C2 (g/L)* V2) after dilution/ (C1 (g/L)) before dilution
    - (V1) before dilution= (0.144 (g/L)*1000) after dilution/ (C1 (g/L)) before dilution
- Also we know that S(g/L) = N*Eq.Wt

So

$$(V_1)_{\text{before dilution}} = (143.793)_{\text{after dilution}}/(N*Eq.Wt)_{\text{before dilution}}$$

$$(V_1)_{\text{before dilution}} = (143.793)_{\text{after dilution}}/(N*31.606)_{\text{before dilution}}$$

$$(V_1)_{\text{before dilution}} = 4.55/(N)_{\text{before dilution}}$$

Or

$$\text{mL KMnO}_4 = \frac{4.55}{\text{normality KMnO}_4}$$

- To this volume add 2 to 3 ml conc H_2SO_4 and $NaHSO_3$ solution drop wise, with stirring, until the permanganate color disappears. Boil to remove excess SO_2, cool, and dilute to 1000 ml with distilled water. Dilute this solution further to measure small amounts of manganese.
- Hydrogen peroxide, H_2O_2, 30%.

- Nitric acid, HNO_3, conc.
- Sulfuric acid, H_2SO_4, conc.
- Sodium nitrite solution:
    - ➢ Dissolve 5.0 g $NaNO_2$ in 95 ml distilled water.
- Sodium oxalate, $Na_2C_2O_4$, primary standard.
- Sodium bisulfite: Dissolve 10 g $NaHSO_3$ in 100 ml distilled water.

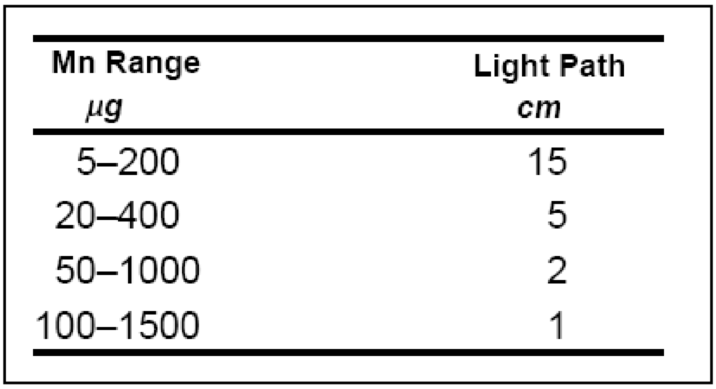
9.6. Procedure:

9.6.1. Treatment of sample:

- **If a digested sample has been prepared according to directions for reducing organic matter and/or excessive chlorides in Section 3030G,**
- Pipette a portion containing 0.05 to 2.0 mg Mn into a 250-ml conical flask. Add distilled water, if necessary, to 90 ml and proceed.
- To a suitable sample portion add 5 ml special reagent
- Add 1 drop H_2O_2.
- Concentrate to 90 ml by boiling or dilute to 90 ml.
- Add 1 g $(NH_4)_2S_2O_8$,
- Bring to a boil, and boil for 1 min. Do not heat on a water bath.
- Remove from heat source, let stand 1 min,
- Cool under the tap. (Boiling too long results in decomposition of excess persulfate and subsequent loss of permanganate color; cooling too slowly has the same effect.)
- Dilute to 100 ml with distilled water free from reducing substances and mix.
- Prepare standards containing 0, 5 … 1500 µg Mn by treating various amounts of standard Mn solution in the same way.

9.6.2. Photometric determination:

- Use a series of depend on your range.
- Make photometric measurements against a distilled water blank. The following table shows light path length appropriate for various amounts of manganese in 100ml final volume:



Mn Range μg	Light Path cm
5–200	15
20–400	5
50–1000	2
100–1500	1

- Prepare a calibration curve of manganese concentration vs. absorbance from the standards and determine Mn in the samples from the curve.
- Correction for turbidity or interfering color:
  - Avoid filtration because of possible retention of some permanganate on the filter paper.
  - If visual comparison is used, the effect of turbidity only can be estimated and no correction can be made for interfering colored ions.
- When photometric measurements are made, use the following ‘‘bleaching’’ method, which also corrects for interfering color:
  - As soon as the photometer reading has been made, add 0.05 ml H_2O_2 solution directly to the sample in the optical cell.
  - Mix and, as soon as the permanganate color has faded completely and no bubbles remain, read again.
  - Deduct absorbance of bleached solution from initial absorbance to obtain absorbance due to Mn.

9.7. Calculation:

- Take the reading directly from the curve in mg Mn/l if you use 100 ml sample,
- else multiply the reading by the dilution to 100ml.

للاقتراحات والشكاوى قم بمسح الصورة (QR)

قام بإعداد الإصدار الأول من هذا البرنامج:

د/ محمد بكر محمد	المعمل المرجعى – الشركة القابضة
د/طارق رشدى	المعمل المرجعى – الشركة القابضة
د/ عاصم عبدالرحمن	المعمل المرجعى – الشركة القابضة
د/محمد أحمد السيد	المعمل المرجعى – الشركة القابضة
د/إبراهيم شوقى	المعمل المرجعى – الشركة القابضة
د/ صبرى زغلول وهبة حنا	المعمل المرجعى - الشركة القابضة
د/تامر إمام	المعمل المرجعى – الشركة القابضة
د/ سناء أحمد الإله	شركة مياه الشرب والصرف الصحى بالفيوم
د/ شعبان محمد على	شركة مياه الشرب والصرف الصحى بالفيوم
د/ حمدى عطيه مشالى	شركة مياه الشرب والصرف الصحى بالغربية
د/ سعيد أحمد عباس	شركة مياه الشرب والصرف الصحى بالغربية
د/ عبدالحفيظ السحيمى	شركة مياه الشرب بالقاهرة الكبرى
د/ مى صادق	شركة مياه الشرب بالقاهرة الكبرى

قام بإعداد الإصدار الثانى من هذا البرنامج:

د/ محمد أحمد السيد	المعمل المرجعى لمياه الشرب- الشركة القابضة
د/ محمد حسين بركات	المعمل المرجعى لمياه الشرب- الشركة القابضة
كيميائى/ صابر داوود عبد الله	شركة مياه الفيوم
كيميائى/ سعيد أحمد عباس الضاحى	شركة مياه الغربيه
كيميائى/ محمود أحمد السيد عز العرب	شركة مياه سوهاج

قام بالمشاركة والمراجعة وابداء الرأى لهذا البرنامج:

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كيميائية/ أمل منصور	شركة مياه البحيرة
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كيميائية/ شيماء محمد عبد المجيد محمد	شركة مياه القليوبية
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كيميائية/ عزة محمد عبد الحى	شركة مياه الدقهلية
كيميائى/ عماد زيدان	شركة مياه الاسكندرية
كيميائى/ محمد امام محمد	شركة مياه الجيزة
د/ محمد حسنى شلتوت	المعمل المرجعى لمياه الشرب- الشركة القابضة
كيميائى/ محمد رفعت محمود	شركة مياه الجيزة
كيميائى/ محمد عابدين إبراهيم	المعمل المرجعى لمياه الشرب- الشركة القابضة

كيميائى/ محمد عبد الفتاح السيد خليل	شركة مياه الجيزة
كيميائية/ مروة محمد خليف	شركة مياه البحيرة
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كيميائية/ نوال محمد محمد عبد الله	شركة مياه الشرقية

قام بالتنسيق الفني والإخراج لهذا الإصدار:

كيميائى/ محمود جمعه	الإدارة العامة للمسار الوظيفى- الشركة القابضة