

Method for Chloride Determination by Ferric Thiocyanate, Version 2.0

1 PRINCIPLE

This method is designed for the determination of chloride in water, soil, and other forms of samples. The sample is prepared offline if necessary and then introduced to the FIALab analyzer. When chloride is mixed with mercuric (II) thiocyanate, it complexes with Hg(II). The thiocyanate that is released combines with Fe(III) ions present in the reagent to form ferric thiocyanate, which can be measured spectrophotometrically.

This method is designed to be run on the FIAlyzer-1000 or FIAlyzer-FLEX.

2 SUMMARY

This method is designed for the determination of chloride in water, soil, and other forms of samples. The method is capable of detecting chloride in the range of 0.5-20mg Cl/L. For more information, see the section on performance metrics.

3 COMPLIANCE

The method follows Standard Method 4500-Cl- E., 4500-Cl- G.

4 SAFETY

The toxicity or carcinogenicity of all reagents used in this method must be taken into account and therefore each chemical listed below should be handled accordingly.

Each laboratory is responsible for maintaining compliance with OSHA regulations regarding the safe handling of the chemicals specified in this method. Material Safety Data Sheets (MSDS) should be made available to all personnel using the method.

All waste materials should be disposed of in a responsible manner, in accordance with federal, state, local, and any other applicable regulations.

The following chemicals have the potential to be highly toxic or highly hazardous; for detailed explanations consult the MSDS:

- **Mercuric Thiocyanate**
- **Methanol**

5 EQUIPMENT AND SUPPLIES

- **Equipment:**
 - Balance, analytical, with a 0.01 g resolution
 - Pipettes for making standards

- **Glassware:**
 - Class A volumetric flask, 1L, QTY 2
 - Graduated cylinder, 100mL, QTY 1
 - Glass storage container, 1L, clear, QTY 2

- **Autosampler (for high sample loads):**
 - Cetac ASX-280/560 (recommended) or AIM-3200/3300

6 REAGENTS AND STANDARDS

Chemical part numbers refer to Fisher Scientific unless noted otherwise.

Chemical	Chem. Formula	CAS#	Supplier PN
Deionized Water	H ₂ O	7732-18-5	
Mercuric thiocyanate solution. 4.17 g/L in methanol.			478516
Ferric nitrate solution. 202 g/L in 0.4M nitric acid.			313416

▪ Preparation of Reagents

- **Carrier:** Matrix match carrier to samples. Salt solution to seawater samples, extraction solution for soil samples, etc.
- **Reagent 1:** Chloride reagent (1 L)
 - Add 150mL of mercuric thiocyanate solution and 150mL of ferric nitrate solution to 600mL of DI water.
 - Add deionized water to a total volume of 1L.
 - Mix well and store in a glass bottle.
 - The reagent should be a light orange color with no particles in it.
- **Probe Wash Solution:** Water with 0.1% Brij L23 (1L)
 - Add 3.3mL Brij L23 to 800mL of deionized water, dilute to 1L.
 - Mix well and store in a glass bottle.
 - The wash solution should be clear with no particles in it.

▪ Notes on reagent shelf life:

- Use of high quality laboratory glass bottles is important.
- Reagent 1 should be prepared every 4 weeks.

▪ Preparation of Standards

- Dilute 1000 mg/L Cl⁻ stock solution with carrier to the desired range of chloride standards.

7 SAMPLE COLLECTION AND PRETREATMENT

This protocol only covers the analysis process. Sample collection and pretreatment depends on the type of sample and will have to be determined separately.

8 INSTRUMENT SETUP – MID-RANGE

- Flow injection analysis apparatus parameters:

Component	Specifications	FIALab PN
Analyzer	FIAlyzer-1000 or FIAlyzer-FLEX flow injection analyzer	*Inquire
Spectrometer	FLAME-T-VIS-NIR Spectrometer. 350-1000 nm.	64019
Light source	HL-2000-LL, tungsten-halogen, 360-2000 nm.	17041
SMA-Z flow cell	Light path – 10mm	29028
Peristaltic pump tubing	1.02mm/0.04in ID (white/white)	*Inquire
Peristaltic pump tubing	0.76mm/0.03in ID (black/black)	*Inquire
Sample injection loop	105 μ L – 9.0in/23.0cm of Teflon capillary tubing with 0.03 in/0.71 mm ID	270040
Reaction coil 1	750 μ L - 65.0in/165cm of Teflon capillary tubing with 0.03 in/0.75 mm ID	270040

9 SOFTWARE PARAMETERS:

Parameter	Value
Pump Speed	30%
Primary Spectrometer Wavelength	480nm
Reference Wavelength	650nm

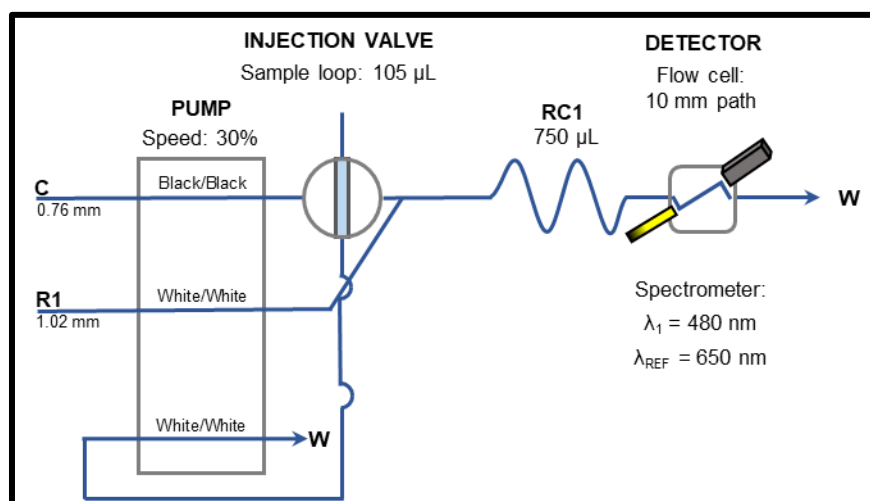


Fig. 1- Flow schematic for chloride determination.

10 FIASOFT METHOD

- The program script using an autosampler is shown below. For manual sample introduction see the FIASoft manual.

'Chloride method script.

FIALab Injection Valve Sample Load
FIALab Peristaltic Pump CounterClockwise(%) 30
Autosampler Wash
Next Sample
Delay (sec) 60

Loop Start

Autosampler Wash
Analyte New Sample
Next Sample
FIALab Injection Valve Sample Inject
Delay (sec) 3
FIALab Injection Valve Sample Load

Spectrometer Reference Scan
Spectrometer Absorbance Scanning
Delay (sec) 30
Spectrometer Stop Scanning

Loop End

Autosampler Rinse
Delay (sec) 60
Autosampler Wash
Delay (sec) 30
Autosave Data C:\Users\FIALab\Desktop\Autosave Data\DateTime
FIALab Peristaltic Pump Off

11 PERFORMANCE METRICS

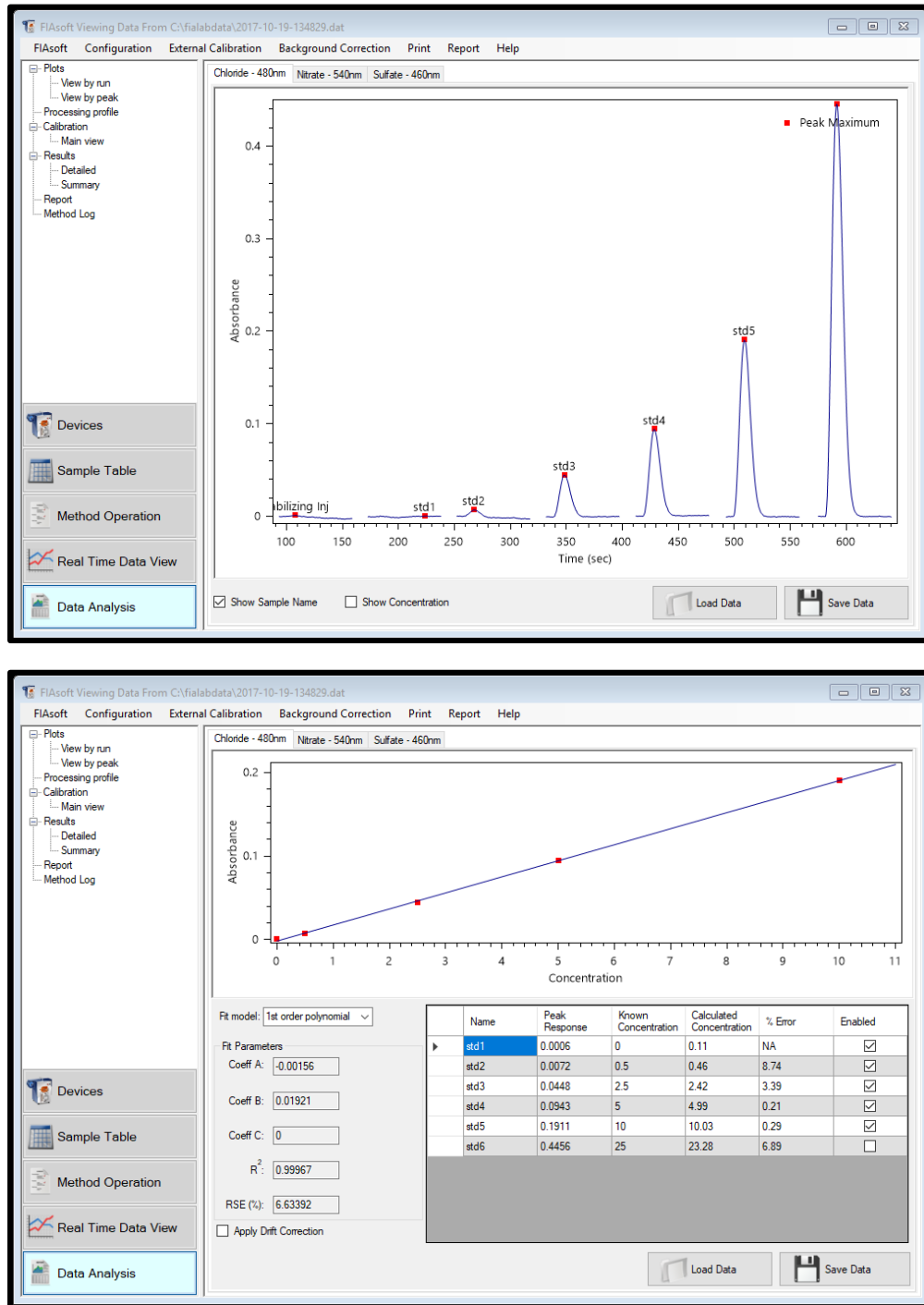


Fig. 2 – Example plot and calibration data for chloride.

- Lower limit of detection: 0.2mg Cl/L – 5.6×10^{-6} mol/L
- Lower limit of quantification: 0.5mg Cl/L – 14×10^{-6} mol/L
- Upper limit of detection: 20mg Cl/L – 0.56×10^{-3} mol/L
- Sample throughput: 90 samples / hour
- Startup + Calibration: 5 minutes
- Shutdown: 5 minutes

Note: due to the orange color of R1, using an optical path of longer than 10mm is not feasible.