WaSH-Mia/SATREPS: Manual

1	Water Security Map (Quantity Aspect) Preparation Manual
2	Field Survey and Water Sample Transport for Chemical and Isotope Analysis
3	Analytical Methods for Microbiological Evaluation of Water Samples
4-1	Analytical Methods for Water sample Target : N, P, Metal, COD and HCO3-
4-2	Handbook for Installation, Operation, and Maintenance of Locally fitted, compact, and distributed (LCD) water treatment system
5	Manual for the Socio-Economic Survey on Household Water Use
6	Manual for Web Mapping of Water Security Information

WaSH-Mia/SATREPS: Manual No.1

Water Security Map (Quantity Aspect) Preparation Manual

Please **consult** one of the followings person before using the data for any purpose

1.0 Bhesh Raj Thapa, bthapa.ioe@gmail.com

2.0 Hiroshi Ishidaira. ishi@yamanashi.ac.jp

3.0 Futaba Kazama, kfutaba@yamanashi.ac.jp

Background

Water security (and its reverse - water scarcity) is more than the sustainable access to adequate quantities and acceptable quality of water for people and economic activities. It is also about the healthy aquatic ecosystem and protecting us against water related disaster in a climate of peace and political stability (ADB, 2016; UN-Water, 2013). Security is an imbalance between supply and demand that varies with local condition (Fischer et al., 2015). Translating water security in numerical terms helps clarity and understand coherently the concept, and reduce ambiguity. Therefore, several indicator-based water security-related indices are developed to quantify water insecurity or the reverse (Lautze and Manthrithilake, 2012; Rijsberman, 2006).

Water security is considered as one of the 21st century challenges for science and society, and for Kathmandu Valley where water supply in quantity and quality has not been adequate where its long-term water supply is not assured due to high water demand, water contamination and so on, caused by population growth and industrialization etc.

With the aim to enhance the management system on potable water resources in Kathmandu Valley, the project for Hydro-Microbiological Approach for Water Security in Kathmandu valley has been implemented since May 2014 for 5 year. The project has 5 major components and five working group (WG) are working under those components. Through the various activities for achieving the project purpose, the project aims to understand status of water environment in the valley. This project is creating water security maps of the Kathmandu valley considering water quantity, quality, and microorganisms. Knowing the spatial and temporal distribution of those components, the project has been developing different types of locally-fitted, compact and distributed (LCD) water treatment technology. Which will be small scale, energy saving, and highly efficient water treatment system, that suited the local condition and can treat the locally found contaminants. The project also envisages establishing a common ground of water security among stakeholders in the valley so that it becomes a Kathmandu model replicable to growing urban settlements of developing countries.

The knowledge of water security and spatio-temporal mapping of those associated water security factor (quantity, quality, and microorganisms) is the first step to know the situation of water security. The integration of those three factors and interpretation of those result is quite challenging. Proper methodology need to be followed to integrate those factors like multiple criteria decision making techniques (AHP) to prepare the integrated water security map. Hence, in this manual, we are dealing all three factors separately in separate section. This manual is mainly focusing on water quantity part done by WG-1 without considering water quality and microbiology part.

The main objectives of WG-1 are 1) to conduct studies on the spatio-temporal distribution of water resources and the long term variation trends, 2) to develop

integrated water security map of potable water resources, and 3) to clarify possibilities of developing alternative techniques to utilize water resources. Hence in this manual, the discussion will be focused and can answer: what types of data need to be collect? what kind of models can be applied to assess the water balance in different component of hydrological cycle? How those data can be used to prepare the water security map in terms of quantity? What could be the alternative techniques that can utilize the available water resources in optimal way? In this manual, the discussion to prepare water security map is in detail and rest of the part described in very precisely.

Material and Methods

In this section, most of the methods are discussed in sequential order to obtain the objectives outlined in background section. In this manual, we are trying to generalize the work but most of the description is based on the project activities, hence methods may be more specific for Kathmandu valley.

Objective-1

To achieve this objective, the whole process can be divided in several sub-section like data collection, spatial and temporal climatic and non-climatic long term variation trends, hydrological modelling, and hydro-geological modelling.

Data collection:

The climatic data such as precipitation, temperature, wind speed, humidity, solar radiation, evaporation, discharge, water withdrawal, river network, land use, geology, soil type, digital elevation model, population, population projection rate, administrative boundary, hydrological boundary, groundwater level data etc. were collected from concerned authorities. The data gaps were identified and missing data on each component were filled using appropriate techniques.

Trend Analysis:

Trend analysis is a rampant procedure of collecting information and attempting to spot a pattern. In this project, the historical climatic data were collected and pattern for precipitation, temperature, and discharge were evaluated (2001-2010), for detail please refer (Thapa et al., 2017). Future projections were also evaluated from year 2011-2099 using ACCESS 1.0 climate projection data for RCP 4.5 and 8.5.

Hydrological modelling:

Several hydrological model are available to access the water resources; it varies from lumped to distributed. In this study, three model HBV, BTOPMC and SWAT models were applied to estimate the water balance component in hydrological cycle. All the three model performance is almost same, hence due to widely applied and easy interpretation SWAT model was used for further investigation. In Kathmandu Valley,

fresh water is available in mountainous regions of valley, which can be used for drinking purpose. Hence SWAT model was used to estimate the fresh water available in mountainous region. To prepare the water security map, the knowledge on water availability estimation and their regular update is necessary. In this manual, the description of how to prepare model in SWAT and how to update with new data set has been discussed. The detail on hydrological model preparation in SWAT is described in **Annex-1**. In addition to this, we applied HBV and BTOPMC model, which is not described in detail but the data prepared for model are compiled in data **Data_HBV** and **Input_BTOPMC** folder.

Hydrogeological modelling:

Several hydrogeological model are available to access the groundwater resources. In this study, MODFLOW based hydrogeological model Visual MODFLOW Flex was used to evaluate the groundwater resources. The detail on procedure and data are discussed in **Annex-2**.

Objective-2

To achieve this objective, the data on water availability from hydrological model, water supply for potable use from different reports, and water demand for domestic purpose need to be accessed. In this objective water security maps were prepared based on the water supply and demand and possible interventions and update can be done based on the water availability in different time period.

Water Security Mapping:

In this study, household water security (WSI) index were defined as the ratio of water supplied for potable use to water demand for household use considering 50 lpcd and 135 lpcd as per capita water use. The detail on procedure, data required and mapping strategy for each service area are discussed in **Annex-3**.

Annex-1:Setting-up SWAT Model (SWAT2012) for a Watershed

SWAT model is widely used watershed model for estimating water quantity and quality. The step wise process for setting up SWAT model can be accessed from web like https://web.ics.purdue.edu/~vmerwade/education/arcswat.pdf.

In this section we tried to describe key steps to set-up the SWAT Model.

Following are key/broader steps to set-up SWAT model.

- Prepare gridded data of following three layers (DEM, land use and Soil). It is **NOT NECESSARY** that they should be of same spatial resolution; however, is **NECESSARY** to be in same **projected** (e.g. UTM45N) coordinate system.
    - DEM (Digital Elevation Model), we can download DEM data from web like https://lta.cr.usgs.gov/SRTM1Arc https://asterweb.jpl.nasa.gov/gdem.asp
    - Land use/cover (LULC): It is necessary to have four-character Code for each land use/cover types. Therefore, insert a column and decode lulc into four-character code. SWAT understands each lulc based on that code. That code should be unique. If the SWAT2012.mdb file already have similar type of land use, the code could be matched with the existing code in the database. In case not, we need to assign unique one that does not match with existing code in the SWAT2012.mdb (stored in the C > SWAT > ArcSWAT > Databases). For property of the new lulc type, try to match them with existing one in the SWAT database and copy their properties. It is possible that more than one lulc can be assigned the same code (while preparing gridded data).
        - After preparing the gridded data with unique lulc Code, check SWAT2012.mdb file stored in the path mentioned above. If one or more of those lulc types do not exist in that database (**crop** sheet in the MDB file), add them. Otherwise, it creates problem while running SWAT.
    - Soil: Assign unique soil name and corresponding code for dominant soil (e.g. Calcaric Cambisols, CMc). Then check the SWAT2012.mdb file in the path mentioned above. Look into "**usersoil**" sheet. If those soil types do not exist in the sheet, insert them one-by-one. One can copy their properties from other projects set-up for the same region.
- Update following sheets in SWAT2012.mdb (located at following path: C > SWAT > ArcSWAT > Databases) based on types of soil, land use/cover and meteorological stations in the study area.
    - Crop: to update land use/cover database
    - Usersoil: to update soil types and their properties as per the soil in the study area. Soil database is linked using unique field such as "MUID or CPNM or SNUM".
    - WGEN_user: to compile statistical properties of the meteorological stations in the study to allow SWAT fill missing values based on those statistical properties. Following Excel macro can be used for the purpose:
        - WGN Maker 4.1 (http://swat.tamu.edu/software/links/).
- Arrange input data in following order for easy handling (it, however, is not compulsory!).
    - 01_DEM
    - 02_Land use/cover: landuse data as well as "look-up table". Lookup tables are in ".dbf" format. The file can be opened using "Libro Office", the freely available office package.

- 03_Soil: soil data (shape file or gridded data)
- 04_Weather:
  - Rainfall data (mm): Lookup table with station names and locations (batch file in .txt format); data files for each station. Even though the data files are in projected coordinate system, location in such lookup table can be defined using latitude and longitude (degree-decimal system as well).
  - Temperature (°C): Lookup table with station names & locations (batch file); data file for each station. Both minimum and maximum temperature should be in the same file.
  - Relative humidity data (fraction): This should be one value for a day (or an average of two values observed in a day). Lookup table with station names & locations (batch file); data file for each station.
  - Solar radiation data (W/m^2): if sunshine hours (hrs) data is available, it should be converted into solar radiation (W/m2) unit before preparing text file.
  - Wind speed (m/s): it if is available in other units, it should be converted into m/s before preparing text file. For example, unit of wind speed data available with DHM is in km/h. We should convert it into m/s before preparing input files for SWAT2012.
- 05_Tables: prepare following "lookup tables". It should be in ".txt" format. (If you did not prepare lookup table, you can assign different type of landuse/landcover and soil type during HRU analysis, landuse/soil/slope definition)
  - Lulc lookup: follow appropriate format (value and name separated by comma)
  - Soil lookup: follow appropriate format (value and name separated by comma)
  - It is good to insert those two tables right inside respective data folder.
- 06_Baseline and future climate (for climate change impact studies)
  - ?

- Set-up SWAT project
  - New Project > define path and other parameters (as required) > Follow instructions.
- Watershed delineation
  - Upload DEM
  - Stream definition: DEM-based (if no information on existing streams available)
  - Create flow direction & flow accumulation: it automatically calculates area & number of cells (if the DEM is in projected coordinate system)
- Create stream network and outlet points. It automatically creates outlet points for all the tributaries, which can be edited (as required!, you can create outlet in your interest point to get output at that point) and will later be used to delineate sub-watersheds.
- Define basin outlet and create basin and watershed boundaries

STEP-wise GUIDELINE for SETTING UP A SWAT PROJECT

1) SWAT Project Setup:

- New project > define path of project directory, SWAT project geodatabase (.mdb), Raster storage database (.mdb), and SWAT parameter geodatabase (.mdb)

2) Watershed Delineator > Automatic Watershed Delineation

- Select DEM raster and define Z-unit as “meters” from “DEM projection setup”; make sure cell sizes are in meter. In case of Kathmandu, cell size is 30m x 30m (or cell area = 0.09 ha).
- Stream definition: DEM-based; define flow direction and accumulation (Area: in ha for stream calculations; lower thresholds yield more number of streams). If that cell is not active: click on “pre-defined streams …” button and again back to “DEM-based” button. Then the cell should be visible.
- Click on “flow direction and accumulation” button: it may take a bit time to generate flow direction and flow accumulation raster.
- Wait until “End of DEM grid pre-processing” message is displayed.
- Click on “Stream networks” button: Wait until “End of Stream Network Processing” message is displayed. It will then show stream networks and monitoring points for sub-basin delineation.
- Outlet and Inlet definition: The location of outlet points, reservoirs, etc. can be prepared as dBase file and imported as “Add point source to each sub-basin” too.
    i. Define sub-basin outlet at all the hydrological stations whose discharge data are available. They are in addition to those points defined automatically by SWAT.
    ii. Furthermore, delineate sub-basins at the points where you want outputs.
    iii. Also identify other key points (e.g., water diversion points, etc.) and delineate sub-basins above those points.
- Select and define watershed outlets: click on “whole watershed outlet selection” button, select outlet point by left clicking on mouse and dragging a square around the outlet point. After the outlet is selected, click on “Delineate watershed” button. Wait until “watershed delineation completed” message is pop up.
- Note down sub-basin ID (Grid-code) that contributes to hydrological station at its outlet
    i. Right click on “watershed” raster; select the sub-basin above the hydrological station in ArcMap; read Grid-code of the sub-basin and note down it as sub-basin ID for that particular hydrological station.
- Click “Calculate sub-basin parameters” button to get sub-basin parameters for all the sub-basins.
    i. After this calculation, a new layer (MonitoringPoint) will be added on ArcMap. This is basically the same points defined during watershed delineation, but have more basin-related information added automatically on it.
- Add/Delete Reservoirs
    i. If there are diversion points (Dams or Reservoirs) for water (e.g., irrigation, hydropower), we have to add/define them at the time of setting-up the model. Click on Add on right side of “Add or delete reservoir” button and follow the instructions.
- To see the watershed report: **Watershed Delineator > watershed report** > Topographic Report > OK.
    i. It stores information about minimum and maximum elevation and % of area below each meter rise in elevation with the min-max range and % of watershed area for the entire watershed as well as each sub-basin.

3) **HRU Analysis**:
- ***Land use/soil/slope definition***: upload those data and link with SWAT table using “Lookup Tables” for soil and land use. Click on User Table, and select appropriate Look Up Table. Click on Reclassify Button. The Reclassification will be completed automatically.

- *Look-up table of soil*: please make sure header is as follows: "VALUE", "NAME". If you don't have look up table you can define directly here with soil type defined similar to your soil in user soil.
- *Look-up table of land use/cover*: header should have two files (value & name), but their names does not matter. If you don't have look up table, you can define directly with similar type of land use type.
- *Slope range*: generally make 3 slope ranges (sometimes even higher); look at the generated slope map; if it does not represent well the area, change the class and or thresholds for each → decision-making is required at this stage. For starting purpose, we can consider 0-5, 5-15, and 15-9999. Wait until slope re-classification message is displayed.
- If all the data tabs (land use, soil and slope) are opened, the "**Overlay**" button is activated. Click on that button and wait until following message is displayed "Finished Land Use/Soil/Slope Definition".

- ***HRU definition***: based on percentage of area of land use, soil and slope to be considered in defining HRUs → Decision-making is required at this stage. For starting purpose, we can consider 20, 20, and 20 for land use, soil and slope.
- ***HRU Analysis Report***:
  - *Land Use, Soils, Slope Distribution* Report: it keeps a record of following for each sub-basin: i) total areas; ii) type of land uses and respective areas within the sub-basin; iii) type of soils and respective areas within the sub-basin; iv) type of slope categories and respective areas under each slope classes number of HRUs, and types of land use/soil/slope under each sub-basin.
  - *Final HRU Distribution Report*: it keeps records number as well as IDs of HRUs under each sub-basin.

4) **Write Input Tables**:
   - ***Weather Data Definition***:
     - ✓ Prepare text files (with SWAT-compatible format) of precipitation, temperature, evaporation, humidity, solar radiation (W/m2), and wind speed (m/s). One station should have one text file for each parameter.
       - Make sure start and end date for T & P are the same.
     - ✓ Prepare "location table" (is same like Look-up table, with a bit different format) for each of the six parameters.
       - Make sure "Location Table" for weather parameters are stored in the same folder in which weather data (i.e., rainfall, temperature, humidity, etc.).
     - ✓ Specify location of all the location tables under **Write Input Tables > Weather Stations**.
   - ***Write SWAT Database Tables****:* select all the tables by clicking on "Select All" and then create tables by clicking on "Create Tables". After successful completion "Done Building Selected Tables!" message will display.
     i. When selecting all and pressing on Create Tables, it asks for our decision to replace various parameters, should we replace them or NOT?

ii. Do we need to update database after that? What does it mean?

5) **SWAT Simulation**

- Run SWAT: Specify Starting date; Ending date; Rainfall distribution type (use default of Skewed normal); SWAT.exe version (e.g. 64-bit release); and printout settings for output time step/parameters/variables.
    - Specify number of years to skip (NYSKIP as 1 or more year; to stabilize the model before taking outputs)
    - Click on Setup SWAT Run. Wait until finished message is displayed.
    - Click on Run SWAT.

6) Reading SWAT Output: To output the results into database.

- SWAT Simulations > Read SWAT Output.
    - Please explore various options. To export discharge data in and out of a particular reach, click on **output.rch** check box. It is the most essential one to extract discharge data for calibration. If we are interested into sub-basin results, click on "**output.sub**" check box.
    - Click "Import Files to Database" > OK (after displaying following message: Done writing files to database)
- See the results: Go to project directory > Scenarios > Default > Tableout (OR, click on Open SWATOutput.mdb tab in the Read Swat Output window.
    - For inflow and outflow related to the Reach: Click "**output.rch**" for river flow output. For definition of headers please refer **tblRchDef** sheet in the mdb file.
        - Inflow/Outflow to/from the reach are stored in column 5 & 6 of the **rch** sheet.
        - To confirm which one is relevant for calibrating a particular station, we have to look carefully in ArcMap whether the location of calibration point is after flow entering the reach or before flow entering the reach.
    - For water balance components of a particular sub-basin: we can click on **sub** sheet, where we can find information on water balance components for each sub-basin.
        - For definition of headers, please refer the sheet "**tblSubDef**".
    - To select data of particular sub-basin (or reach) of interest: click on the heading "SUB", deselect all, and select the sub-basin of your interest (that contributes to the particular discharge station). Then it shows discharge data for that particular station only.
        - Now, copy data and paste in Excel. Then plot it along with observed data, calculate statistical indicators for performance measure, understand the output and decide next move for "Calibration"
- Checking mass balance for hydrology, solutes, etc.: Review SWAT Output > Run SwatCheck > SetUp > Examine Model Output > Wait for a while until it the processing is completed.
    - Now we can see Simulation details on right hand side (e.g., simulation length, warm up years (i.e., NYSKIP), number of HRUs/sub-basins, etc.
    - Go to "Hydrology" tab: It shows a figure with water balance components for the **entire basin** in a diagram. It also shows water balance ratios. Please pay particular attention to evapotranspiration, baseflow and surface runoff ratios. If they somehow are reasonable, perhaps, the model simulates well the water balance components.

- To see the monthly value of water balance components: please click the tab "**Show Av. Monthly Basin Values**".
- For the various water balance components under each land use category: click on "Land Use Summary" tab.
- For reservoir-related summary: click on Reservoirs tab.
- For sediment-related summary: click on Sediment tab.

- To see annual summary of time-series data for every year: click on "**Open output.std**"
- To see all input tables for each sub-basin and HRU: click on "**Open input.std**"
- Saving simulation: click on Save Simulation. (**If you think this simulation is ok)**

7) **Setting default simulation**: SWA Simulation > Default SWAT Simulation > Follow instruction. (**if you think, this simulation is the base simulation for further calibration, you can set it as default simulation)**

8) **Carrying out calibration manually**:
   - SWAT Simulation > Manual Calibration Helper. try to understand the parameters to be calibrated and their effects on the model performance, the continue the process until observed and simulated discharges are visually as well as statistically comparable to an acceptable degree.
     - Edit SWAT Input > Watershed Data > General Data (. BSN)
     - Edit SWAT Input > Sub Basins' Data

9) Carrying out calibration automatically (just summary, please go through user manual)
   - Please follow the instruction at swat cup user manual (http://swat.tamu.edu/media/114860/usermanual_swatcup.pdf)
   - SWAT-CUP is interface that was developed for SWAT automatic calibration and easily linked with SWAT.
   - Install the SWAT-CUP in the same directory as SWAT
   - Open the project: click on start icon  at left. Choose a new project
   - Import a TxtInout directory from SWAT project Scenario folder and set out the swat version and processor architecture.
   - Set the project type (processing for eg. SUFI2) and set the project name and directory
   - Select the variable through which you want to calibrate the model like .**sub, .hru, .rch**.
   - Edit the calibration inputs in **par_inf.txt.** In this section, you need to define no of parameter, their range, and type very carefully.
   - Edit Sufi2_Swedit: you can define the no of simulation
   - Edit File.cio: You can define no of simulation year, skip year, starting year, ending days of simulation.
   - Observation data preparation: it is quite tricky and need to prepare data in prescribed form. You can watch this video (https://www.youtube.com/watch?v=hllrJah3wbc)
   - Extraction: Edit var-file_rch.txt……Define your outlet no carefully
   - Objective function: Edit var-file_name.txt…by changing the no for appropriate objective function.

Annex-2: Setting-up Visual MODFLOW (VMOD) Flex, 2014 for a groundwater simulation

VMOD Flex is widely used powerful software package that provides the tool for building three dimensional groundwater conceptual and numerical models using raw GIS data objects. The step wise process for setting up VMOD Flex model can be accessed from web like

http://trials.swstechnology.com/software/VMODFlex/2014/VMODFlex_UsersManual.pdf

In this section we tried to describe key steps to set-up the VMOD Flex Model.

Following are key/broader steps to set-up VMOD Flex model.

- Prepare gridded data of required layers that depends upon the available data and modeling strategy. In this model we called it as surface. Prepare the required layers, in the case of Kathmandu (DEM as ground, based on the lithology information having X, Y, Z information (Shallow Aquifer layer, Aquitard layer, and Deep Aquifer layer)). It is **NOT NECESSARY** that they should be of same spatial resolution; however, is **NECESSARY** to be in same **projected** (e.g. UTM45N) coordinate system. VMODFLEX does not support the Geographic coordinate system, hence need to be projected.
    - DEM (Digital Elevation Model), we can download DEM data from web like https://lta.cr.usgs.gov/SRTM1Arc https://asterweb.jpl.nasa.gov/gdem.asp
    - Other surface data can be exported from .XLS,.TXT, .CSV etc. or polygon data like shape file or any other format like jpg, tif. Asci and can be converted into gridded data. For this you can create surface using imported data sets in any form.
- Prepare others data like pumping well information in prescribed format in excel, observation well data in prescribed format in excel.
- Prepare river network and their information like elevation, bed level, conductivity, thickness, width etc. if there is drainage in your study area, prepare those information for drainage also.
- Please think for the zonation (it may be in polygon or whole structure). This is required for assigning the hydraulic conductivity, storage coefficient. Which is mainly depends upon the geology and soil type and hence need to prepare different zone based on the properties. Don't make more no of zone, it will be difficult to handle and you can make same zone for similar types of geological settings.
- Prepare the recharge, evaporation, flux or any other information need to be incorporate in groundwater model. That depends upon how much information you can produce and also relevant for groundwater simulation. For more in detail please refer groundwater simulation related theory.
- Arrange input data in one folder for easy handling (it, however, is not compulsory!).

STEP-wise GUIDELINE for SETTING UP A VMODFLOW PROJECT

While starting the setup, you can start either with numerical modelling or conceptual modelling. It is recommended to prepare conceptual model for new project and numerical model for old project.

1) Project Setup:

- New project > define project name and set directory, Set unit for each like conductivity, length, pumping rate, recharge, specific storage, time as per your data availability.
- Also set the coordinate system (e.g. local Cartesian) and datum (e.g. World Geodetic System 1984) and click Ok.
- Select conceptual modelling and the conceptual model workflow will load. Define the objectives of your model and the default parameters. For conductivity, storage etc. and start date of simulation.
- Click  (next step) to proceed

2) Collect Data Objects

- Import or create the data objects you wish to use for building the conceptual model like:
  - ❖ DEM and shape file for creating surface
  - ❖ Boundary condition Like recharge, river, evaporation and other files as boundary condition (at this stage, you can import, create new data objects 9by digitizing) or create surfaces (from points data objects). Import the data object and select data type like point, polygon etc. and then click finish.
  - ❖ Create surface as per requirement. Repeat these steps to import the remaining
  - ❖ Click next step toproceed, where you will arrive at the define conceptual model.

3) Define Conceptual Model

- Provide a name for conceptual boundary (i.e. horizontal boundary (polygon file)) for modeled area.

4) Define structure

- This is basically creation of horizon considering the geological surfaces (like DEM and other surface layer) as inputs and three dimensional model can be created. You need to define the types of horizon (like base, erosional etc.) by adding surface using  .
- Preview the horizon and create horizon using next button.

5) Define Property zone

- There are two ways to define property zone either structural zones (one zone have same properties) and polygon data objects (you can create several zones based on properties)
- You can click one of the way to define property and select the required layer and properties type (like conductivity, initial heads, storage coefficients)
- You need to repeat this process for all the property type and for all zone as per your requirements.
- Click next step to proceed to the selection screen. Please choose the defining boundary condition or define grid or mesh. For Kathmandu case, please select boundary condition.

6) Define Boundary Condition

- In this step, select boundary condition type (River, Recharge, Evaporation, constant head, drainage etc.) as per requirement and fill the required data.
- After This you can add the pumping well information in prescribed format (please use the provided excel format for data preparation). Import excel sheet as well format.

7) Select grid Type

- In this step, you can choose one from define finite difference grid, define finite element mesh, and define unstructured grid. For Kathmandu valley, you can select first one and follow the following steps.

- ❖ Save the Name of grid, define no of rows and column as per your required grid size. Finer grid will take more time to run the model. You can make coarser grid for whole area and can create child grid in your interested area with finer grid also.
- ❖ Click next step to proceed. Better to edit here, if you need to change any properties here in conceptual model. After converting it into numerical model will be little bit difficult that conceptual model.

8) Convert to Numerical Model

- Click on the convert to numerical model button to proceed. Please wait it will take several minutes depending upon your model until the message conceptual model to numerical model conversion has completed. If you have some error in any boundary condition, message wil show error, please check it carefully.
- Click next step and next tab will be active with numerical model. Please use those tab for further work.

……..

1) Define Properties

- At this step, you can add/edit/delete properties (i.e. conductivity, storage coefficient, and initial head)
- You can see the properties values and their spatial distribution. You can also see the properties values in different view by clicking different view like row view, column view, and layer view. You can also assign the specific row and column to look their properties.
- After this click next button

2) Define Boundary condition

- At this step, you can add/edit/delete boundary condition (i.e. River, recharge, Constant Head etc.)
- Click next step. You will arrive at select the next step options

3) Define Observation Well/Particles/Zone Budget Zones

- Please add the observation well by clicking define observation well and import it from the main window (you need to make it's format in well while converting the prescribed excel file)
- If you are doing particle tracking then you can define particles using define particles.
- If you want to see the water budget in different zone, then you can define zones using polygon object using define zone budget zones.

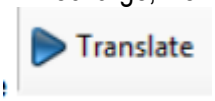
4) Select Run Type

- At this step, you select run type either PEST run or Single run. If you want to use PEST run, please go through PEST run manual. For Kathmandu valley case, we will use single run. Click single run.
- After clicking single run, there is several options available like engine (MODFLOW 2000 or 2005, check one of them), check modpath, zone budget as per your requirement.
- Click the compose engine button to proceed
- Click next step button

5) Translate

- At this stage translate button is active but we need to carefully define the option that includes.
  - ❖ Output folder (define as you required)
  - ❖ Start date (this date is same as previously defined date)
  - ❖ Setting (steady or Transient analysis)
  - ❖ Time steps (monthly, daily, yearly etc.)
  - ❖ Solver (which solver, MODFLOW 2000, 2005 or NWT etc.)

- ❖ Recharge, Rewetting options etc.)

- Click 

button to proceed. It will take certain time. It will convert various input files.
- Click next step to proceed, you will arrive at run

6) Run Numerical Engine

- Click the run button on the main workflow. It will take time, once finished. Click the next step button. After that vie result button will be activated.

7) View Result

- You can then choose to view results in the form of Maps (contour or color shading) or Charts
- You can compare the head distribution with observed data and look on the different performance parameters.

……..

Calibration and validation

- ❖ **Edit the Properties and boundary Condition**
  - You can edit the conductivity, initial head, and storage coefficient values through define properties tab. You can change it as per your knowledge to get the good correlation with observed data.
  - In addition to this, if you want to change the boundary condition data. You can add/edit/delete boundary condition as per requirement from define boundary condition.
- ❖ After editing those properties we need to translate every time and run the model. After that, please check the performance and repeat these steps upto satisfactory performance.

Annex-3: Water Security Index (WSI) Preparation using water quantity data

Water security (and its reverse - water scarcity) is more than the sustainable access to adequate quantities and acceptable quality of water for people and economic activities. It is also about the healthy aquatic ecosystem and protecting us against water related disaster in a climate of peace and political stability. Security is an imbalance between supply and demand that varies with local condition. Translating water security in numerical terms helps clarity and understand coherently the concept, and reduce ambiguity. Therefore, several indicator-based water security-related indices are developed to quantify water insecurity or the reverse . Based on available literature, the overall water security contains mainly five components such as basic needs, agricultural production, environmental flows, risk management, and independence. ADB basically calculating national water security index looking into five components i.e. household, economic, urban, environmental, resilience to water-related disaster . In this study, the focused on the household water security index (WSI) containing three components access to piped water supply, access to improved sanitation, and hygiene. For this study, we are assuming Kathmandu Upatyaka Khanepani Limited (KUKL) will provide safe water that will be piped water supply with improved sanitation and hygiene. Hence we are just focusing on water quantity aspect, which is limitation of this study.

Household water security index (WSI) is calculated only considering the quantity aspect assuming KUKL will provide good quality of water as:

WSI = (Amount of water supply, S) / (Potable water demand, D)

This amount of water supply will be linked with available water, hence we will discuss about the water availability also. Let's talk in each components in detail.

Water Availability (WA)

Water availability means the amount of fresh water available in different sub-watershed or service area that can be used for drinking purpose. For this watershed hydrological model SWAT can be used. For the each sub-watershed fresh water available from mountains can be accessed using the methods described in paper

Thapa, B.R., Ishidaira, H., Bui, T.H., Shakya, N.M., 2016a. Evaluation of water resources in mountainous region of Kathmandu Valley using high resolution satellite precipitation product. J. JSCE, Ser. G (Environmental Res. 72, 27–33

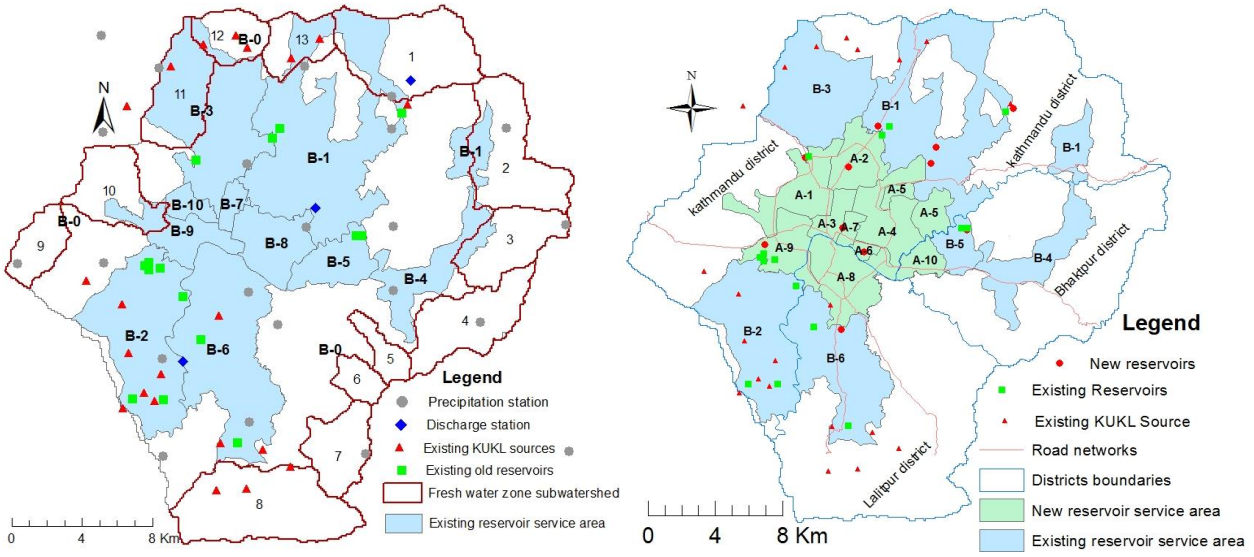
The SWAT modelling can be done using the methods described in annex-1. The water available in each sub-watershed were accessed from output of SWAT.mdb files for the respective sub-watershed using respective reach (.rch) output.

Top access the water available in groundwater component, groundwater modelling can be done as described in annex-2.

In this section we are just providing the basic idea. For more in detail, you can refer annex1 and 2 with corresponding referred manuals and paper.

Service area and data availability:

Water supply is basically amount of water supplied in each service area of KUKL through reservoir tank. In this study, we are just focusing on potable water supply by KUKL for household drinking purpose. KUKL has plan to supply water to each service are up-to 135 lpcd (liter per capita a day) after completion of the Melamchi Water Supply Project (MWSP). Recently KUKL is supplying water through 10 service area and has plan to change to 16 through additional 10 new reservoir tank as shown in figure below. How to prepare those map will be discuss later in very short.



Service Area (SA) No	Service area name served by existing reservoirs	Service Area (SA) No	Service area name served by existing reservoirs	Service Area (SA) No	Service area name served by new reservoirs	Service Area (SA) No	Service area name served by new reservoirs
B-1	Mahankalchour	B-6	Lalitpur	A-1	Balaju North	A-6	Minbhavan East
B-2	Kritipur	B-7	Kamaladi	A-2	Bansbari North*	A-7	Anamnagar East
B-3	Maharajgunj	B-8	Baneshowr	A-3	Panipokhari East	A-8	Khumaltar North
B-4	Bhaktapur	B-9	Tripureshowr	A-4	Mahankalchour North	A-9	Kritipur North
B-5	Madhyapur Thimi	B-10	Chhetrapati	A-5	Arubari North	A-10	Tigeni North

Figure 1: Study area showing a) Conservation zone for freshwater, KUKL's existing sources and service areas, and hydro meteorological stations; b) Planned water supply service areas after Melamchi Water Supply Project (MWSP). New reservoir service area will get water from MWSP and Existing reservoir will get water from existing network

Water supply data and respective service area were taken from KUKL, MWSP, KVWSMB reports and data. Those service area and respective supply may change with due course of time, hence how to prepare those and how to update those map need to know. We have following data in different form:

- Service area map (New and Old Service area in JPG form)
- Ward and VDC level population data
- No of reservoir tanks available, No of surface source and their link, their production and contribution in each reservoir tank.
- Water delivered/supplied from each reservoir tank in each area i.e. service area in dry and wet season
- Population projection data from Central Bureau of Statistics (CBS) and Population data for year 2011 at ward/VDC level.

Supply (S)

To calculate supply following steps need to be followed:

- Prepare the shape file of service area. We have **JPJ** file hence need to perform geo-referencing in GIS platform. If you have already shape file, it will be easy to prepare map.
- Prepare the database for each service area
    - In our case, we have water production and water supply data from respective service area through respective reservoir tank from KUKL report and MWSP reports.
    - It can be changed with due course of time hence need to update in different phases of MWSP.

Demand (D)

To calculate Demand following steps need to be followed:

- Using the prepared shape file, calculate (estimate) the population in each service area. We have VDC and ward level information on population, which need to be summed up and convert it into service area based on the area. If some ward lies in two or more service area, we can use reciprocal method based on area lies.
- In case of Kathmandu Valley, we have 2011 population data from CBS. We can use it as base data but we need to convert it into 2017 or 2018 as current year. Hence we need projection rate for each ward and VDC.
- In Kathmandu, ward or VDC level projection data is not available. We have district wise projection rate from year 2011-2030 estimated by CBS. Those data gives un-realistic population projection hence need to make it more realistic.
- To make it realistic, we can use 2001 and 2011 CBS population data to estimate the ward/VDC level projection rate. Which will gives us old projection rate at ward/VDC level.
- The following formula can be used to estimate the new projection rate at ward/VDC level using the district wise projection rate and can be summed up for each service area.

The new growth rate at ward or VDC level (NGR) is estimated as

$$NGR_i = \frac{NGR_j}{OGR_j} OGR_i \qquad (1)$$

Where, NGR is new growth rate, OGR is old growth rate subscript *i* represents ward level for municipalities and VDCs and *j* is corresponding district (Kathmandu, Lalitpur, and Bhaktapur). OGR_i and OGR_j are calculated as the growth rate calculated from the population census data of year 2001 and 2011. NGR_j is obtained from projected growth rate for corresponding district.

- The following formulas can be used to estimate the population for different year using different projection rate.

  The ward and VDC level annual population beyond 2011 was projected based on exponential growth formula as follows as estimated by:

  $$P_t = P_0 * e^{rt} \qquad (2)$$

  Where, P_t is Population at time t, P_0 is Population at time t_0, r is New growth rate (NGR) calculated from Eq. (1) it can, t is Time in year (number of periods)

- Using equation 1 and 2, population for different year at each service area can be estimated.
- If we know the population in each service area for different year, the water demand (D) can be calculate using:

  Demand (D) = Population in respective service area *135 LPCD

- Knowing the Demand and Supply, Household water security index for respective service area for different year can be calculate as:

  WSI= Supply (S)/Demand (D)

- After calculating all those data, we can create the attribute table in shape files with respective service area and can be mapped using GIS.

WaSH-Mia/SATREPS: Manual No.2

Field Survey and Water Sample Transport for Chemical and Isotope Analysis

Standard operating procedure for field survey and prepare the sample transport

Analysis target and relevance

Target: *Nitrate, Ammonia, Iron, Nitrogen isotope in Nitrate and Nitrogen isotope in Ammonia.*

The National Drinking Water Quality Standards, 2062 issued by the Ministry of Physical Planning and Works clearly states that drinking water should be free from *some excess chemical constituent*.

Category	Parameter	Unit	Maximum concentration limit
Chemical	Nitrate-nitrogen	mg/L	11.3
	Ammonia-nitrogen	mg/L	1.2
	Iron	mg/L	0.3
Isotopes	Nitrogen in nitrate	‰	No limit
	Nitrogen in Ammonia	‰	No limit

Various forms of nitrogen exist in the environment. Nitrate-nitrogen (NO_3-N) is hazardous to health causing blue-baby syndrome and gastrointestinal cancer. Ammonia-nitrogen (NH_4-N) is of pungent odor and less hazardous however, the oxidation of this increases NO_3-N concentration in the drinking water. Iron (Fe) is not directly hazardous but is toxic to human body at high dosages.

Standard operating procedure for field survey and prepare the sample transport

Sample site selection

Selection procedure

Simple random sampling carried out for groundwater analysis.

Possible situations covered during sampling;

- Land use (agricultural and buildup area),
- population density (very high > 10000/sq.km, high 5000-10000/sq.km, medium 1000-5000/sq.km and low <1000/sq.km)
- pre-historic town or newly build town
- newly build or old well

Wells selected after the questionnaire survey of its availability and use.

Groundwater source selection

Depending upon the availability and popularity

1. Shallow dug well (< 50m)
2. Shallow tube well (popular in the area with less open space)
3. Stone spout (traditional belief)
4. Springs
5. Rivers
6. Deep tube wells (> 50 m)

Source prioritization

1. Community wells
2. Private house using for drinking

Standard operating procedure for field survey and prepare the sample transport

Materials required

For sampling:

1. Cooling bag
2. Sterile 100 ml bottle and 100ml for duplicate sample
3. Bucket and rope
4. Ice packs
5. Gloves
6. Paper towel
7. Markers
8. Scissor
9. Water proof labelling tape

On site analysis:

1. GPS
2. Multi-probe (pH, EC, DO, Temperature)
3. Water logger

Standard operating procedure for field survey and prepare the sample transport

Sample collection:

Water samples are in a chemically dynamic state and the moment they are removed from the sample site, chemical, biological and physical processes can change their composition.

The general rule of sampling is to take extreme care to avoid contaminating the sample container and the water sample.

1. Autoclave the plastic bottle as required to sterilize.

2. Label the bottle and place them along with ice packs in a cooling bag.

3. Prepare gloves, ethanol, paper towel, bucket and pack them accordingly.

4. Transport the sample to the laboratory in a cooling bag filled with ice packs (Temperature: 2-8°C) as soon as possible.

Standard operating procedure for field survey and prepare the sample transport

Sampling technique

The sampling bottles are to be rinsed two to three times with the sample.

During the sampling, utmost care should be taken for the presence of air bubbles. The bottles should be filled completely with the samples with little air space. This is done by tightening the cap filled with the samples after sampling. (Figure 1)

1. If the sampling is from a tap, make sure to remove the stagnant water in a pipe by running the tap for some minutes.

2. If the sampling is from a well, make sure to plunge the bucket deep down near to the base to obtain original samples than surface contaminated water.

3. If the sampling is from tube wells (shallow/deep), make sure to pump it for certain time to flush the stagnant water stored inside the pipe. The flushing time depends on the sampling source.

4. If the sampling is from river, make sure to plunge the sampling bottle inverted up to certain depth and gently straighten inside the water releasing the surface contamination. Sampling should be done from the central run than the sideways due to the land surface interaction.

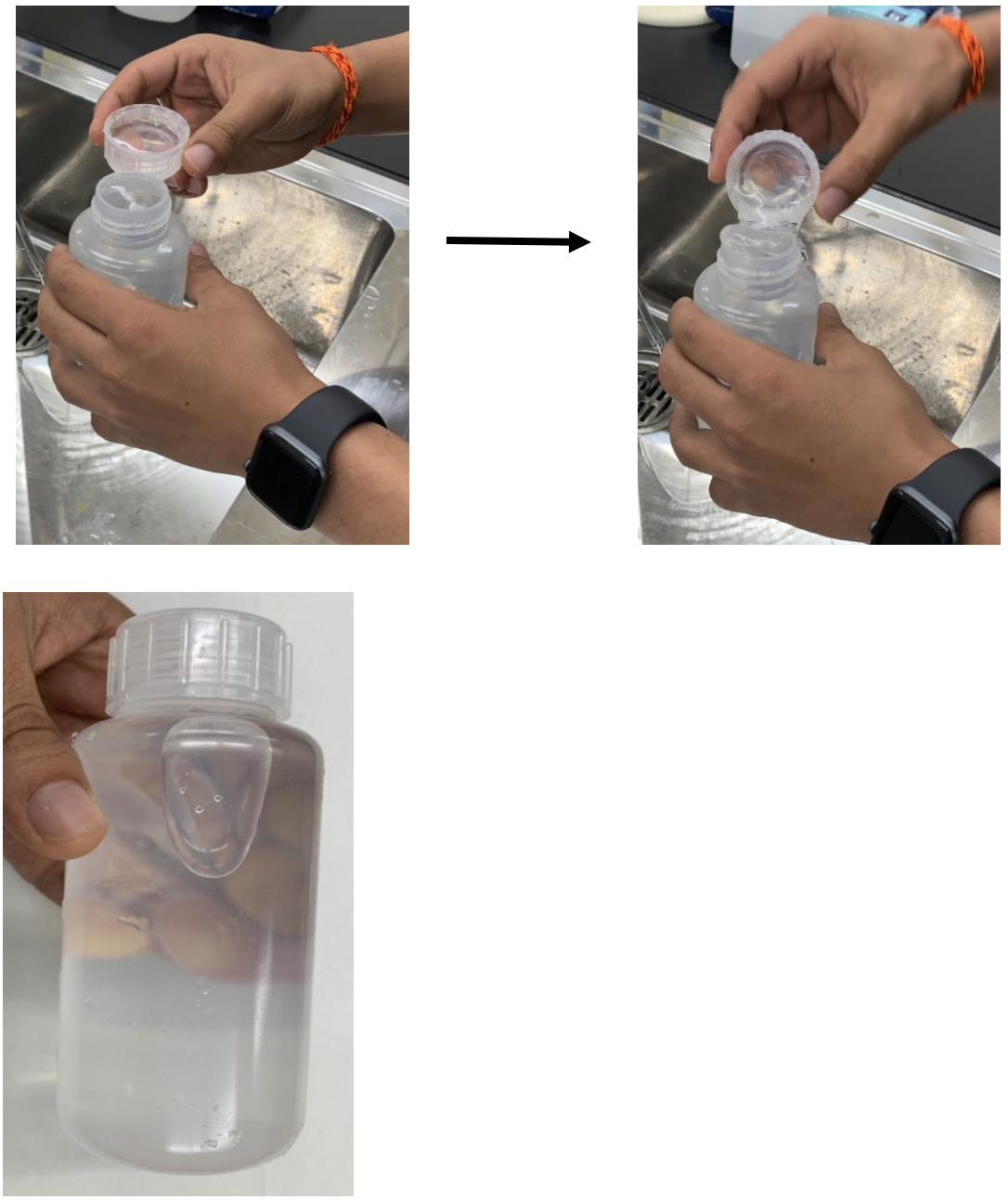


Figure 1. Reducing the air space during sampling.

Standard operating procedure for field survey and prepare the sample transport

Sample gathering:

1. Once the sample has been received in the laboratory or a gathering place, utmost care should be taken regarding the sampling IDs. Cross check for the samples.

2. It is preferable to give site specific IDs for e.g. A1, A2, …., B1, B2, …… along with date, time and location information during the sampling. As soon as the sample reaches laboratory or the final collection place, the site specific IDs are to be changed to standard IDs. For eg. A1 collected from shallow dug well of Baneshwor it is noted as KTM1, A2 collected from Anamnagar is noted as KTM2 and so on.

3. If the samples in the laboratory need some days for analysis or need to further transport, the samples are to be preserved in deep freezer with the temperature (-4^{O}C). Before storing into the freezer, some air space is to be made in the sampling bottle. This prevents the sampling bottle to rupture due to the increment in the sample volume during freezing.

4. Samples are to be packed in the zip lock plastic bags with the clear indication of the sample number on the bags for sample management.

WaSH-Mia/SATREPS: Manual No.3

Analytical Methods for Microbiological Evaluation of Water Samples

Standard operating procedure for fecal indicator bacteria analysis

Analysis target and relevance

Target: *Escherichia coli* and total coliforms

The National Drinking Water Quality Standards, 2062 issued by the Ministry of Physical Planning and Works clearly states that drinking water should be free from *E. coli* and total coliforms.

Category	Parameter	Unit	Maximum concentration limit
Microbiological	*E. coli*	MPN/100 ml	0
	Total coliforms	MPN/100 ml	0 (95% of samples)

MPN - Most Probable Number

Escherichia coli are the predominant member of the facultative anaerobic microorganisms of the human colonic normal flora. The bacterium's only natural habitat is the large intestine of warm-blooded animals and since *E. coli*, with some exceptions, generally does not survive well outside of the intestinal tract, its presence in environmental samples, food, or water usually indicates recent fecal contamination.

Materials required

For sampling:

1. Cooling bag
2. 70% ethanol
3. Sterile 100 ml bottle
4. Bucket and rope
5. Few Ice packs
6. Gloves
7. Paper towel
8. Markers
9. Sodium thiosulphate solution (5000 ppm)

For laboratory analysis:

1. Laboratory coat
2. UV lamp
3. Colilert reagent
4. Quanti- tray
5. Quanti-tray sealer
6. Incubator
7. Autoclave
8. Glass bottle
9. 25 ml pipette
10. 10 ml pipette
11. Pipette
12. Distilled water plant
13. Sterilized pure water (MilliQ)
14. Micropipette
15. 1000 µl tips

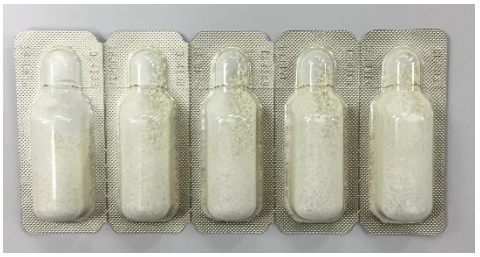


Fig. 1 Colilert reagent

Preparation of 70% ethanol

Add 30% of Pure Water to 70% of 100% Ethanol to make a mixture of 70% Ethanol. For example- While making a 500 ml solution of 70% ethanol, add 350 ml of 100% ethanol to150 ml of Pure water.

Autoclaving

Autoclaving is done at a temperature of 121°C for 15 minutes at a pressure of 15lbs.

Preparation of 5000 ppm sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$)

Take 1.56gm of 100% Sodium Thiosulfate 5-Hydrate and dissolve it in 200 ml of Pure Water (MilliQ). Then autoclave the glass bottle containing the mixture prior to use.

Sample collection:

The general rule of sampling is to take extreme care to avoid contaminating the sample container and the water sample.

1. Autoclave the plastic bottle as required to sterilize.

2. Label the bottle and place them along with Ice packs in a cooling bag.

3. Prepare gloves, 70% ethanol, paper towel, bucket and pack them accordingly.

4. Fill the bottle with the sample and add sodium thiosulphate solution to the sample collected. Sodium thiosulphate stops disinfection from chlorine and has no action on the sample itself.

5. Transport the sample to the laboratory in a cooling bag filled with Ice packs maintaining cold chain (Temperature: 2-8°C) as quickly as possible.

6. If the sampling is from a tap, make sure to disinfect the tap and let the tap run for a minute first. This removes stagnant water. Disinfection can be done with 70% ethanol or sodium hypochlorite solution.

7. If the sampling is from a well or river or lake, make sure to plunge the bottle with neck downwards to prevent any surface film from entering the bottle.

At the laboratory:

1. Once the sample has been received in the laboratory, place 103 ml of sample water in a sterilized glass bottle using a dispenser with 25 ml pipette.

2. Open a pack of Colilert reagent and add all the contents into the transparent glass bottle containing the sample.

3. Shake the bottle until the reagent dissolves completely and pour the sample into a Quanti- Tray 2000. Make sure no bubbles appear by gently tapping it with your fingers.

4. Seal the Quanti- Tray using the Quanti- Tray sealer and incubate at 35°C ± 0.5°C for 24 hours. Check the results after incubation.

Figure 2. Sealing of Quanti- tray once the sealer has attained the temperature of 180°C.

Results Interpretation:

1. **No discoloration** in wells= **Absence of *E. coli* and total coliforms**
2. **Yellow discoloration** only= **Presence of total coliforms only**

   If there is yellow discoloration, place the tray under a UV lamp in a dark room to check for fluorescent wells.

   Figure 3. Yellow discoloration showing presence of total coliform.
3. **Yellow discoloration and fluorescent wells= Presence of *E. coli***

Figure 4. Fluorescent wells showing presence of *E. coli*

Quantifying the *E. coli* and total coliforms in the water sample using Most Probable Number (MPN) method.

1) First download the MPN generator software from the link given below.

   https://www.idexx.co.uk/en-gb/water/resources/mpn-generator/

2) There are 49 large and 48 small wells in the Quanti - Tray 2000. Count the number of boxes with the yellow discoloration.

3) Select Colilert option in Method option and coliform as analyte. Then enter the number (e.g.- 24 in positive large wells and 25 in positive small wells) and click calculate to quantify the number of total coliforms present in 100 ml of water sample.

4) Likewise, change the analyte to *E. coli* and enter the number of large and small wells with fluorescence to get the MPN for *E. coli*.

Serial dilution

When all the wells are colored we cannot get an exact number of total coliforms or *E. coli*. The software only shows a probable number i.e >2419.6 which could mean 2500 or even 25000.

So, to get a definite number of coliforms or *E. coli* present in the water sample we need to perform serial dilution.

Dilution is done by:

1) First prepare 103ml of water sample in a sterile glass water and prepare another glass bottle with 103 ml of sterile pure water (MilliQ) in it.

2) Pipette 1ml (1000 µL) of the water sample into the glass bottle containing 103 ml of sterile pure water. Now, this is a diluted sample of 10^2.

3) Add the colilert reagent into the diluted the sample. Incubate for 24 hours and count the number of boxes with the discoloration and calculate the number of bacteria present as mentioned above.

4) Your no. of bacteria is the given Most Probable Number x 10^ 2.

5) Even after the 10^ 2 dilutions, if all the wells are still colored yellow then you further dilute if by 10^4, 10^6 and so on.
6) To dilute it by 10^4 first prepare 10^2 diluted sample and again prepare another glass bottle containing 103 ml of sterile pure water (MilliQ) and add 1ml (1000 µL) of diluted sample from the glass bottle containing 10^2 dilution. Then, add the colilert reagent and incubate before counting the wells for total coliforms and *E. coli*.

7) Use the software mentioned above to get the exact number of bacteria and its MPN would be the given number x 10^ 4.

8) If it still has yellow discoloration after 10^ 4 dilutions, then you continue doing similarly with 10^6 and so on.

WaSH-Mia/SATREPS: Manual No.4-1

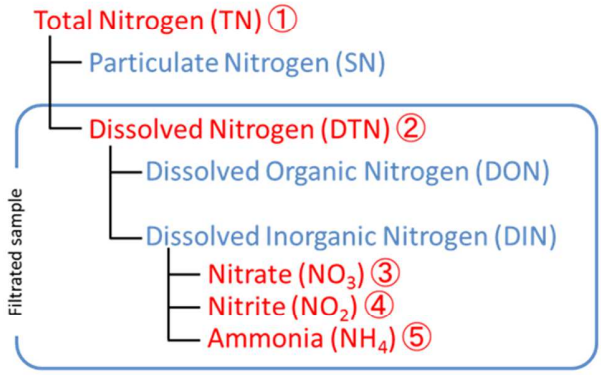
Analytical Methods
for Water sample Target :
N, P, Metal, COD and $HCO3^-$

Contents

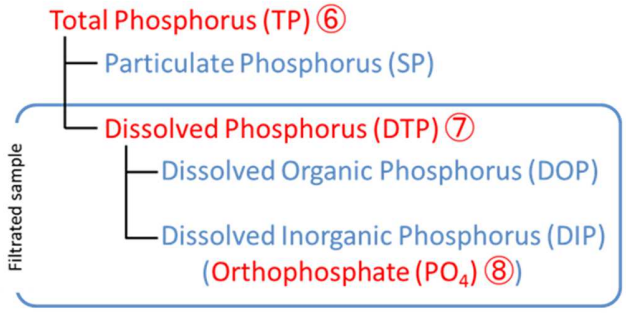
List of Lecture on analysis

①—⑬ : analysis targets

1. Nitrogen



2. Phosphorus



3. Metal

- Total Iron (T-Fe) ⑨
- Acid soluble Iron (AS-Fe) ⑩
  include: Fe^{2+}, Fe^{3+}, Iron complex compound, $Fe(OH)_3$, Clay particles…
  These can change easily a form by an environmental change.
- Ferrous ion (Fe^{2+}) ⑪

- Dissolved Manganese (D-Mn)⑫

4. Chemical Oxygen Demand (COD_{Cr}) ⑬

5. Bicarbonate (HCO_3^-) ⑭

▪ Method for Cleaning Equipment

・ before use in experiment (for volumetric flask)

Rinse the volumetric flask in pure water 3 times

・ cleaning solution

Put cleaning powder (50g), and pour water (10L) into the bucket.

* the ultrasonic cleaning machine: 30g cleaning powder/10L

This solution can be use several times.

・ after use in experiment

1. Throw away the inside (if there are stains, rub equipments with a sponge).
2. Wash equipments in (tap) water several times.
3. Fill equipment with the cleaning solution of the bucket, sink equipments, and keep overnight.
   * if you use the ultrasonic cleaning machine, set a timer at 20 minutes, and start to wash.
4. Take out equipments.
5. Wash equipments with tap water until a bubble disappears.
6. Rinse equipments in pure water 3 times.
7. Upend equipments to the basket, and put it in a drying cabinet.
8. After dry, cap the bottle, or put the equipments into a bag, then keep in shelf.

▪ Sampling and storage method of sample

・ Target : nonmetal

《sampling》 Bring back samples to the laboratory. If it need to filter, filtration do in laboratory.

《storage》 Stored in refrigerator (analysis period is less than 1week), Keep in freezer (more than 1week)

・ Target : metal

《sampling》 Fill bottle directly from sampling source and stopper (if it need to filter, filtration do onsite).
Sample with 2ml-HCl/100ml-sample at time of collection.

《storage》 Stored at room

▪ Preparation of Standard Solution (Weight method)

Equipment :

- pipette (10mL, 5mL, 1mL)
- Screw Bottle (30mL)
- Pure water

Apparatus :

- chemical balance

Procedure :

1. Power on chemical balance. Wait until end of calibration.
2. Put a Screw bottle on the balance, close the cover, wait, and push a "tare" button.
3. Weigh out the required amount of "Stock sol." or "Std. Sol. A (5mg/L)" (refer to table 1-6), and close a cover.
4. Wait, then record actual weight.
5. Add pure water until total weight to 25 gm.
6. Wait, then record actual gross weight.
7. Cap a Screw bottle, and mix it well.
8. Calculation of concentration (mg/L)

$$\text{Actual concentration} = \text{concentration of Std. Sol. (or } \mathbf{A}) \times \frac{\text{actual weight(g)}}{\text{actual gross weight(g)}}$$

①-③TN/DTN/NO_3-N Standard solutions: (0.05 ~ 5 mg-N/L)

Chemical : Nitrate Nitrogen Standard Solution (1000*mg- NO_3-N/l)

*when calculate, use the written value of the standard solution bottle.

Table.1 TN/DTN/NO_3-N Standard solutions

Required concentration : mg-N/L	5 (Std. Sol. A)	4	3	2	1	0.5	0.2	0.1	0.05
weight of Std. sol. (1g/L) : g	0.125	0.10	0.075	0.050	—	—	—	—	—
weight of **Std. sol. A** (5mg/L) : g	—	—	—	—	5.0	2.5	1.0	0.5	0.25
actual weight : g									
actual gross weight : g									
Actual concentration : mg-N/L									

③-2 NO_3-N Standard solutions of second derivative method: (5 ~ 25 mg-N/L)

Chemical : Nitrate Nitrogen Standard Solution (1000*mg- NO_3-N/l)

*when calculate, use the written value of the standard solution bottle.

Table.2 NO_3-N Standard solutions of second derivative

Required concentration : mg-N/L	25	20	15	10	5
weight of Std. sol. (1g/L) : g	0.625	0.50	0.375	0.25	0.125
actual weight : g					
actual gross weight : g					
Actual concentration : mg-N/L					

④ NO_2-N Standard solutions: (0.02 ~ 0.5 mg-N/L)

Chemical : Nitrite Nitrogen Standard Solution (1000*mg- NO_3-N/l)

*when calculate, use the written value of the standard solution bottle.

Table.3 NO_2-N Standard solutions

Required concentration : mg-N/L	5 (**Std. Sol. A**)	0.5	0.2	0.1	0.05	0.02
weight of Std. sol. (1g/L) : g	0.125	—	—	—	—	—
weight of **Std. sol. A** (5mg/L) : g	—	2.5	1.0	0.5	0.25	0.1
actual weight : g						
actual gross weight : g						
Actual concentration : mg-N/L						

⑤ NH_4-N Standard solutions: (0.05 ~ 5 mg-N/L)

Chemical : Ammonium Nitrogen Standard Solution (1000*mg- NO_3-N/l)

*when calculate, use the written value of the standard solution bottle.

Table.4 NH_4-N Standard solutions

Required concentration : mg-N/L	5 (Std. Sol. A)	4	3	2	1	0.5	0.2	0.1	0.05
weight of Std. sol. (1g/L) : g	0.125	0.10	0.075	0.050	—	—	—	—	—
weight of **Std. sol. A** (5mg/L) : g	—	—	—	—	5.0	2.5	1.0	0.5	0.25
actual weight : g									
actual gross weight : g									
Actual concentration : mg-N/L									

⑥-⑧ TP/DTP/PO_4-P Standard solutions: (0.01 ~ 5 mg-P/L)

Chemical : Phosphorus Standard Solution (1000*mg- PO_4-P/l)

*when calculate, use the written value of the standard solution bottle.

Table.5 TP/DTP/PO_4-P Standard solutions

Required concentration : mg-P/L	5 (Std. Sol. A)	4	3	2	1	0.5	0.2	0.1	0.05
weight of Std. sol. (1g/L) : g	0.125	0.10	0.075	0.050	—	—	—	—	—
weight of **Std. sol. A** (5mg/L) : g	—	—	—	—	5.0	2.5	1.0	0.5	0.25
actual weight : g									
actual gross weight : g									
Actual concentration : mg-P/L									

⑨-⑪T-Fe / AS-Fe/ Fe^{2+} Standard solutions: (0.2 ~ 1 mg/L)

Chemical : Iron Standard Solution (1000*mg/l)

*when calculate, use the written value of the standard solution bottle.

**need to add conc. HCl at all bottles. Because iron absorb to bottle.

Table.6 Fe^{2+}/T-Fe Standard solutions

Required concentration : mg-Fe/L	5 (Std. Sol. A)	1	0.8	0.6	0.4	0.2
weight of Std. sol. (1g/L) : g	0.125	—	—	—	—	—
weight of **Std. sol. A** (5mg/L) : g	—	5.0	4.0	3.0	2.0	1.0
actual weight : g						
Add conc .HCl (ml)	0.3	0.3	0.3	0.3	0.3	0.3
actual gross weight : g						
Actual concentration : mg-Fe/L						

⑫ D-Mn Standard solutions: (0.1 ~ 4 mg/L)

Chemical : Manganese Standard Solution (1000*mg/l)

*when calculate, use the written value of the standard solution bottle.

Table.7 T-Mn Standard solutions

Required concentration : mg-Mn/L	5 (Std. Sol. A)	4	3	2	1	0.5	0.1
weight of Std. sol. (1g/L) : g	0.125	0.10	0.075	0.050	—	—	—
weight of **Std. sol. A** (5mg/L) : g	—	—	—	—	5.0	2.5	0.5
actual weight : g							
actual gross weight : g							
Actual concentration : mg-Mn/L							

① Total Nitrogen Analysis by Ultraviolet Spectrophotometric Screening Method

(ref. : Standard Methods for the Examination of Tap Water in Japan)

***volume is different**

Equipment:

- 200ml measuring cylinder
- transfer pipet
- pipette(10ml, 1ml)
- bottle
- 100 ml Beaker
- tubes with cap
- silica cuvette(1cm) : *cannot use glass cuvette, that block UV light.

Apparatus:

- Analytical balance
- Spectrophotometer

Required Chemicals:

1. Distilled water
2. Potassium persulfate (freshly prepared) : for analysis of Nitrogen
3. Sodium hydroxide : for analysis of Nitrogen
4. Conc. HCl : G.R.
5. Nitrate Nitrogen Standard Solution (1000mg- NO_3-N/l)

Preparation of reagents:

1. Sodium hydroxide/Potassium persulfate (Digestion Solution): (0.4ml/tube)
   *Total Nitrogen are converted to Nitrate.
   Dissolve 4gm NaOH to 100 ml distilled water, stir it with the help of magnetic stirrer. After dissolve, add 3 gm of Potassium persulfate. Then stir.
2. Hydrochloric acid solution, HCl, 1N : same of Nitrate (0.48ml/tube)
   To 110ml of distilled water, add 10 ml of Hydrochloric Acid
3. Preparation of Nitrate Standard solutions: (0.05 ~ 5 mg/l) same of Nitrate
   See Table.1

Procedure: see Fig. 1

a. Sample Preparation:
   i. triplicate all the samples
   ii. Take 2ml of samples.
   (Dilute the sample (if required) and take 2 ml of each)
   * had better check nitrate concentration by pack test.
   iii. Add 0.4 ml of Digestion Solution to each sample.
   iv. Autoclave all the samples for 30 minutes at 121°C.
   v. After cooling, add 0.48ml of the 1N HCl to the samples, and mix.
   vi. Wait until hydroxide precipitates.

b. Standard solutions preparation:
   duplicate blank and all the standard solutions
   Treat blank and std. solutions in same manner as samples.

c. Photometric measurement:
   Measure the absorbance at 220nm and 275nm.
   220nm : to obtain NO_3^- reading
   275nm : to determine interference due to dissolved organic matter

Calculation:

For samples, blank and std. solutions, subtract two times the absorbance reading at 275nm from the reading at 220nm to obtain absorbance due to NO_3^-:

$$2DS = Abs_{220} - 2*Abs_{275}$$

where:
2DS = absorbance due to NO_3^-
Abs_{220} = the absorbance reading at 220nm
Abs_{275} = the absorbance reading at 275nm.

Construct a standard curve by plotting absorbance due to NO_3^-(2DS) against NO_3^--N concentration of standard. Using corrected sample absorbances, obtain sample concentrations directly from standard curve.

② Dissolved Nitrogen Analysis by Ultraviolet Spectrophotometric Screening Method

(ref. : Standard Methods for the Examination of Tap Water in Japan)

***volume is different**

Equipment:

- 200ml measuring cylinder
- transfer pipet
- pipette(10ml, 1ml)
- bottle
- 100 ml Beaker
- tubes with cap
- silica cuvette(1cm) : *cannot use glass cuvette, that block UV light.
- syringe
- syringe filter (0.2µm) : i.e. cellulose acetate

Apparatus:

- Analytical balance
- Spectrophotometer

Required Chemicals:

1. Distilled water
2. 3 gm, Potassium persulfate (freshly prepared) : for analysis of Nitrogen
3. 4 gm, Sodium hydroxide : for analysis of Nitrogen
4. 10 ml, Conc. HCl : G.R.
5. Nitrate Nitrogen Standard Solution (1000mg- NO_3-N/l)

Preparation of reagents:

1. Sodium hydroxide/Potassium persulfate (Digestion Solution): (0.4ml/tube)
   *Dissolved Nitrogen are converted to Nitrate.
   Add 4gm NaOH to 100 ml distilled water, stir it with the help of magnetic stirrer. After dissolve, add 3 gm of Potassium persulfate. Then stir.
2. Hydrochloric acid solution, HCl, 1N : same of Nitrate (0.48ml/tube)
   To 110ml of distilled water, add 10 ml of Hydrochloric Acid
3. Preparation of Nitrate Standard solutions: (0.05 ~ 5 mg/l) same of Nitrate
   See Table.1

Procedure: see Fig. 1

a. Removal of suspended particles:
   Filter through a syringe filter (0.2μm)
b. Sample Preparation:
   i. duplicate all the samples
   ii. Take 2ml of samples.
   (Dilute the sample (if required) and take 2 ml of each)
   * had better check nitrate concentration by pack test.
   iii. Add 0.4 ml of Digestion Solution to each sample.
   iv. Autoclave all the samples for 30 minutes at 121°C.
   v. After cooling, add 0.48ml of the 1N HCl to the samples, and mix.
   vi. Wait until hydroxide precipitates.
c. Standard solutions preparation:
   duplicate blank and all the standard solutions
   Treat blank and std. solutions in same manner as samples.
d. Photometric measurement:
   Measure the absorbance at 220nm and 275nm.
   220nm : to obtain NO_3^- reading
   275nm : to determine interference due to dissolved organic matter

Calculation:

For samples, blank and std. solutions, subtract two times the absorbance reading at 275nm from the reading at 220nm to obtain absorbance due to NO_3^-:

$$2DS = Abs_{220} - 2*Abs_{275}$$

where:
2DS = absorbance due to NO_3^-
Abs_{220} = the absorbance reading at 220nm
Abs_{275} = the absorbance reading at 275nm.

Construct a standard curve by plotting absorbance due to NO_3^-(2DS) against NO_3^--N concentration of standard. Using corrected sample absorbances, obtain sample concentrations directly from standard curve.

TN, DTN

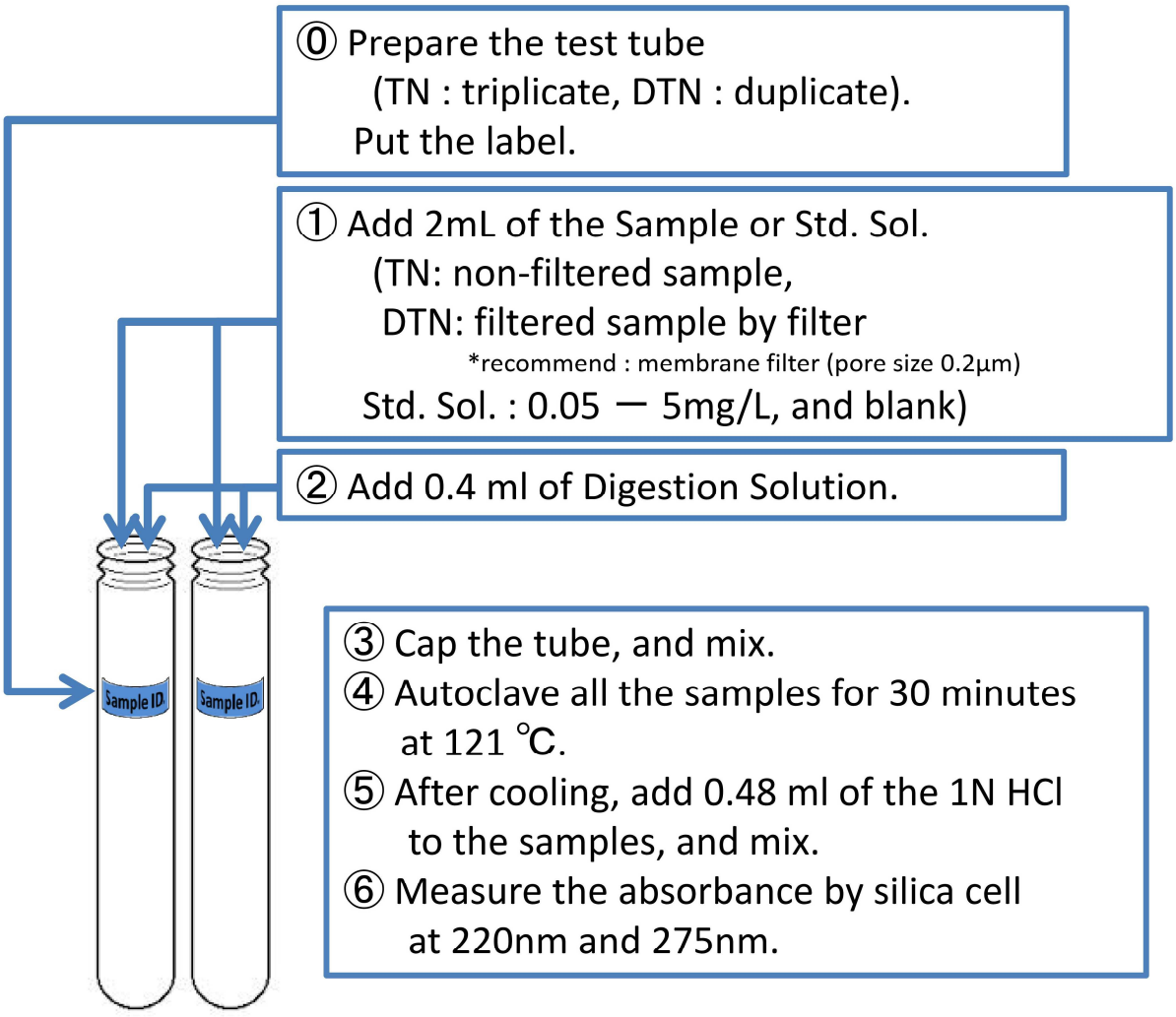


Fig. 1. Flow chart of the analytical procedure for TN/DTN.

③ Nitrate Analysis by Ultraviolet Spectrophotometric Screening Method

(only in the case of low organic matter contents)

(ref. : Standard methods 22nd edition 4500-NO_3^-B)

***volume is different**

Equipment:

- 200ml measuring cylinder
- transfer pipet
- pipette(10ml, 1ml)
- bottle
- tubes with cap
- silica cuvette(1cm) : *cannot use glass cuvette, that block UV light.
- syringe
- syringe filter (0.2μm) : i.e. cellulose acetate

Apparatus:

- Analytical balance
- Spectrophotometer

Interference:

Dissolved organic matter, surfactants, NO_2^-, and Cr^{6+} interfere. Various inorganic ions not normally found in natural water, such as chlorite and chlorate, may interfere. inorganic substances can be compensated for by independent analysis of their concentrations and preparation of individual correction curves.

Required Chemicals:

1. Freshly prepared nitrate free water
2. 10 ml, Conc. HCl : G.R.
3. Nitrate Nitrogen Standard Solution (1000mg- NO_3-N/l)

Preparation of color reagent:

1. Hydrochloric acid solution, HCl, 1N : (0.1ml/tube)
   To 110ml of distilled water, add 10 ml of Hydrochloric Acid
2. Nitrate Standard solutions: (0.05 ~ 5 mg/l)
   See Table.1

Procedure: see Fig. 2

a. Removal of suspended particles:
   Filter through a syringe filter (0.2µm)

b. Sample Preparation:
   duplicate all the samples
   Dilute the sample (if required)
   * had better check nitrate concentration by pack test.
   To 5 ml of sample, add 0.1 ml of Hydrochloric acid solution, mix thoroughly.

c. Standard solutions preparation:
   duplicate blank and all the standard solutions
   To 5 ml of blank and std. solutions, add 0.1 ml of Hydrochloric acid solution, mix thoroughly.

d. Photometric measurement:
   Measure the absorbance at 220nm and 275nm.
   220nm : to obtain NO_3^- reading
   275nm : to determine interference due to dissolved organic matter

Calculation:

For samples, blank and std. solutions, subtract two times the absorbance reading at 275nm from the reading at 220nm to obtain absorbance due to NO_3^-:

$$2DS = Abs_{220} - 2*Abs_{275}$$

where:
2DS = absorbance due to NO_3^-
Abs_{220} = the absorbance reading at 220nm
Abs_{275} = the absorbance reading at 275nm.

Construct a standard curve by plotting absorbance due to NO_3^-(2DS) against NO_3^--N concentration of standard. Using corrected sample absorbances, obtain sample concentrations directly from standard curve.

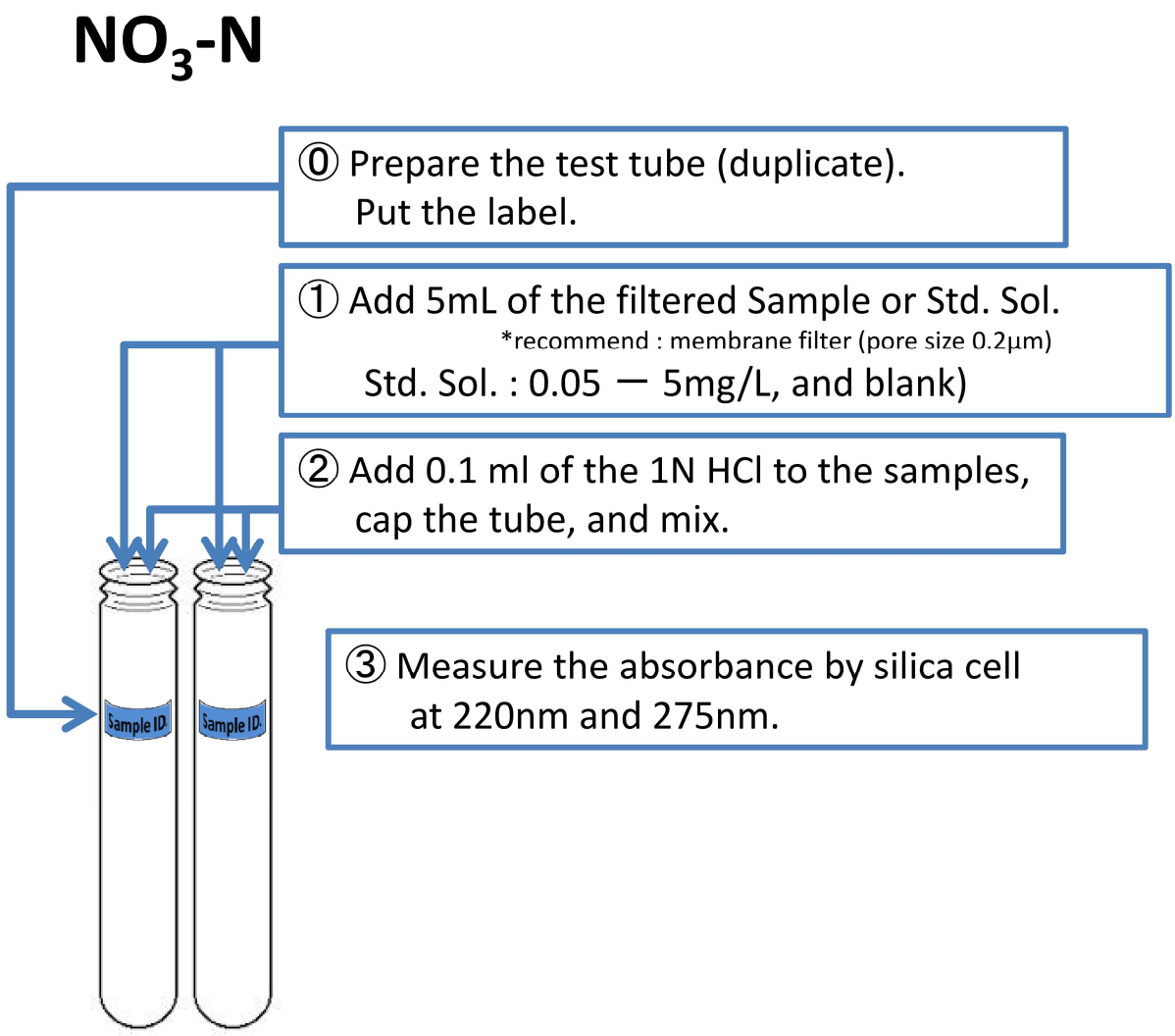


Fig. 2. Flow chart of the analytical procedure for NO_3.

③-2 Nitrate Analysis by Second-Derivative Ultraviolet Spectrophotometric Method

(ref. : Standard methods 22nd edition 4500-NO_3^-C)

***volume is different**

Equipment:

- transfer pipet
- pipette(10ml, 1ml)
- bottle
- tubes with cap
- silica cuvette(1cm) : *cannot use glass cuvette, that block UV light.
- syringe
- syringe filter (0.2μm) : i.e. cellulose acetate

Apparatus:

- Spectrophotometer

Interference:

The nitrate UV spectrum is similar to that of nitrate. However, nitrite concentrations usually are much lower than nitrate concentrations. Bicarbonate absorbs weakly at wavelengths below 210 nm, but does not affect the second-derivative signal of nitrate. Bromide interferes at seawater concentrations (68 mg Br-/L, salinity 35%) so this method cannot be used to determine nitrate in seawater. Neither Fe nor Cu interferes at 2mg/L but both metals seriously interfere at 20mg/L. The method has been tested only for potable water. Its suitability for nitrate determination in seawater has not been tested.

Required Chemicals:

4. Freshly prepared nitrate free water
5. 10 ml, Conc. HCl : G.R.
6. Nitrate Nitrogen Standard Solution (1000mg- NO_3-N/l)

Preparation of color reagent:

1. Hydrochloric acid solution, HCl, 1N : (0.1ml/tube)
   To 110ml of distilled water, add 10 ml of Hydrochloric Acid
2. Nitrate Standard solutions: (5 ~ 25 mg/l)
   See Table.2

Procedure: see Fig. 3

a. Removal of suspended particles:
   Filter through a syringe filter (0.2μm)

b. Check the absorbance of sample:
   Pipet 5.0 ml sample into the tube, add 0.1ml of 1N HCl, and shake
   Scan from 250 nm to 200 nm, and check the maximum absorbance point in the range 230 to 220 nm
   * if absorbance is beyond 0.5 Abs, dilute sample with nitrate-free water

c. Sample preparation:
   Put in 9 ml the sample (or diluted sample) into the tubes, 0.2 ml 1N HCl, 1 ml standard solution to tubes
   * standard solution : blank, 1, 2, 3, 4, 5 mg-N/ml
   each concentration prepare duplicate tubes

d. Photometric measurement:
   Measure the absorbance every 1.0nm in the range 231 to 219 nm, and record each value

Calculation:

(1) For each tube, compute second-derivative spectrum by above absorbance of each wavelength, and find maximum values (see Fig.4)

(2) Use the simplified least-squares procedure to simultaneously smooth and differentiate spectra
Perform least-squares linear regression using the second derivatives of the blank and standard spectra
Sample concentration is (Fig.4):

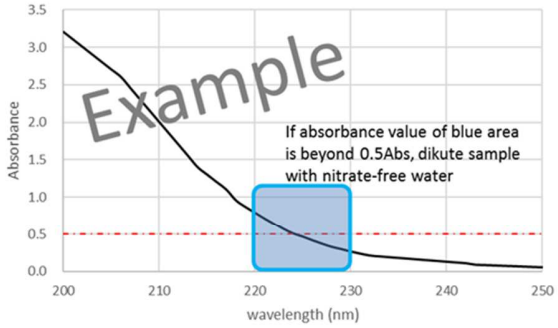
$$C(mg-N/l) = \frac{Int}{Slp} \times \frac{1}{V}$$

where:
Slp : slope of regression line,
Int : intercept of regression line, and
V : sample volume (ml).

NO_3-N (Second-derivative method)

1. Check the absorbance of sample

Pipet 5mL filtered sample and 0.1mL of 1N HCl
Scan from 250 to 200nm



2. Measurement

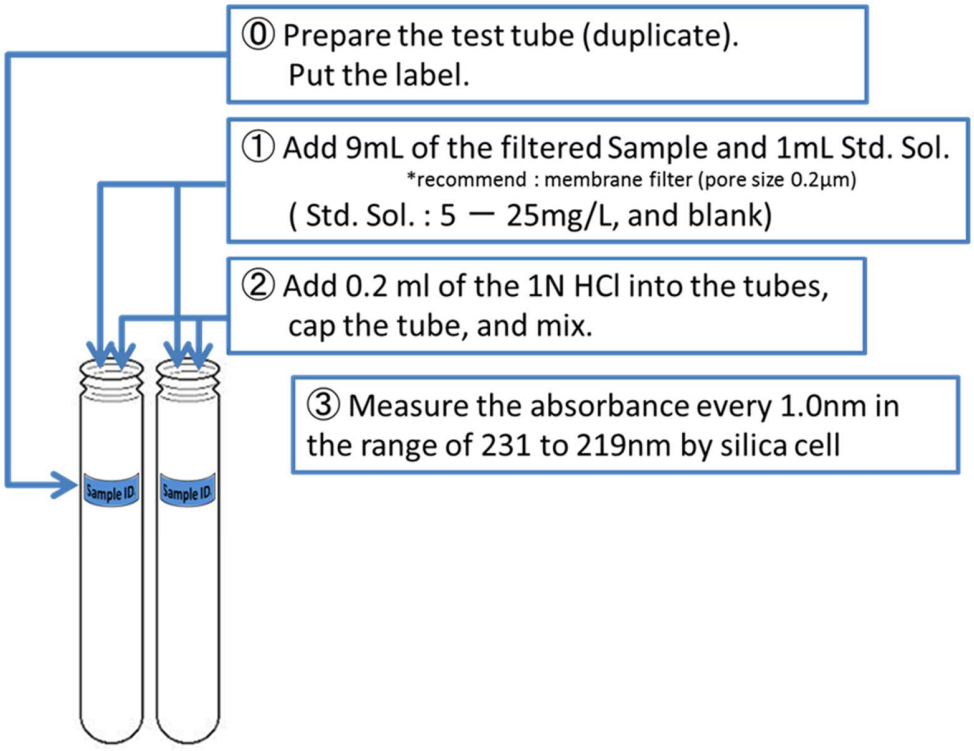


Fig. 3. Flow chart of NO_3 second derivative method

NO_3-N (Second-derivative method)

3. Calculation

(1) Second-derivative

For each tube, compute second-derivative spectrum by above absorbance of each wavelength, and find maximum values

Absorbance	add NO3-N (μg)					
WL(nm)	2.5	2	1.5	1	0.5	0
219	0.8680					0.1204
220	0.7902					0.1176
221	0.7117					0.1155
⋮	⋮					⋮
229	0.2981					0.0995
230	0.2650					0.0972
231	0.2371					0.0956

← actual concentration

Absorbance values

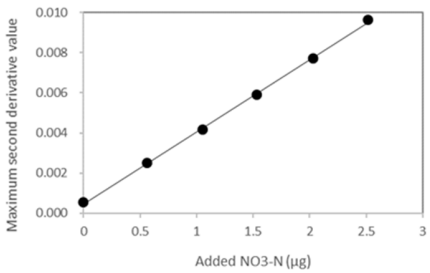
Ex) second-derivative at X nm

$$2DV_X = \frac{\left(\frac{Abs_{X+1}-Abs_X}{WL_{X+1}-WL_X}\right)-\left(\frac{Abs_X-Abs_{X-1}}{WL_X-WL_{X-1}}\right)}{(WL_{X+1}-WL_{X-1})} = \frac{Abs_{X+1}-2*Abs_X+Abs_{X-1}}{(WL_{X+1}-WL_{X-1})}$$

2nd derivative	add NO3-N (μg)					
WL(nm)	2.5	2	1.5	1	0.5	0
220	−0.0004					0.0004
⋮	⋮					⋮
230	0.0026					0.0004

Where:
DV : second-derivative value
Abs_{X+1},Abs_X,Abs_{X-1} : absorbance at X+1, X, X-1 nm
WL_{X+1},WL_X,WL_{X-1} : Wavelength

(2) Make a least-squares linear regression



$$S = Int + A \times Slp$$

Where:
S : maximum second-derivative value
A : amount of added NO3-N (μg)
Int : intercept of regression line
Slp : slope of regression line

(3) Calculate the concentration

$$C = \frac{Int}{Slp} \times \frac{1}{V}$$

Where:
C : concentration (mg/L)
Int, Slp : intercept and slope of above line
V : sample volume (ml)

Fig. 4. Flow chart(2) of NO_3 second derivative method

④ Nitrite Analysis by Colorimetric Method

(ref. : Standard methods 22nd edition 4500-NO_2^-B)

***volume is different**

Equipment:

- volumetric flask (100ml, 50ml)
- transfer pipet
- 100ml measuring cylinder
- pipette(10ml, 1ml)
- bottle
- 100 ml Beaker
- tubes with cap
- glass cuvette(1cm)
- syringe
- syringe filter (0.2µm) : i.e. cellulose acetate

Apparatus:

- Analytical balance
- Spectrophotometer

Required chemicals:

1. Freshly prepared nitrite free water
2. 10 ml, Phosphoric Acid (85%) : E.P.
3. 1 gm, Sulfanilamide : G.R.
4. 0.1 gm, N-(1-Naphthyl) ethylenediamine dihydrochloride : G.R.
5. Nitrite Nitrogen Standard Solution (1000mg- NO_2-N/l)

Reagents

1. color reagent : (0.2mL/tube)

   To approximately 80ml of distilled water, add 10 ml of Phosphoric Acid (85%), 1 gm Sulfanilamide and 0.1 gm N-(1-Naphthyl) ethylenediamine dihydrochloride and make the total volume of 100 ml.

   ** Store the color reagent in dark glass bottle and keep in refrigerator.

   *Note: This color reagent can be used for a month.

2. Nitrite Standard solutions: (0.02~0.5 mg/l)

   See Table.3

Procedure: see Fig. 5

a. Removal of suspended particles:
   Filter through a syringe filter (0.2µm)
b. Sample Preparation:
   duplicate all the samples
   Dilute the sample (if required)
   * had better check nitrite concentration by pack test.
   To 5 ml of sample, add 0.2 ml of color reagent, mix thoroughly, and leave for 20 minutes in room temperature.
c. blank and Standard solutions preparation:
   duplicate blank and all standard solutions
   To 5 ml of blank and std. solutions, add 0.2 ml of color reagent, mix thoroughly, and leave for 20 minutes in room temperature.
d. Photometric measurement:
   Measure the absorbance at 543nm.

Calculation:

Prepare a std. curve by plotting absorbance of std. against NO_2^--N concentration. Compute sample concentration from the curve.

**The std. solution has certain absorbance and develops the color after adding color reagent. But sometimes, the samples have higher absorbance than the std. solution but results no color development even after adding color reagent. In such a situation, we have to measure the absorbance of the sample without color reagent and reduce the absorbance value from the sample with color reagent. We use this deducted absorbance as a reading.
Note: The disappearance of the color might be from the organic material present in the sample.

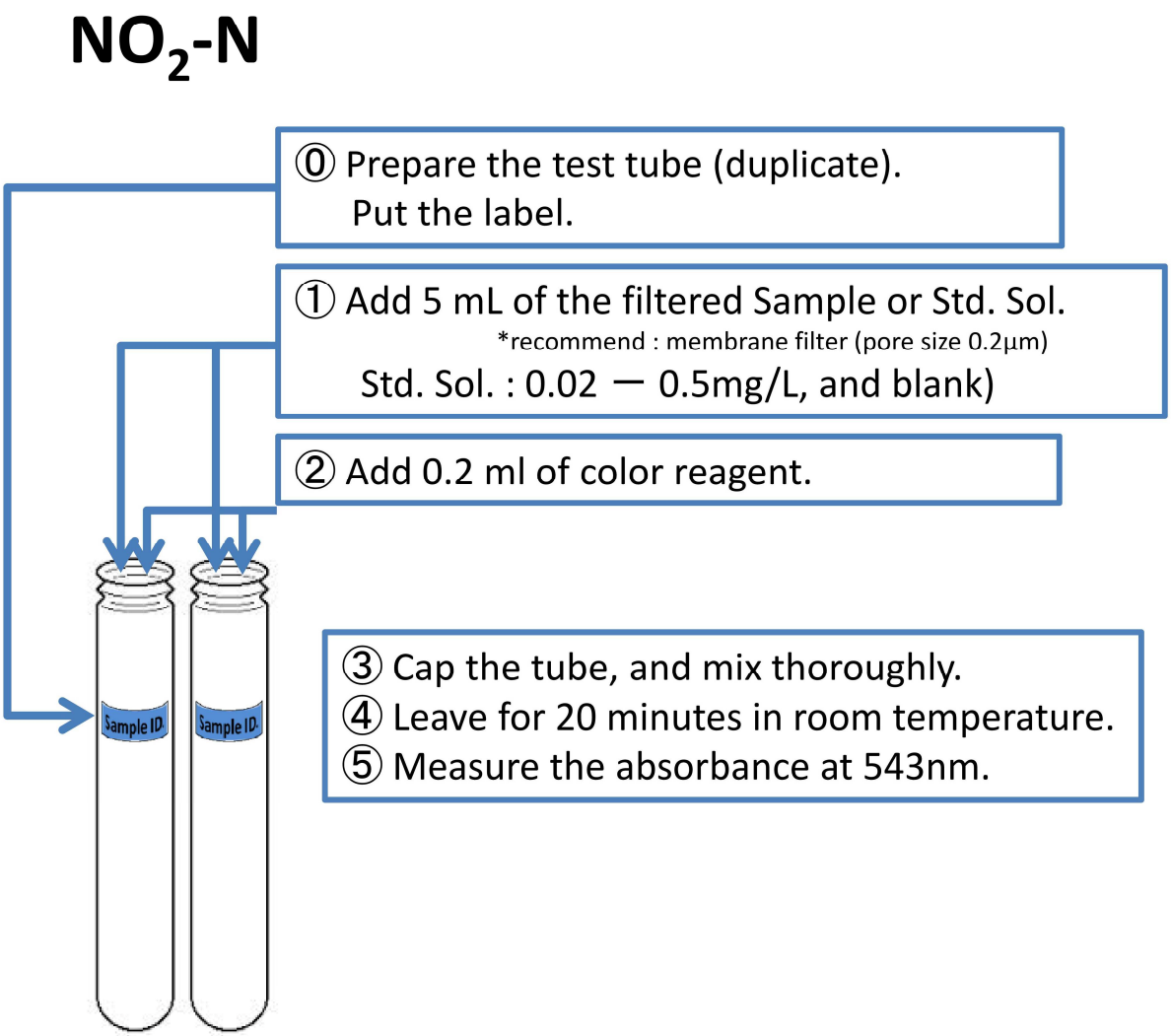


Fig. 5. Flow chart of the analytical procedure for NO_2.

⑤ Ammonia Analysis by Phenate Method

(ref. : Standard Methods for the Examination of Tap Water in Japan)

***volume is different**

Equipment:

- volumetric flask (500ml, 100ml, 50ml)
- transfer pipet
- pipette(10ml, 1ml)
- bottle
- 100 ml Beaker
- tubes with cap
- glass cuvette(1cm)
- syringe
- syringe filter (0.2µm) : i.e. cellulose acetate

Apparatus:

- Analytical balance
- Spectrophotometer

Interference:

If hydrogen sulfide is present, remove by acidifying samples to pH 3 with dilute HCl and aerating vigorously until sulfide odor no longer can be detected.

Required Chemicals:

1. Distilled water
2. 5 gm Phenol : G.R.
3. 0.025 gm, Sodium Nitroprusside : G.R.
4. 10 ml, Sodium Hypochlorite (5%) : Chemically Pure
   *If fresh Sodium Hypochlorite then, it is 12%
5. 15 gm, Sodium Hydroxide : for analysis of Nitrogen
6. Ammonium Nitrogen Standard Solution (1000mg-NH_4-N/l)

Reagent:

1. Phenol/Sodium nitroprusside solution (Solution A): (1ml/tube)

   To approximately 400 ml water, add 5 gm of Phenol, 0.025 gm of Sodium Nitroprusside and dilute to 500 ml.

   **Prepare this solution one day before use/ analysis, to make phenol dissolve

   **Store this solution in dark bottle. This Solution can be used for a month.

2. Sodium hypochlorite solution (effective chlorine concentration: 0.1w/v%) (Solution B):
   (1ml/tube)
   Dissolve commercial sodium hypochlorite solution (50/C mL, C : effective chlorine concentration) and 7.5 gm of Sodium Hydroxide in 100ml water and dilute to 500 ml.
   ** Store this solution in dark bottle, and refrigerate.
   * This solution can be used in a range of the effective chlorine concentration (0.05-0.1w/v%).
3. Ammonium Nitrogen Standard Solution: (0.05 ~ 5 mg/l)
   See Table.4

Procedure: see Fig. 6

a. Removal of suspended particles:
   Filter through a syringe filter (0.2µm)
b. Sample Preparation:
   duplicate all the samples
   i. Take 2 ml of samples.
      (Dilute the sample (if required), and make the final volume of 2 ml in a tube.)
      * had better check ammonium concentration by pack test.
   ii. Add 1 ml of solution A, to all samples blank and std. solution; and shake gently so that no bubbles are formed.
   iii. Add 1 ml of solution B and gently shake, after cap.
   iv. Leave the samples for 1 hour at room temperature (20-40°C)
   v. After an hour, bluish green color develops.
c. Standard solutions preparation:
   duplicate blank and all the standard solutions
   Treat blank and std. solutions in same manner as samples.
d. Photometric measurement:
   Measure the absorbance at 640nm.

Calculation:

Prepare a std. curve by plotting absorbance of std. against NH_3-N concentration. Compute sample concentration from the curve.

NH_4-N

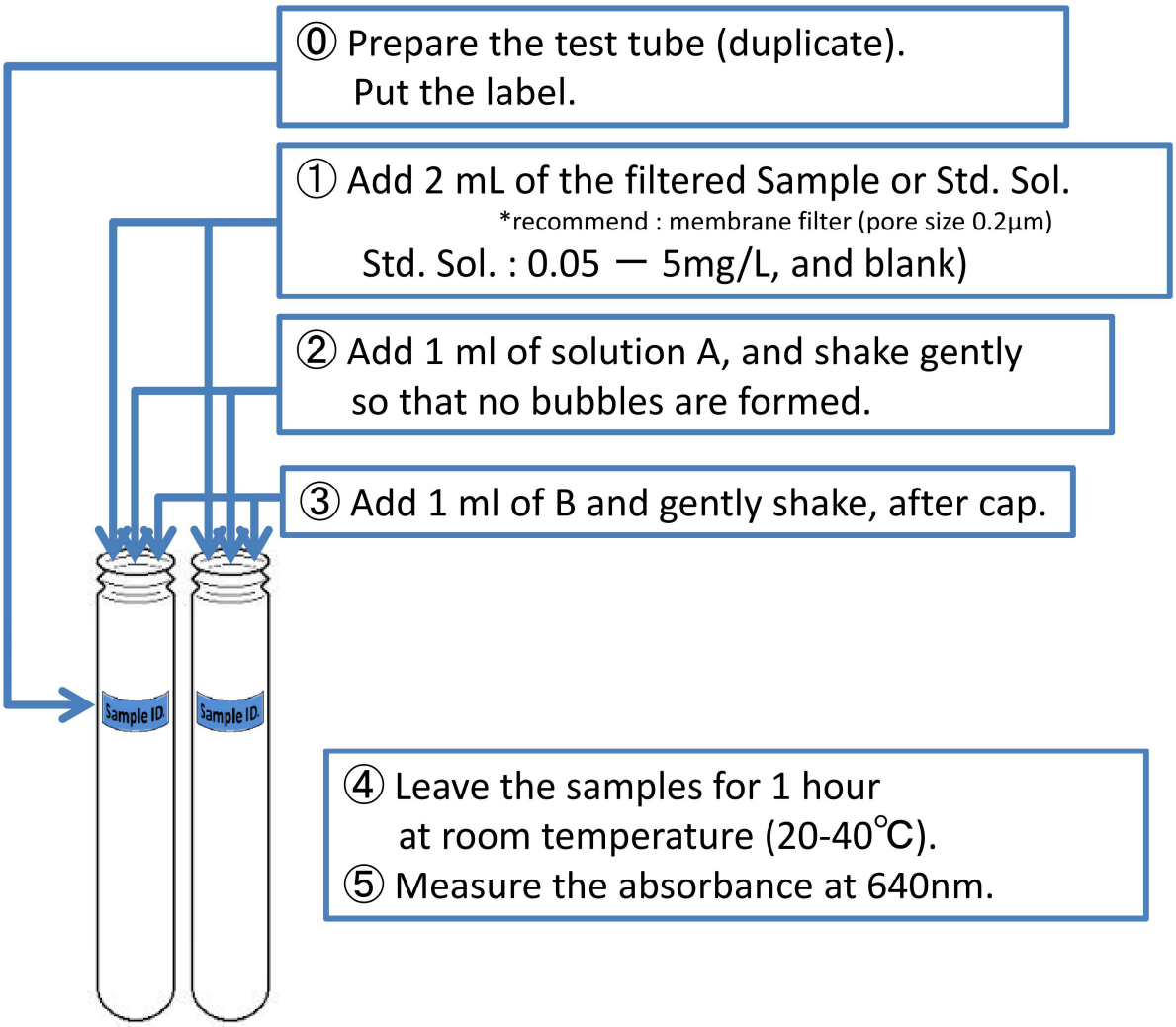


Fig. 6 Flow chart of the analytical procedure for NH_4.

⑥ Total Phosphorus Analysis by Persulfate Digestion Method

(ref. : Standard Methods for the Examination of Tap Water in Japan)

***volume is different**

Equipment:

- volumetric flask(500ml, 100ml)
- pipette(10ml, 5ml)
- measuring cylinder(200ml, 50ml)
- bottle
- 100 ml Beaker
- tubes with cap
- glass cuvette(1cm)

Apparatus:

- Magnetic stirrer
- Analytical balance
- Spectrophotometer

Required Chemicals:

1. Distilled water
2. 4 gm, Potassium persulfate (freshly prepared) : for analysis of Phosphorus
3. 50 ml, Conc. H_2SO_4 : G.R.
4. 0.24 gm Potassium antimonyl tartrate: G.R.
5. 6gm, Ammonium molybdate : G.R.
6. gm Ascorbic Acid : G.R.
7. Phosphorus Standard Solution (1000mg-PO_4-P/l)

Preparation of reagents:

1. 4% Potassium persulfate Solution (Digestion Solution): (0.4ml/tube)
   *Total Phosphorus are converted to orthophosphate.
   Prepare Potassium persulfate 4% Weight by Volume. Add 4 gm of Potassium persulfate to 100 ml distilled water. Then stir it with the help of magnetic stirrer.
2. Sulfuric Acid (Solution A): same of orthophosphate
   To approximately 100 ml water, add **50 ml** of Conc. H_2SO_4.
3. Potassium antimonyl tartrate solution (Solution B):
   To approximately 300 ml water, add 0.24 gm of Potassium antimonyl tartrate, 6 gm of Ammonium molybdate, and dissolve. Then, add 120mL of Solution A. Let it cool and then make a final volume of 500 ml in a volumetric flask.
4. L-ascorbic Acid (Solution C): same of orthophosphate
   To **100 ml** of distilled water, add **7.2 gm** of L-ascorbic Acid
   ****This reagent can be used only for a week, even refrigerated.**
   ****It is colorless when freshly prepared and color changes to light yellow when kept for long time)**
5. Combined reagent (Solution D): same of orthophosphate (0.2ml/tube)
   Combine Solution B and C in the ration 5:1

6. Phosphorus Standard Solutions: (0.01 ~ 5 mg/l) same of orthophosphate
   See Table.5

Procedure: see Fig. 7

a. Sample Preparation:
   i. triplicate all the samples
   ii. Take 2ml of samples.
   (Dilute the sample (if required) and take 2 ml of each)
   * had better check Phosphorus concentration by pack test.
   iii. Add 0.4 ml of Digestion Solution to each sample.
   iv. Autoclave all the samples for 30 minutes at 121°C.
   v. After cooling, add 0.2ml of the Solution D to the samples.
   vi. Leave the samples for 15 minutes at room temperature (20-40°C), before taking the readings.

b. Standard solutions preparation:
   duplicate blank and all the standard solutions
   Treat blank and std. solutions in same manner as samples.

c. Photometric measurement:
   Measure the absorbance at 880nm.

Calculation:

Prepare a std. curve by plotting absorbance of std. against P concentration. Compute sample concentration from the curve.

⑦ Dissolved Phosphorus Analysis by Persulfate Digestion Method

(ref. : Standard Methods for the Examination of Tap Water in Japan)

***volume is different**

Equipment:

- volumetric flask(500ml, 100ml)
- pipette(10ml, 5ml)
- measuring cylinder(200ml, 50ml)
- bottle
- 100 ml Beaker
- tubes with cap
- glass cuvette(1cm)
- syringe
- syringe filter (0.2µm) : i.e. cellulose acetate

Apparatus:

- Magnetic stirrer
- Analytical balance
- Spectrophotometer

Required Chemicals:

1. Distilled water
2. 4 gm, Potassium persulfate (freshly prepared) : for analysis of Phosphorus
3. 50 ml, Conc. H_2SO_4 : G.R.
4. 0.24 gm Potassium antimonyl tartrate: G.R.
5. 6gm, Ammonium molybdate : G.R.
6. 7.2 gm Ascorbic Acid : G.R.
7. Phosphorus Standard Solution (1000mg-PO_4-P/l)

Preparation of reagents:

1. 4% Potassium persulfate Solution (Digestion Solution): same of Total Phosphorus

   (0.4ml/tube)

   *Dissolved Phosphorus are converted to orthophosphate.

   Prepare Potassium persulfate 4% Weight by Volume. Add 4 gm of Potassium persulfate to 100 ml distilled water. Then stir it with the help of magnetic stirrer.
2. Sulfuric Acid (Solution A): same of orthophosphate

   To approximately 100 ml water, add 50 ml of Conc. H_2SO_4.
3. Potassium antimonyl tartrate solution (Solution B):

   To approximately 300 ml water, add 0.24 gm of Potassium antimonyl tartrate, 6 gm of Ammonium molybdate, and dissolve. Then, add 120mL of Solution A. Let it cool and then make a final volume of 500 ml in a volumetric flask.

4. L-ascorbic Acid (Solution C): same of orthophosphate
   To 100 ml of distilled water, add 7.2 gm of L-ascorbic Acid
   **This reagent can be used only for a week, even refrigerated.
   **It is colorless when freshly prepared and color changes to light yellow when kept for long time)
5. Combined reagent (Solution D): same of orthophosphate (0.2ml/tube)
   Combine Solution B and C in the ration 5:1
6. Phosphorus Standard Solutions: (0.01~1.0 mg/l) same of orthophosphate
   See Table.5

Procedure: see Fig. 7

a. Removal of suspended particles:
   Filter through a syringe filter (0.2µm)
b. Sample Preparation:
   i. duplicate all the samples
   ii. Take 2ml of samples. (Dilute the sample (if required) and take 2 ml of each)
   * had better check Phosphorus concentration by pack test.
   iii. Add 0.4 ml of Digestion Solution to each sample.
   iv. Autoclave all the samples for 30 minutes at 121°C.
   v. After cooling, add 0.2ml of the Solution D to the samples.
   vi. Leave the samples for 15 minutes in room temperature(20-40°C), before taking the readings.
b. Standard solutions preparation:
   duplicate blank and all the standard solutions
   Treat blank and std. solutions in same manner as samples.
c. Photometric measurement:
   Measure the absorbance at 880nm.

Calculation:

Prepare a std. curve by plotting absorbance of std. against P concentration. Compute sample concentration from the curve.

TP, DTP

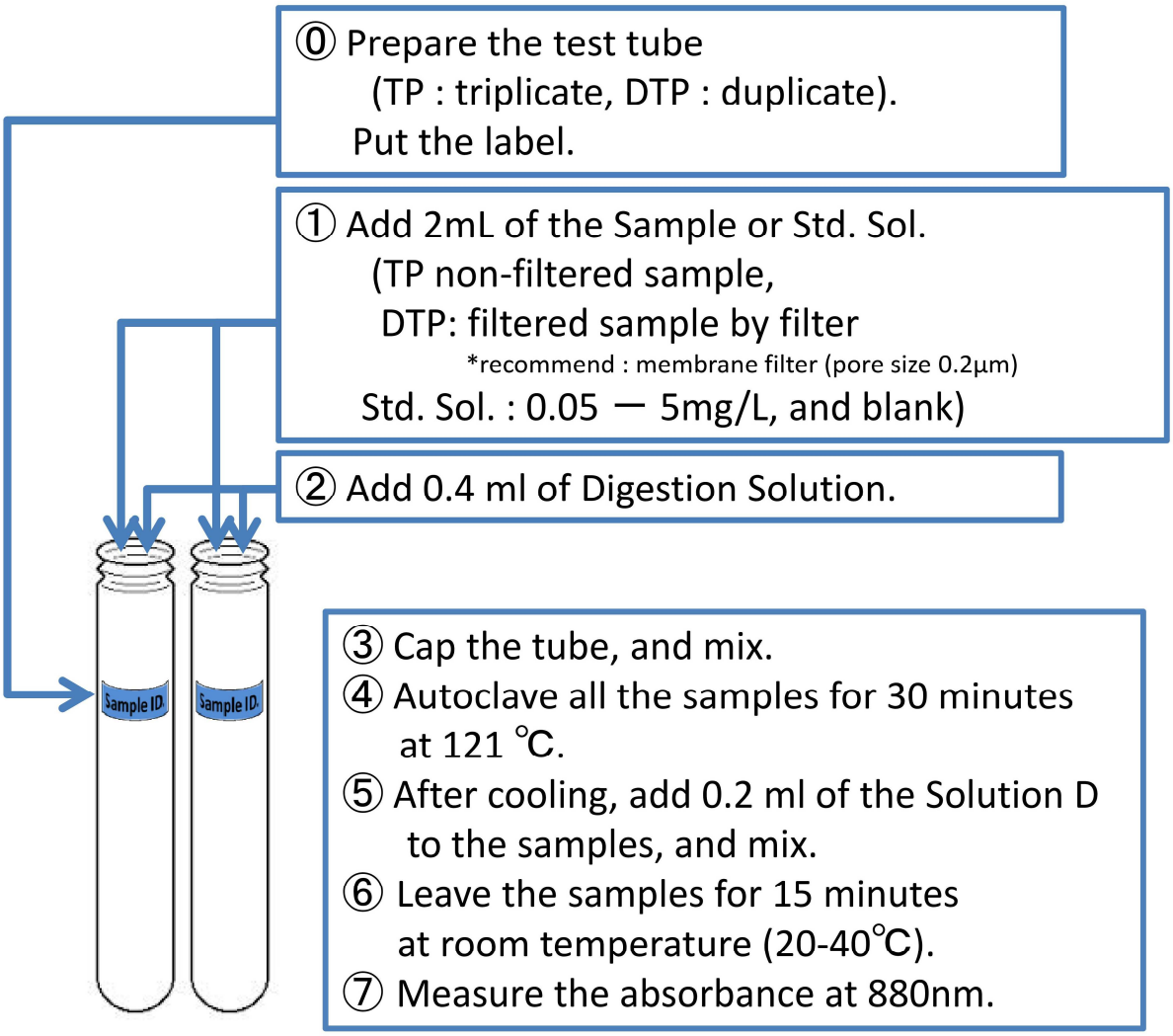


Fig. 7 Flow chart of the analytical procedure for TP/DTP.

⑧ Orthophosphate Analysis by Ascorbic Acid Method

(ref. : Standard Methods for the Examination of Tap Water in Japan)

***volume is different**

Equipment:

- volumetric flask(500ml, 100ml)
- transfer pipet
- pipette(10ml, 5ml)
- measuring cylinder(200ml, 50ml)
- bottle
- 100 ml Beaker
- tubes with cap
- glass cuvette(1cm)
- syringe
- syringe filter (0.2µm) : i.e. cellulose acetate

Apparatus:

- Magnetic stirrer
- Analytical balance
- Spectrophotometer

Interference:

ferric ion (1mg/L<)

Required Chemicals:

1. Distilled water
2. 50 ml, Conc. H_2SO_4 : G.R.
3. 0.24 gm Potassium antimonyl tartrate: G.R.
4. 6gm, Ammonium molybdate : G.R.
5. 7.2 gm Ascorbic Acid : G.R.
6. Phosphorus Standard Solution (1000mg-PO_4-P/l)

Preparation of reagents:

1. Sulfuric Acid (Solution A):
   To approximately 100 ml water, add 50 ml of Conc. H_2SO_4 .
2. Potassium antimonyl tartrate solution (Solution B):
   To approximately 300 ml water, add 0.24 gm of Potassium antimonyl tartrate, 6 gm of Ammonium molybdate, and dissolve. Then, add 120mL of Solution A. Let it cool and then make a final volume of 500 ml in a volumetric flask.
3. L-ascorbic Acid (Solution C):
   To 100 ml of distilled water, add 7.2 gm of L-ascorbic Acid.
   **This reagent can be used only for a week, even refrigerated.
   **It is colorless when freshly prepared and color changes to light yellow when kept for long time)

4. Combined reagent (Solution D): (0.2ml/tube)
   Combine Solution B and C in the ration 5:1
5. Orthophosphate Standard Solutions: (0.01~1.0 mg/l)
   See Table.5

Procedure: see Fig. 8

a. Removal of suspended particles:
   Filter through a syringe filter (0.2μm)
b. Sample Preparation:
   duplicate all the samples
   Dilute the sample (if required)
   * had better check Phosphorus concentration by pack test.
   To 2 ml of blank and std. solutions, add 0.2 ml of Solution D, mix thoroughly, and leave for 15 minutes in room temperature(20-40°C).
c. Standard solutions preparation:
   duplicate blank and all the standard solutions
   Treat blank and std. solutions in same manner as samples.
d. Photometric measurement:
   Measure the absorbance at 880nm.

Calculation:

Prepare a std. curve by plotting absorbance of std. against PO_4 concentration. Compute sample concentration from the curve.

PO_4

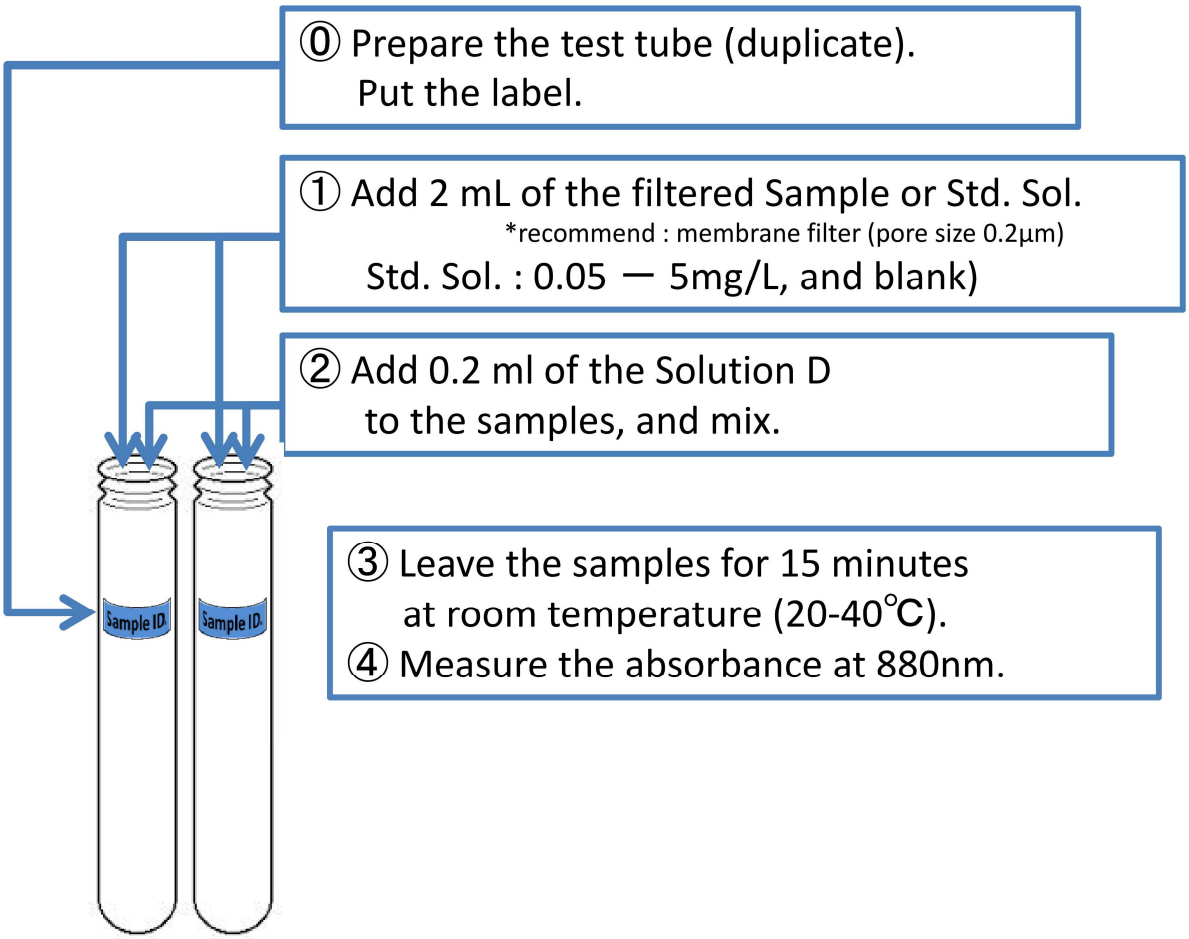


Fig. 8 Flow chart of the analytical procedure for PO_4.

⑨ Total iron by Phenanthroline Method

(ref. : Standard Methods 22nd edition 3500-Fe B)

Required Apparatus:

1. Volumetric flask (20ml, 100ml)
2. 100ml measuring cylinder
3. Pipette (10ml and 1ml)
4. Screw bottle (30 mL)
5. 100ml beaker
6. Analytical balance
7. Spectrophotometer
8. Glass cuvette (1.5ml)
9. Syringe
10. Syringe filter (0.2 μm): cellulose acetate
11. Hot plate
12. Teflon beaker

Required chemicals:

1. Freshly prepared nitrite free water
2. Conc. Hydrochloric acid
3. Hydroxylamine Hydrochloride ($NH_2OH \cdot HCL$)
4. Ammonium Acetate ($NH_4C_2H_3O_2$)
5. 1,10-phenanthroline monohydrate ($C_{12}H_8N_2 \cdot H_2O$)
6. Iron Stock Solution

Preparation of color reagent:

Store reagents in glass-stoppered bottles.
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

1. Hydrochloric acid, HCl, conc, containg less than 0.5 ppm iron:
   Add 5ml of Hydrochloric acid, to 55 ml of distilled water.
   *This solution is stable indefinitely if tightly stoppered.
2. Hydroxylamine solution:
   Dissolve 10g Hydroxylamine Hydrochloride in 100 mL water.
   *This solution is stable for several months

3. Ammonium acetate buffer solution:

Dissolve 250 g Ammonium Acetate in 150 mL water. Add 700 mL conc (glacial) acetic acid. Because even a good grade of Ammonium Acetate contains a significant amount of iron, prepare new reference standards with each buffer preparation.

* This solution is stable indefinitely if tightly stoppered.

4. Phenanthroline solution:

Dissolve 100 mg 1,10-phenanthroline monohydrate, in 100 mL 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

5. Iron standard solution (0~1.0mg/L)

See Table.6

Procedure: see Fig. 9

a. Removal of suspended particles:

Filter the sample through a syringe filter (0.2μm)

b. Sample Preparation:

Duplicate all the samples

Mix sample thoroughly and measure 50.0 mL into a 125-mL erlenmeyer flask.

Dilute the sample (if this sample volume contains more than 200μg iron use a smaller accurately measured portion and dilute to 50ml.)

Add 2 mL conc HCl and 1 mL $NH_2OH \cdot HCl$ 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 or 20 mL.(if the sample is ashed, take up residue in 2 mL conc HCl and 5 mL water)

Cool room temperature and transfer to 50- or 100-mL volumetric flask.

Add 10 mL $NH_4C_2H_3O_2$ buffer solution and 4 mL phenanthroline solution, and dilute to mark with water.

Mix thoroughly and allow a minimum of 10 min for maximum color development.

c. Blank and Standard Solutions Preparation:

Duplicate the blank and all standard solutions.

Treating in the same way as samples.

d. Photometric measurement:

Measure the absorbance at 510nm.

Calculation:

Prepare a standard curve by plotting absorbance of standard against Fe concentration. Compute sample concentration from the curve.

$$\text{mg Fe/L} = \frac{\mu\text{g Fe (in 100 mL final volume)}}{\text{mL sample}}$$

* Report details of sample collection, storage, and pretreatment if they are pertinent to interpretation of results.

** The standard solution has certain absorbance and develops the color after adding color reagent. But sometimes, the samples have higher absorbance than the standard solution but results no color development even after adding color reagent. In such a situation, we have to measure the absorbance of the sample without floor reagent and reduce the absorbance value from the sample with color reagent. We use this deducted absorbance as a reading.
Note: The disappearance of the color might be from the organic material present in the sample.

T-Fe

Preparation of sample

⓪ Prepare the Teflon beaker(duplicate). Put the label.
① Measure 50mL sample or Std. Sol. into a Teflon beaker.
(Std. Sol. : 0.2 ― 1mg/L, and blank)
② Add 2mL conc HCl and 1mL Hydoroxylamine solution.
③ Add a few glass beads and heat to boil at Hot plate.
④ Continue boiling until volume is reduced 15 to 20mL.
⑤ Cool to room temperature.

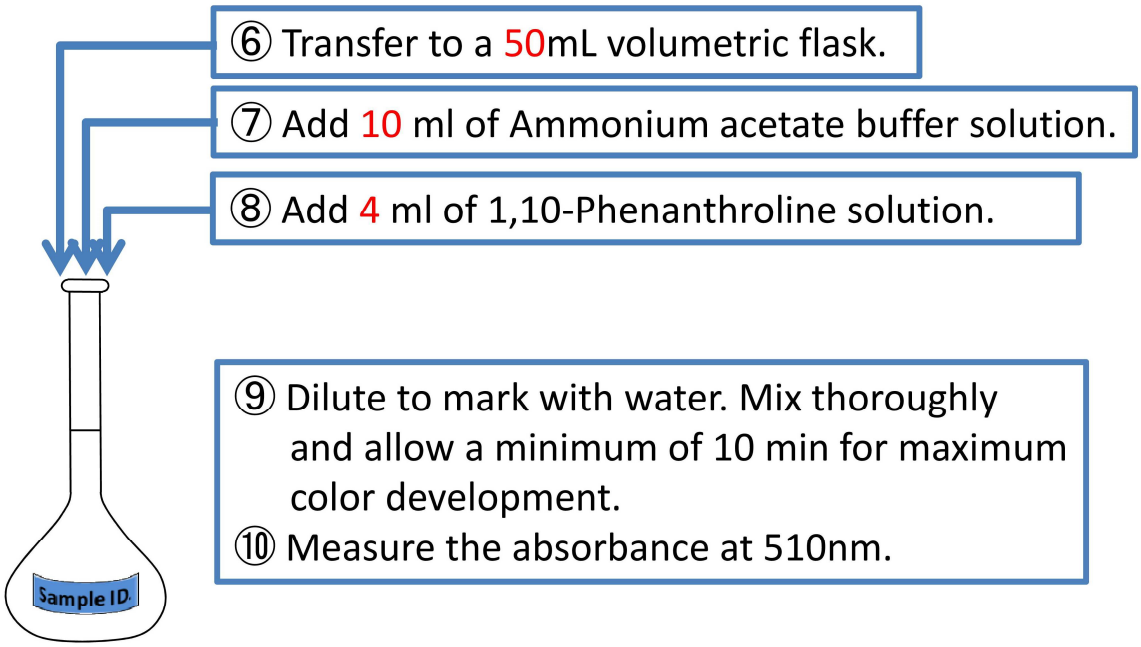


Fig. 9 Flow chart of the analytical procedure for T-Fe.

⑩ Acid soluble iron by Phenanthroline Method

(ref. : water quality research method (Japan))

***volume is different**

Equipment:

- measuring cylinder (200mL, 1L)
- volumetric flask (20ml, 1L)
- transfer pipet
- pipette(10ml, 1ml)
- bottle
- 300 ml Beaker
- tubes with cap
- Teflon beaker
- glass cuvette(1cm)

Apparatus:

- Magnetic stirrer
- Analytical balance
- Spectrophotometer

Required Chemicals:

1. Distilled water
2. Conc. HCl : containing less than 0.5 ppm iron
3. 1,10-Phenanthroline monohydrate : G.R.
4. Ammonium acetate : G.R.
5. conc (glacial) Acetic acid : G.R.
6. Hydroxylamine Hydrochloride
7. Ammonium hydroxide(28%)
8. Fe Standard Solution (1000mg- Fe/l)

Preparation of reagents:

1. 1,10-Phenanthroline solution : (1ml/tube)
   Dissolve 0.1 gm 1,10-Phenanthroline monohydrate, in 100 ml distilled water by stirring and heating to 80℃ (do not boil). Heating is unnecessary if 2 drops conc HCl are added to the water.
   **** Store this solution in dark bottle, and refrigerate.**
   **** Discard the solution if it darkness.**
2. Ammonium acetate buffer solution : (1ml/tube)
   Dissolve 250gm Ammonium acetate in 150mL water. Add 700mL conc (glacial) Acetic acid.
3. Preparation of Iron Standard solutions: (0.05~1 mg/l)
   See Table.6
4. Hydroxylamine solution : (0.4ml/tube of Std.Sol.)
   Dissolve 10g Hydroxylamine Hydrochloride in 100mL water.

5. 3N HCl (1.2ml/each Teflon beaker)
   Add 10ml HCl in 30 ml distilled water.

Procedure: see Fig. 10

a. Sample Preparation:
   ***Sample with 1ml-HCl/100ml-sample at time of collection.**
   Fill bottle directly from sampling source and stopper.
   i. Duplicate all the samples
   ii. Take 10ml portion of acidified samples (50 ml Teflon beaker).
   (Dilute the sample (if required) and take 10 ml of each)
   iii. Add 1.2 ml of 3N HCl to each sample
   iv. Heat for 5 minutes by hotplate
   v. Then, cool. Transfer to a 20ml volumetric flask (if sample is turbid, need to filter)
   vi. Add 0.4 ml Hydroxylamine solution to each tubes
   vii. Add 1.0 ml 1,10-Phenanthroline solution to each tubes
   viii. Add 4 ml of Ammonium acetate buffer solution with vigorous stirring
   ix. Dilute to 20mL, and mix thoroughly
   *Do not expose to sunlight.

b. Standard solutions preparation:
   Duplicate blank and all the standard solutions
   Take 10 ml of blank and std. sol.
   Add 0.2 ml conc HCL.
   Then, treat in same manner as samples (vi-ix).

c. Photometric measurement:
   Measure color intensity within 5 to 10 min at 510nm.

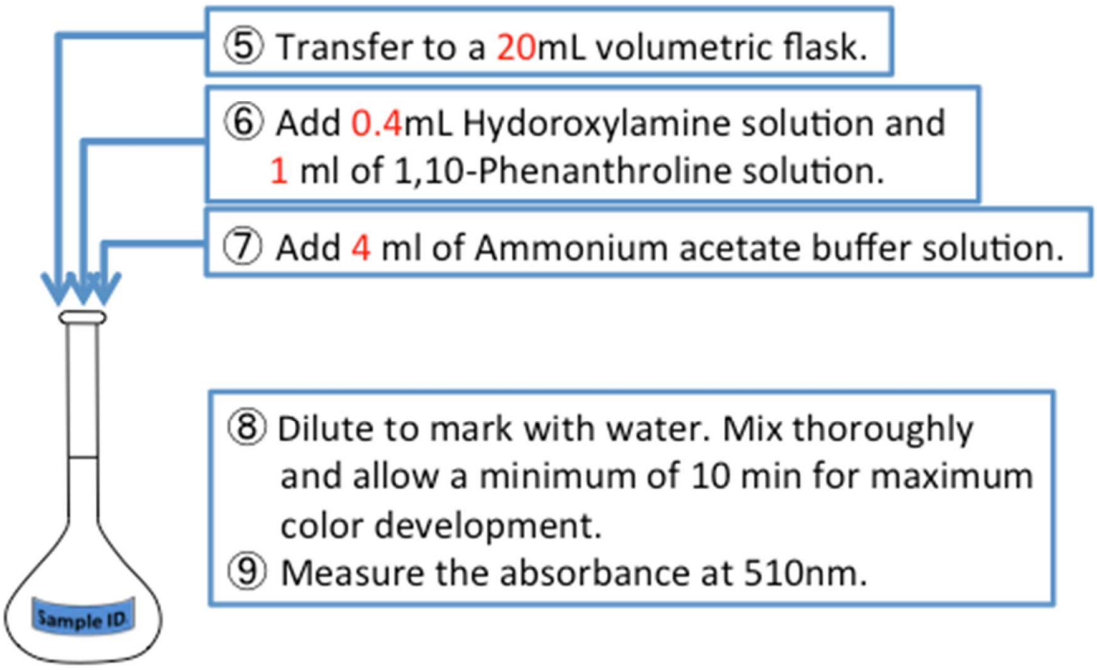
Calculation

Prepare a std. curve by plotting absorbance of std. against ferrous ion concentration. Compute sample concentration from the curve.

AS-Fe

Preparation of sample

⓪ Prepare the Teflon beaker(duplicate). Put the label.
① Measure 10mL sample into a Teflon beaker.
(Std. Sol. : 0.2 — 1mg/L, and blank)
② Add 1.2mL of 3N HCl.
③ Heat for 5minutes by Hot plate.
④ Cool to room temperature.



Procedure for Std. Sol.

(Std. Sol. : 0.2 – 1mg/L, and blank)
- Prepare the test tube(duplicate). Put the label.
- Add 10mL of the Std. Sol.
- ⑦ - ⑨

Fig. 10 Flow chart of the analytical procedure for AS-Fe.

⑪ Ferrous ion by Phenanthroline Method

(ref. : Standard Methods 22nd edition 3500-Fe B)

***volume is different**

Equipment:

- measuring cylinder (200mL, 1L)
- volumetric flask (1L)
- transfer pipet
- pipette(10ml, 1ml)
- bottle
- 300 ml Beaker
- tubes with cap
- glass cuvette(1cm)

Apparatus:

- Magnetic stirrer
- Analytical balance
- Spectrophotometer

Required Chemicals:

1. Distilled water
2. Conc. HCl : containing less than 0.5 ppm iron
3. 1,10-Phenanthroline monohydrate : G.R.
4. Ammonium acetate : G.R.
5. conc (glacial) Acetic acid : G.R.
6. Fe Standard Solution (1000mg- Fe/l)

Preparation of reagents:

1. 1,10-Phenanthroline solution : (2ml/tube)
   Dissolve 0.1 gm 1,10-Phenanthroline monohydrate, in 100 ml distilled water by stirring and heating to 80℃(do not boil). Heating is unnecessary if 2 drops conc HCl are added to the water.
   **** Store this solution in dark bottle, and refrigerate.**
   **** Discard the solution if it darkness.**
2. Ammonium acetate buffer solution : (1ml/tube)
   Dissolve 250gm Ammonium acetate in 150mL water. Add 700mL conc (glacial) Acetic acid.
3. Preparation of Iron Standard solutions: (0.05~1 mg/l)
   See Table.6
4. Hydroxylamine solution : (0.1ml/tube of Std.Sol.)
   Dissolve 10g Hydroxylamine Hydrochloride in 100mL water.

Procedure: see Fig. 11

b. Sample Preparation:

***Sample with 2ml-HCl/100ml-sample at time of collection.**
Fill bottle directly from sampling source and stopper.

i. Duplicate all the samples
ii. Take 5ml portion of acidified samples.
(Dilute the sample (if required) and take 5 ml of each)
iii. Add 2 ml of 1,10-Phenanthroline solution to each sample.
iv. Add 1 ml of Ammonium acetate buffer solution with vigorous stirring.
v. Dilute to 10mL, and mix thoroughly.

*Do not expose to sunlight.

b. Standard solutions preparation:

Duplicate blank and all the standard solutions
Add 0.05 ml conc HCL and 0.1ml Hydroxylamine solution to each tubes.
Then, treat in same manner as samples(iii-v).

c. Photometric measurement:

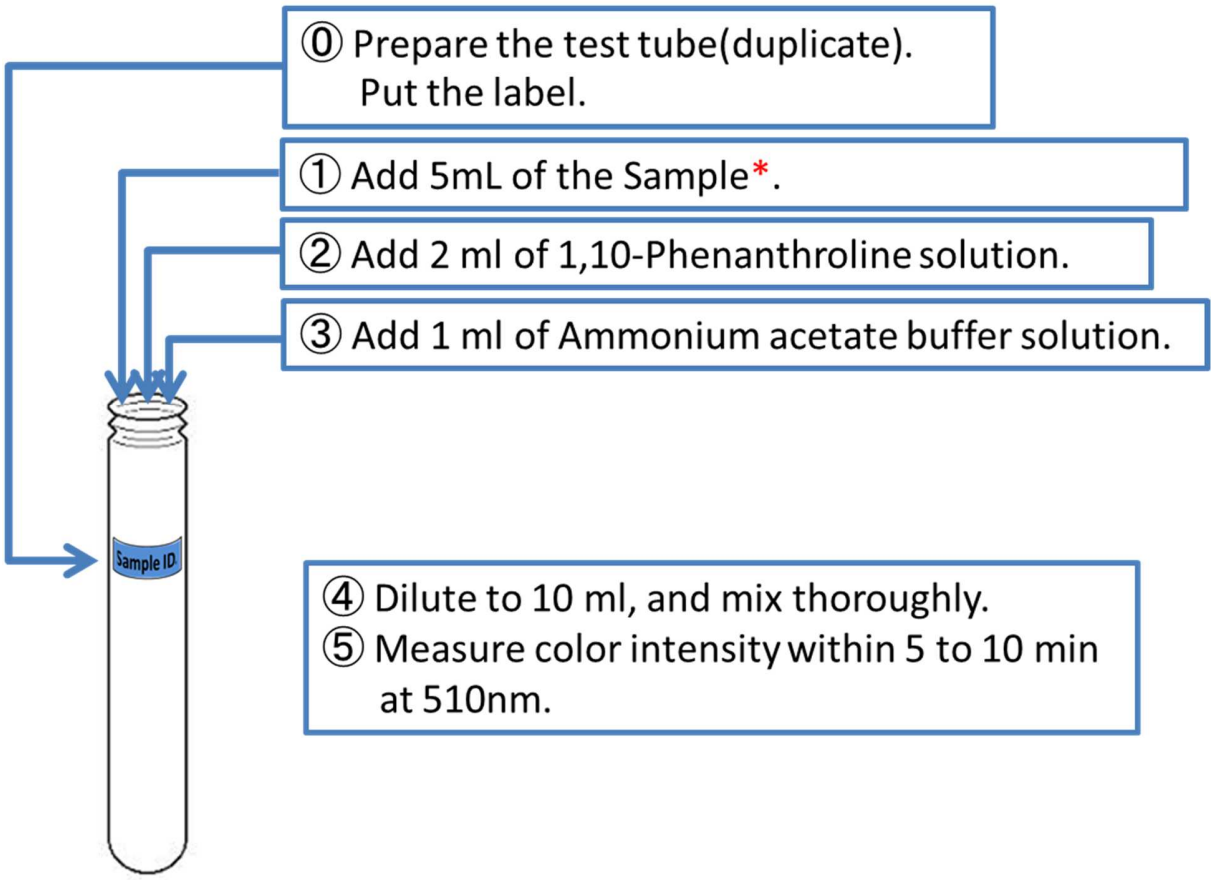
Measure color intensity within 5 to 10 min at 510nm.

Calculation

Prepare a std. curve by plotting absorbance of std. against ferrous ion concentration. Compute sample concentration from the curve.

Fe^{2+}

***Sample with 2ml-HCl/100ml-sample at time of collection.**
Fill bottle directly from sampling source and stopper.



Procedure for Std. Sol.

(Std. Sol. : 0.2 – 1mg/L, and blank)

⓪ Prepare the test tube(duplicate). Put the label.
① Add 5mL of the Std. Sol.
② Add 0.05mL conc HCl and 0.1mL Hydoroxylamine solution.
③ Add 2 ml of 1,10-Phenanthroline solution.
④ Add 1 ml of Ammonium acetate buffer solution.
⑤ Dilute to 10 ml, and mix thoroughly.
⑥ Measure color intensity within 5 to 10 min at 510nm.

Fig. 11 Flow chart of the analytical procedure for Fe^{2+}.

⑫ Dissolved Manganese by Absorptiometric method (Holm aldoxime method)

(ref. : Analytical method of mineral spring in Japan)

Equipment:

- Pipette (1,210 mL)
- Screw bottle (30 mL)
- Beaker
- Tubes and cap
- Volumetric flask(100,200mL,1L)
- Screw bottle (30ml)
- Analytical balance
- UV Spectrophotometer
- glass cuvette (1.5ml)

Required Chemicals:

1. Holm aldoxime reagent
2. buffer solution (pH = 10)
3. L- ascorbic acid sodium salt
4. 0.1M EDTA solution
5. Manganese stock solution (1000mg-Mn^{2+}/L)

Preparation of reagents:

1. Holm aldoxime reagent
   Approximately 100 mL of distilled water , add 8 g of Hydroxylamine hydrochloride (NH_2-OH · HCl). After that add 4ml of 37% formaldehyde (HCHO), adjust the volume of 200ml with distilled water.
2. buffer solution (pH = 10)
   Approximately 300 mL of distilled water , add 68 g of Ammonium chloride (NH_4Cl). After that add 570 mL of conc. NH_3 solution, adjust the volume of 1L with distilled water.
3. 0.1M EDTA solution
   Dissolve 3.7g of Disodium EDTA dihydrate [$(CH_2COO)_2N \cdot CH_2 \cdot CH_2N(CH_2COO)_2H_2 \cdot Na_2 \cdot 2H_2O$] in distilled water adjust the final volume of 100mL.
4. Manganese standard solution (0~5.0mg/L)
   See Table.7

Procedure: see Fig. 12

a.) Suspended particles Removal

- Filter through a syringe filter (0.2 μm)

b.) Sample preparation

i. Duplicate all the samples
ii. Take 20 mL of samples. (Dilute the sample {If required})
iii. Add 1 mL of Holm aldoxime reagent and 0.1M EDTA solution of each tube and close with cap.
iv. Mix and Leave the samples for 5 minutes by control condition at room temperature.
v. As the 20 ~ 27℃, stir in addition L- ascorbic sodium salt 10mg and a 0.1M EDTA 1mL.

*The order of addition of sodium L- ascorbic acid → EDTA.

vi. Leave the samples for 10 minutes by control condition at room temperature.
vii. Measure absorbance by ultraviolet spectrophotometry at 450 nm

c.) Standard solutions preparations

i. Prepare duplicate samples of blank and the standard solutions
ii. Treating in the same way as samples.

Calculation

Prepare a std. curve by plotting absorbance of std. against Manganese concentration. Compute sample concentration from the curve.

D-Mn

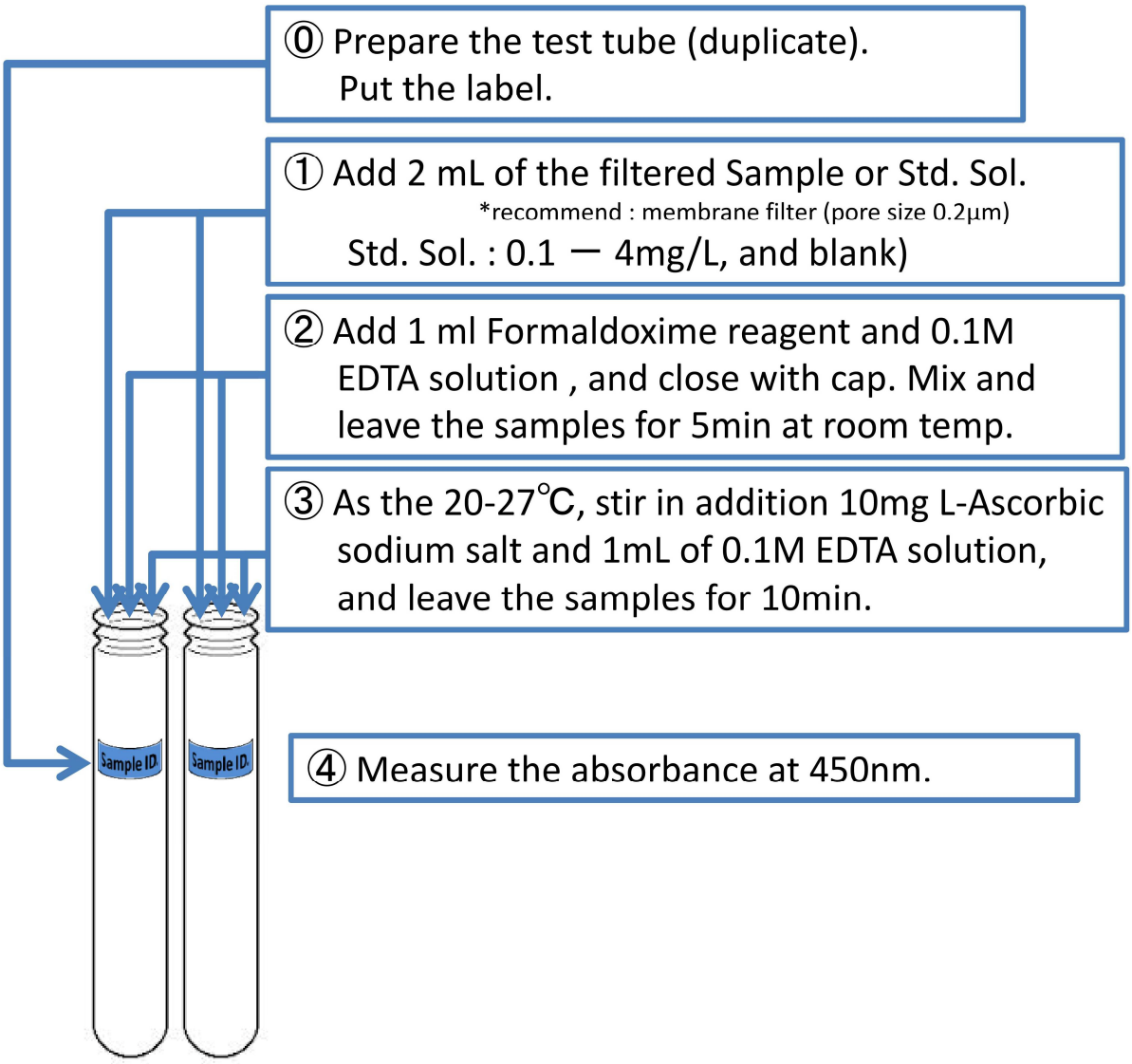


Fig. 12 Flow chart of the analytical procedure for D-Mn.

⑬ COD_{Cr}(Closed Reflux) by Titrimetric Method

(ref. : standard methods 22nd edition 5220 C)

Required Apparatus:

1. volumetric flask (1000ml, 500ml)
2. pipette (10ml, 5ml)
3. 200 ml measuring cylinder
4. bottle
5. 20 ml Ampule (clear) :
   *Wash ampules with 20% H_2SO_4 before first use to prevent contamination.
6. Magnetic stirrer
7. Analytical balance
8. Burette
9. microburet
10. Autoclave

Interference:

Nitrite exerts a COD of 1.1mg O_2/mg NO_2^--N. Because concentration of NO2- in water rarely exceed 1 or 2 mg NO_2^--N/L, the interference is considered insignificant and usually is ignored. To eliminate a significant interference due to NO_2^-, add 10mg Sulfamic acid for each mg NO_2^--N present in the sample volume used; add the same amount of Sulfamic acid to the ampoule containing the distilled water blank.

Required Chemicals:

1. Distilled water
2. conc. Sulfuric Acid : G.R.
3. 1.65 gm, Silver sulfate(Ag_2SO_4) : G.R.
4. 4.903 gm, Potassium dichromate ($K_2Cr_2O_7$) : primary standard grade
   *Previously dried at 150°C for 2h.
5. 33.3 gm Mercuric sulfate ($HgSO_4$) : G.R.
6. 1.485 gm, 1, 10-Phenanthroline monohydrate : G.R.
7. 695 mg, $FeSO_4.7H_2O$: G.R.
8. 425 mg, Potassium Hydrogen Phthalate (KHP): G.R.
   *Previously dried at 110°C.
9. 39.2 gm, $Fe(NH_4)_2(SO_4)_2.6H_2O$: G.R.
10. Sulfamic acid : G.R.

Preparation of reagents:

1. Sulfuric Acid reagent (Reagent A): (3.5ml/ampoule)
   Dissolve 1.65 gm, Silver sulfate (Ag_2SO_4) in 0.3 kg of conc. Sulfuric Acid.
   **Stir it for 1 day

2. Std. Potassium dichromate digestion solution (Reagent B) (0.01667 M): (1.5ml/ampoule)
   To approximately 500 ml of distilled water, dissolve 4.903 gm of Potassium dichromate (99.98% pure), 167 ml of conc. H_2SO_4 and 33.3 gm of $HgSO_4$. Dissolve, cool to room temperature, and then dilute to 1000 ml.
   **Take care when pouring Conc. H_2SO_4, pour slowly (not all at a time) in volumetric flask and stir gently to prevent overheating, keep in water bath with cold water
3. Conc. Ferroin Indicator:
   To approx. 50 ml of distilled water, dissolve 1.485 gm of 1,10-Phenanthroline monohydrate and 695 mg of $FeSO_4.7H_2O$ and dilute to 100 ml.
4. Ferroin Indicator:
   Take 10 ml of Conc. Ferroin indicator and dissolve to 40 ml distilled water.
5. Potassium Hydrogen Phthalate (KHP):COD_{Cr} value ≒ 500mg-O_2/L
   Dissolve 425 mg of KHP in 1000 ml of distilled water.
6. Standard Ferrous Ammonium Sulfate titrant (FAS) (0.10 M):
   Dissolve 39.2 gm, $Fe(NH_4)_2(SO_4)_2.6H_2O$ in distilled water. Add 20 ml of Conc. H_2SO_4 and cool and dilute to 1000 ml.
7. Ferrous Ammonium Sulfate titrant (FAS) (0.02 M):
   200 ml of 0.10M FAS in distilled water make up to 1000mL.

Procedure:

a. For Molarity of FAS solution:
   i. Take 5 ml of Reagent B into 3 beakers each
   ii. Add 10 ml of distilled water in all the beakers
   iii. Put 2 drops of Ferroin indicator
   iv. Titrate against FAS titrant

$$\text{Molarity of FAS solution (M)} = \frac{\text{Reagent B,ml}}{\text{Volume FAS used in titration,ml}} \times 0.1000$$

b. Sample preparation: see Fig. 13

i. triplicate all the samples

ii. place 2.5 ml of sample in ampule, add 1.5 ml of Reagent B. If high concentration of NO_2^--N present, add 10mg Sulfamic acid for each mg NO_2^--N present in the sample volume used
(Dilute the sample (if required) and take 2.5 ml of each)

iii. Carefully run 3.5 ml of Reagent A down inside the ampule so that an acid layer is formed under the sample digestion solution layer.
* Do not mix.

iv. The total volume in the ampule is 7.5 ml.

v. Take the ampules with samples and burn its upper part in order to seal it.

vi. After sealing, shake the ampules gently.
* caution : wear face shield and protect hands from heat produced when contents of ampules are mixed. Mix thoroughly before applying heat to prevent local heating of ampule bottom and possible explosive reaction.

vii. Check the solution color. Color is:
yellow : O.K.
green : △(If sample contents of SS or high DOC concentration, digestion reagent is not enough. Dilute a sample.)
blue : ×(digestion reagent is not enough. Dilute a sample.)

viii. Autoclave the ampules at 127°C for 2 h.

ix. After 2 hrs. of autoclave, cool to room temperature.

x. Open ampules, add 2 drops of Ferroin indicator and stir rapidly on magnetic stirrer while titrating with standardized 0.10M FAS.

xi. The end point is sharp color change from blue-green to reddish brown.

xii. Note down the volume of FAS used.

c. Blank and check solution preparation:

triplicate blank and check solution
Blank : 2.5 ml of distilled water
Check solution : 1 ml of KHP solution, add 1.5ml of distilled water
Treat blank and std. solutions in same manner as samples.

Calculation:

$$\text{COD (mg-O}_2\text{/L)} = \frac{(A-B)\times M\times 8000}{\text{Sample volume ml}}$$

Where,
A= ml FAS used for blank,
B= ml FAS used for sample,
M= Molarity of FAS, and
8000= milliequivalent weight of oxygen ✕1000 mg/L

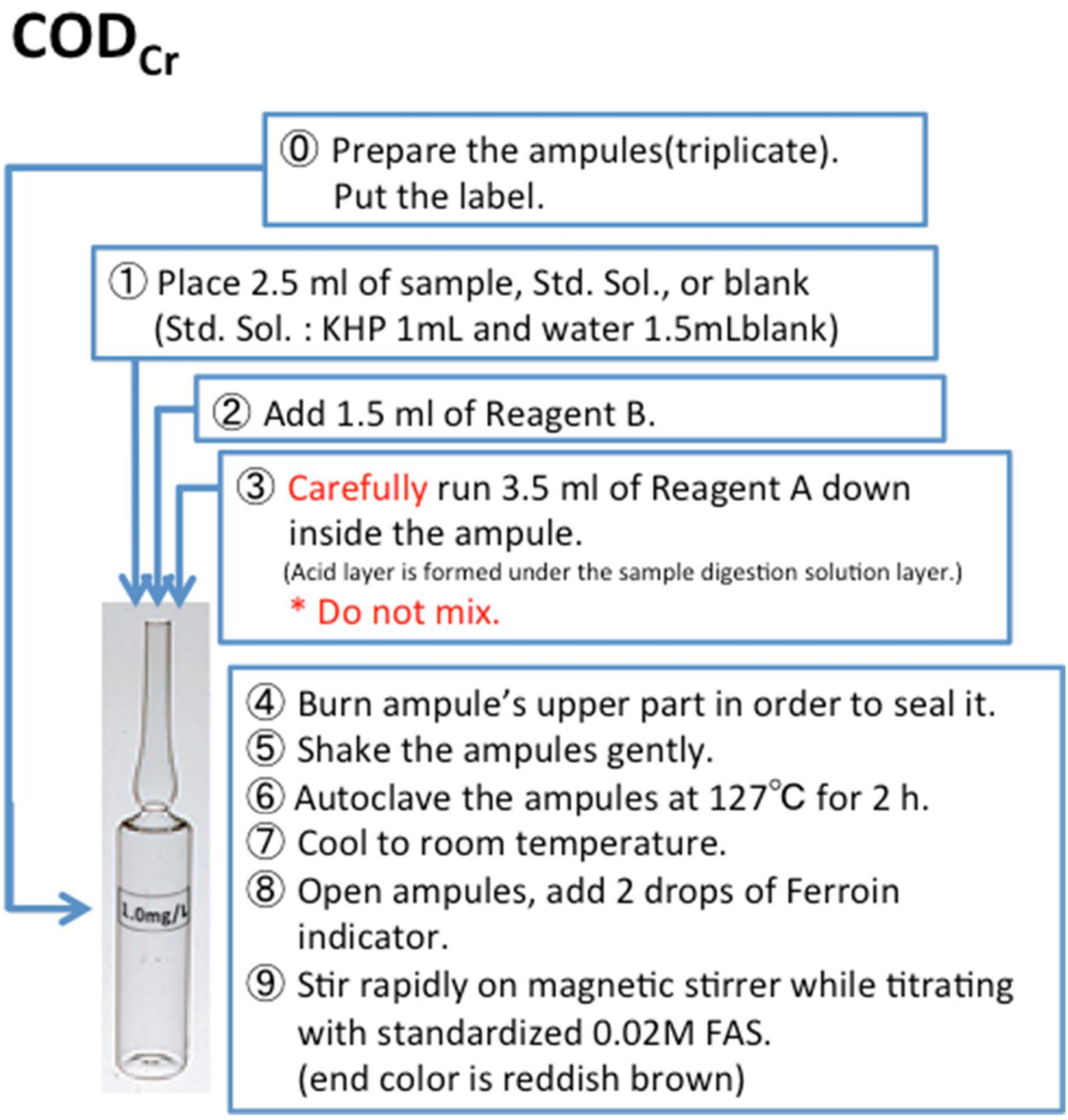


Fig. 13 Flow chart of the analytical procedure for COD_{Cr}.

⑭ Bicarbonate by Titration Method

(ref. : Standard Methods for the Examination of Tap Water in Japan)

Equipment:

- measuring cylinder (50mL, 100mL)
- dropper
- conical beaker(100mL)
- Burette

Apparatus:

- Magnetic stirrer
- Analytical balance

Required Chemicals:

9. Distilled water
10. 0.02N H_2SO_4 : for titration
11. Methyl Red : G.R.
12. Bromocresol Green : G.R.
13. Ethanol : G.R.

Preparation of reagents:

1. 95% Ethanol :
   Mix 95mL Ethanol and 5mL water.
2. MR-BCG indicator : (5 drops/titration)
   Dissolve 0.02 gm Methyl Red and 0.1gm Bromocresol Green, in 100 ml 95% Ethanol.
   * Store the indicator in plastic bottle and keep in refrigerator.

Procedure(Titration): see Fig. 14

vi. Measure 50mL sample into a 100mL conical beaker.
vii. Add 5 drops of MR-BCG indicator and stir rapidly on magnetic stirrer while titrating with standardized 0.02N H_2SO_4 titrant.
viii. The end point is sharp color change from blue (or green) to old pansy.
ix. Note down the volume of 0.02N H_2SO_4 used.

Calculation

$$HCO_3^-(mg/L) = \frac{a(mL)}{v(mL)} \times 0.02(N) \times F \times 61(g/mol) \times 1000(mg/g)$$

Where,
a= ml 0.02N H_2SO_4 titrant used,
v= ml sample volume,
F= factor of 0.02N H_2SO_4.

HCO_3^-

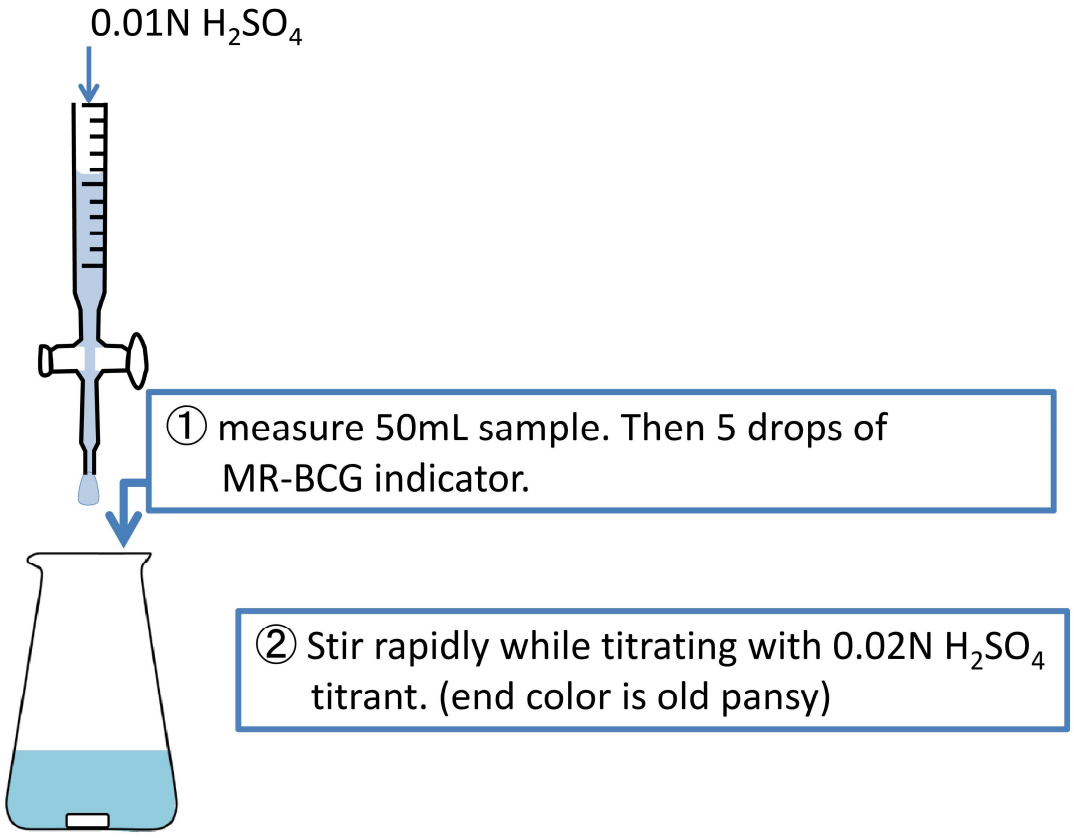


Fig. 14 Flow chart of the analytical procedure for HCO_3^-.

Wastewater treatment (in case of COD_{Cr})

The wastewater of COD_{Cr} method contains high concentration of acid, Mercury, and Chromium. Wastewater treatment process is necessary to throw safely away Drainage.

Water quality standard and Guidelines of those are as follows (table.1):

Table.1 Standard and Guidelines of water quality (mg/L)

		Drainage Standard (Japan)	Drinking water Standard (Japan)	Guidelines for Drinking water (WHO)
pH		5.8 < pH < 8.6		—
Hg		0.005	0.0005	0.001
Cr	Total	2	—	0.05
	Cr^{6+}	0.5	0.05	—

Equipment:

- Beaker
- Glass rod
- ORP meter
- pH test paper
- Filter
- Funnel
- Funnel stand
- Dropper
- Bottle
- PACKTEST (Cr6+, Cr・T, S)
- Mercury measurement set

Required Chemicals: Low purity is enough

1. Iron(II) Sulfate heptahydrate($FeSO_4 \cdot 7H_2O$)
2. Sodium Hydroxide (NaOH)
3. Calcium Hydroxide ($Ca(OH)_2$)
4. Sodium sulfide nonahydrate ($Na_2S \cdot 9H_2O$)
5. Iron(III) Chloride hexahydrate ($FeCl_3 \cdot 6H_2O$)
6. Hydrogen peroxide (30%, H_2O_2)

Preparation of reagents: in case of each 200ml wastewater treatment

1. 20% $FeSO_4$ Solution:
   18g Iron(II) Sulfate heptahydrate in deionized water make up to 50ml
2. 10N NaOH Solution:
   80g Sodium Hydroxide in deionized water make up to 200ml
3. 30% $Ca(OH)_2$ Slurry:
   15g Calcium Hydroxide in deionized water make up to 50ml
4. 10% Na_2S Solution:
   15g Sodium sulfide nonahydrate in deionized water make up to 50ml
5. 15% $FeCl_3$ Solution:
   12.5g Iron(III) Chloride hexahydrate in deionized water make up to 50ml

Procedure: see p.4

a. Reduction of Chromium ($Cr^{6+} \rightarrow Cr^{3+}$)
   Measuring ORP and mixing by wastewater by glass rod while delivering 20% $FeSO^4$ Solution by drops into wastewater. When the ORP value decreases and the color change to blue-green (include Ferroin indicator) or yellow, stop the drop.
b. Check the Chromium(VI) concentration
   Measure Cr^{6+} concentration with Packtest (Cr6+; see p.5). If concentration exceeds the Drainage Standard of Japan, repeat a.
c. Sedimentation (heavy metal)
   ***This process generates gases. Do the work outdoors or inn Fume hoods.**
   (1) Checking pH value by pH test paper and mixing by wastewater by glass rod while adding 10N NaOH. When the pH value is 7-8, stop the addition.
   *** keep in water bath with cold water**
   (2) Then, checking pH value by pH test paper and mixing by wastewater by glass rod while adding 30% $Ca(OH)_2$ Slurry. When the pH value is 9, stop the addition. Cool to room temperature.
d. Filtration
   Set up funnel, pleated filter paper (see p.6), beaker, and the funnel stand. Filter sediment from the liquid.

e. Check the Chromium concentration

Measure Cr concentration with Packtest (Cr・T; see p.7). If concentration exceeds the Drainage Standard of Japan, add a small amount of sulfuric acid, then back to c.

f. Sedimentation (Mercury)

***This process generates H_2S gas. Do the work outdoors or inn Fume hoods.**

Measuring ORP and mixing by wastewater by glass rod while delivering 10% Na_2S Solution by drops into wastewater. When the ORP value is 0 or negative, stop the drop. Add a small volume of 15% $FeCl_3$ Solution and mix. Check the pH value(○：pH > 9, ×：pH<9, add 10N NaOH). Let stand overnight.

g. Filtration

Set up funnel, pleated filter paper, beaker, and the funnel stand. Filter sediment from the liquid.

h. Check the Mercury concentration

First, check that the pH value of liquid is less than 9, and measure S^{2-} concentration (because, S^{2-} affects Hg measurement; see p.8). Measure Hg concentration with Mercury Measurement Set (see p.9-10). If concentration exceeds the Drainage Standard of Japan, back to f.

Sediment : After dry, store the sturdy bag

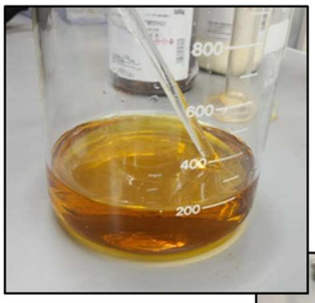
Liquid : colorless → drain

color → apply the liquid to sunlight until the color disappears, then drain

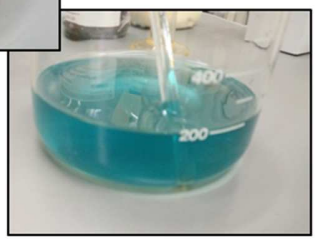
Wastewater Treatment

(in case of COD_{Cr})

a. Reduction

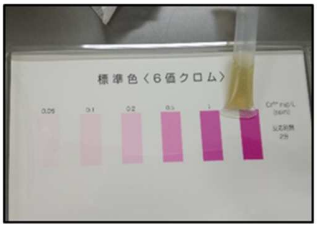


← initial



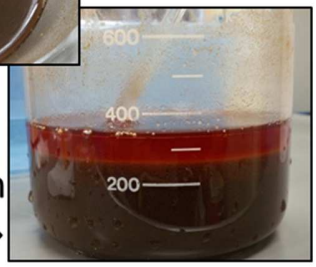
After reduction →

b. Concentration check (Cr^{6+})



c. Sedimentation

← mixing



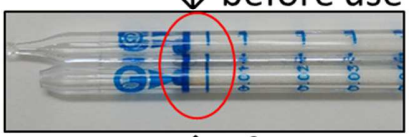
After sedimentation →

d. Filtration

f. Sedimentation(Hg)

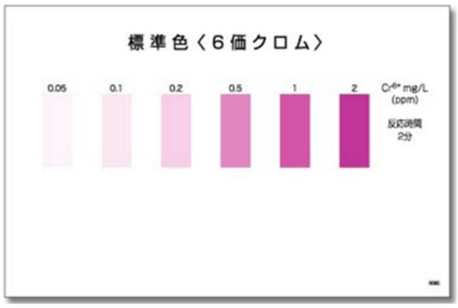
h. Concentration check (Hg)

↓ before use

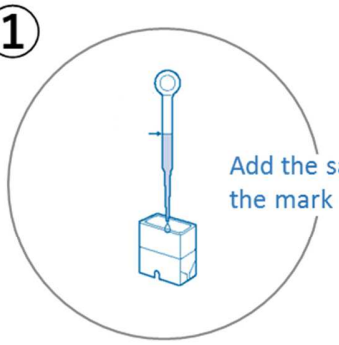


↑ after use

HOW TO USE・・・PACKTEST(Cr6+)

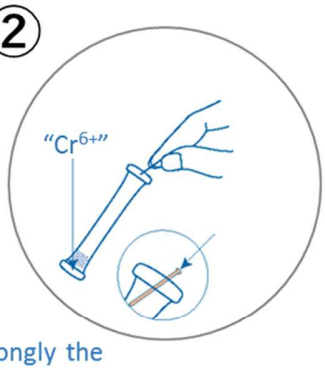


①



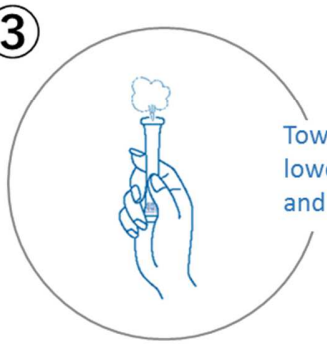
Add the sample with a pipette up to the mark

②



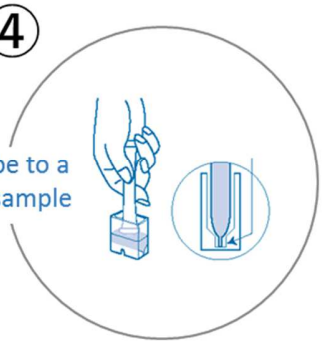
Pull out by pinching this part

③



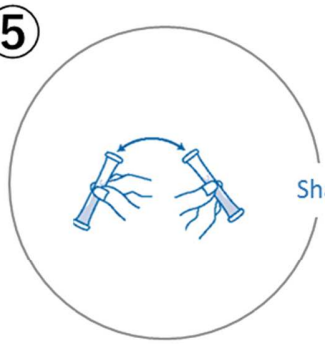
Toward a hole in the top, pinch strongly the lower half of the tube between the finger tips, and bent the tube into the V-shape

④



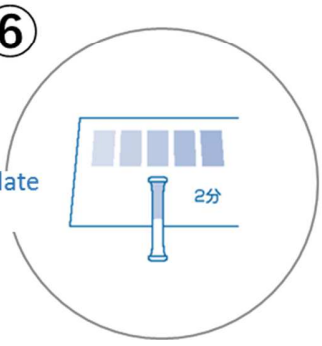
As it is put in the holes in the tube to a bottom of cup, inhale all of the sample

⑤



Shaking 5 times

⑥

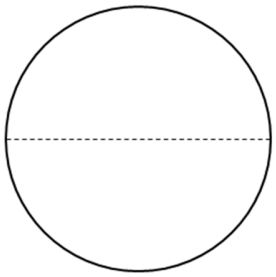


Compare the color of the color plate and tube after 2 minutes

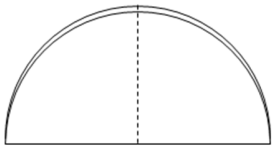
How to make the pleated filter paper

As shown in the following figure, fold the filter paper many times.

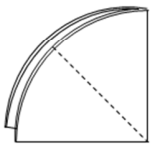
①



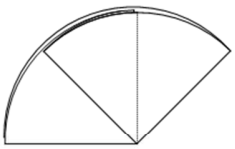
②



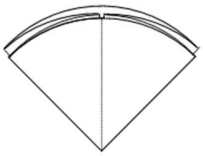
③



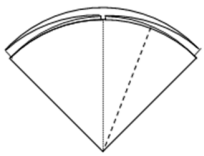
④



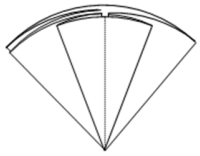
⑤



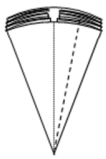
⑥



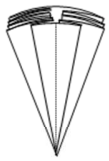
⑦



⑧

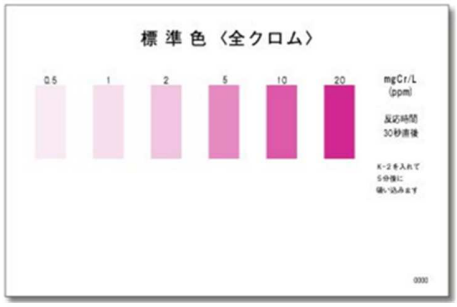


⑨

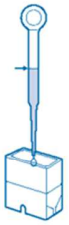


⑩

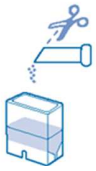
HOW TO USE・・・PACKTEST(Cr・T)



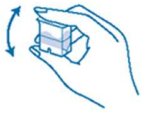
① Add the sample with a pipette up to the mark (0.2mL)



② Add the K-1 solution with a pipette up to the mark (1.5mL)

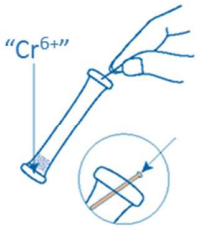


③ Add the K-2 powder



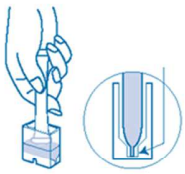
④ Close with the cap, and shake until the reagent has dissolved

⑤ allow to stand for 5 minutes (Shake on the way once or twice)

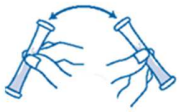


⑥ Pull out by pinching this part

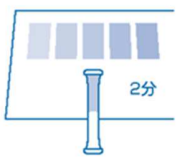
⑦ Toward a hole in the top, pinch strongly the lower half of the tube between the finger tips, and bent the tube into the V-shape



⑧ As it is put in the holes in the tube to a bottom of cup, inhale all of the sample

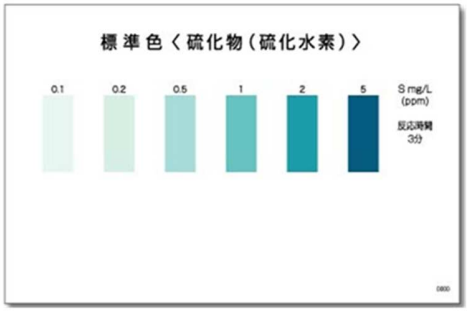


⑨ Shaking 5 times

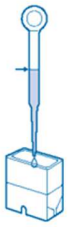


⑩ Compare the color of the color plate and tube after 30-second

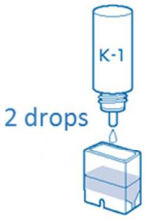
HOW TO USE・・・PACKTEST(S)

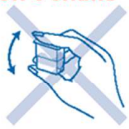


***Work of ①-⑤, be done quickly**

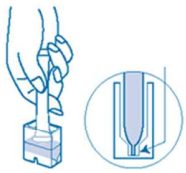


① Add the K-1 solution with a pipette up to the mark (1.5mL)

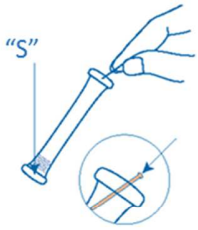




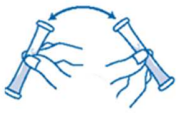
② Add the sample with a pipette up to the mark, and 2 drops pf k-1 solution



⑤ As it is put in the holes in the tube to a bottom of cup, inhale all of the sample

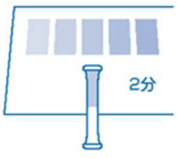


③ Pull out by pinching this part



⑥ Shaking 5 times

④ Toward a hole in the top, pinch strongly the lower half of the tube between the finger tips, and bent the tube into the V-shape



⑦ Compare the color of the color plate and tube after 2 minutes

HOW TO USE

・・・Mercury measurement set

1. Preparation

① Solution B : add a solvent for reagent B to the line and dissolve powder
(Adjusted at the time of use)
② 5M NaOH : 20g Sodium Hydroxide in deionized water make up to 100mL
③ Attach the connection rubber tube to the impinge (Fig.1)
④ Stand 2 tubes in a test tube stand, set 1ml of pipettes in each tubes (Fig.2)

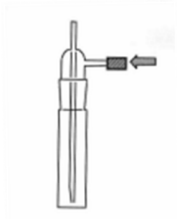


Fig.1 Impinger and the connection rubber tube

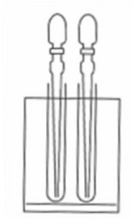


Fig.2 set tubes and pipettes

2. Measurement method

① check the pH value (○ : 1.0 < pH < 11.5,
× : adjust sample so that a pH value becomes a range of 1 to 11.5)
② Transfer the 20ml sample to the impinger
③ Add 1mL Solution A, and 5mL 5M NaOH
④ Add 1mL Solution B
⑤ Break off the both ends of the detector tube and pretreatment tube
⑥ Set as follow(Fig.3):
Confirm the pump handle is fully pushed in. Then insert the detector tube into the rubber inlet with G▶ mark towards the gas sampling pump.

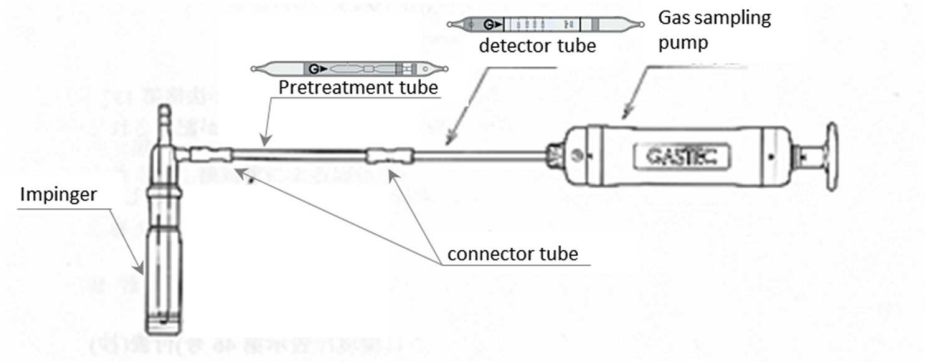


Fig.3 Connection of Mercury measurement kit

⑥ Align the guide marks on the pump shaft red (▲) 100 mL, and pull out the handle until it is locked. Wait until the sampling time has elapsed(1.5min).
⑦ Push back the handle, repeat ⑥ three times (total volume : 400mL)
⑧ After finish the absorption, remove the detector tube. The color in the detector tube changes as the gas is drawn in. Read the measurement at the end of the colored layer. (the color change : white - light orange)

3. Maintenance

Leakage of the gas sampling pump : (see table.1)

If you did not get rid of the bug, please refer to the repair request.

Table.1 The causes and solutions of leakage

	Causes	Solution
Inlet nut	The slack by having forgotten to close	Tighten
Inlet rubber	Damage or aging	Replace the part with new one
Cylinder, Piston	Pollution or lack of grease	Grease up, as follow:

・ Maintenance of the gas sampling pump

(1) Give the tail block turns to the left, uncouple the piston from cylinder

(2) Clean the old grease inside of cylinder and outside of piston off with a soft or paper

(3) Apply grease the inside near the opening of cylinder

(4) Slide down the piston to the cylinder, give the tail block turns to the right, and screw that up tight

(5) Slide the piston in and out approximately 10 times, apply the grease to the cylinder

(6) do the air tightness test of the gas sampling pump, check the performance is good.