Standard Operating Procedure on Ground Water Quality Data Analysis

Step by step guidelines for Ground water quality data analysis

Central Ground Water Board,

Department of Water Resource River Development and Ganga Rejuvenation,
Ministry of Jal Shakti

Standard Operating Procedure on Ground Water Quality Data Analysis

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Executive Summary

Water quality data analysis is the component of the monitoring process that turns collected data into useful information. Analyzing water quality data improves the understanding of the system being monitored and drives management action. Hence, it is essential to prepare a Standard Operating Procedure (SOP) for ground water quality data analysis.

The various monitoring networks to be followed in Central Ground Water Board is discussed in this SOP. The existing and new monitoring stations form the Background Monitoring Networks. Areas which show anomalous concentration of any basic/trace/geogenic /anthropogenic contaminants more than the permissible limit should be monitored regularly as Trend Monitoring Wells. Samples should be collected twice every year i.e., both during Pre-monsoon and post-monsoon. Areas where new geogenic contamination in ground water has been reported or anthropogenic influence has changed the ground water quality be monitored as Special Purpose Monitoring.

Geographical Information System (GIS) tools is used to map and visualize the distribution of various parameters geographically. Time series graphs are used for spotting connections between two or more water quality variables and to identify long-term trends and seasonal variations. Water quality Trend analysis for 5 year or 10 year district-wise/block-wise data is to be carried out during preparation of annual ground water quality report. Based on trend analysis, the reasons for ground water contamination may be assessed and shared with authorities for corrective action.

Suitability of water for drinking purpose is assessed based on BIS and WHO drinking water standards. Various water quality indices like Sodium Absorption Ratio (SAR), Percent Sodium and Residual Sodium Carbonate (RSC), graphical representation like Wilcox diagram and USSL diagram for irrigation suitability and Chloride – bicarbonate ratio for seawater intrusion, Bivariant plot and Scatter plots to visualize the relationship between two water quality parameters or contaminants are demonstrated in this SOP.

The additional parameters to be monitored such as Biochemical Oxygen Demand (BOD), COD, TOC, organic pollutant such as Pesticides, Dioxins, Volatile organic compounds (VOCs), Microbial contaminants like Bacteria, parasites, Total Coliform, Faecal coliform etc, Micro plastics and Pharmaceutical residues, Isotopes studies such asδ18O, δD, δ17O, 14C, 3H, 85Kr, 39Ar, 36Cl, and Radioactive elements like Uranium and Radon etc are placed in accordance with the CGWB uniform protocol for groundwater analysis and as per CGWB Vision 2047.

The SOP also communicates that groundwater quality report shall be shared with States/ UTs, DoDW&S and copy shall be marked to the district administration and any information regarding groundwater contamination shall be brought in to the public domain through CGWB website and NWIC.

Amendment Sheet

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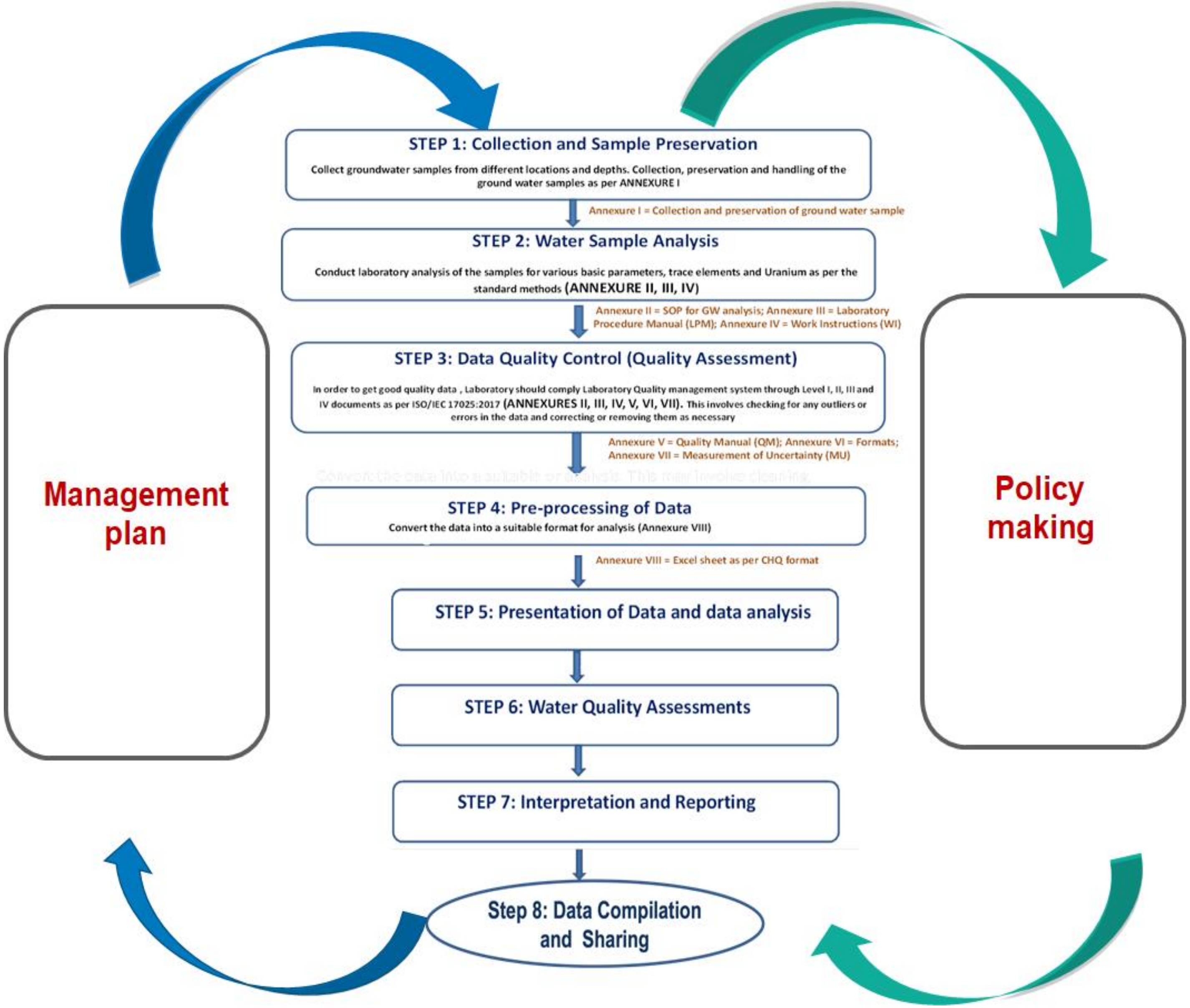
1. Introduction & Scope

Groundwater quality data analysis is crucial for the sustainable management of water resources. Effective groundwater management requires knowledge of the quality of available groundwater resources, identification of potential contamination sources, and development of strategies to prevent contamination. Overall, groundwater quality data analysis is critical for protecting human health and the environment, complying with regulations, promoting economic benefits, and ensuring sustainable water resource management. The Central Ground Water Board (CGWB) disseminates a quantum of groundwater quality data annually. CGWB ensures that significant ground water quality data is widely disseminated through various platforms to support informed decision-making and sustainable groundwater management.

This handbook aims to guide personnel to ensure uniform protocol for ground water quality data analysis and uniform guidelines for ground water sampling, sample preservation, sample analysis techniques, quality control checks, data analysis, Interpretation, reporting, data compiling and sharing of data and report. The subsequent sections outline protocols for new ground water monitoring framework, ground water sampling, their analysis methodology, data preprocessing, data analysis, Interpretation, reporting, data compilation and sharing. This handbook on ground water quality data analysis is a concise portion of Ground *Water Quality data analysis Report* and subject to modification when necessary to adapt to diverse site conditions, equipment constraints, or procedural limitations.

2. Flowchart for Methodology (SOP) on Groundwater Quality data analysis



Management plan

STEP 1: Collection and Sample Preservation

Collect groundwater samples from different locations and depths. Collection, preservation and handling of the ground water samples as per ANNEXURE I

Annexure I = Collection and preservation of ground water sample

STEP 2: Water Sample Analysis

Conduct laboratory analysis of the samples for various basic parameters, trace elements and Uranium as per the standard methods (ANNEXURE II, III, IV)

Annexure II = SOP for GW analysis; Annexure III = Laboratory Procedure Manual (LPM); Annexure IV = Work Instructions (WI)

STEP 3: Data Quality Control (Quality Assessment)

In order to get good quality data , Laboratory should comply Laboratory Quality management system through Level I, II, III and IV documents as per ISO/IEC 17025:2017 (ANNEXURES II, III, IV, V, VI, VII). This involves checking for any outliers or errors in the data and correcting or removing them as necessary

Annexure V = Quality Manual (QM); Annexure VI = Formats; Annexure VII = Measurement of Uncertainty (MU)

Convert the data into a suitable or analysis. This may involve cleaning,

STEP 4: Pre-processing of Data

Convert the data into a suitable format for analysis (Annexure VIII)

Annexure VIII = Excel sheet as per CHQ format

STEP 5: Presentation of Data and data analysis

STEP 6: Water Quality Assessments

STEP 7: Interpretation and Reporting

Step 8: Data Compilation and Sharing

Policy making

- Step by step guidelines for Ground water quality data analysis

- Step 1 to Step 3 related to Ground Water Quality monitoring and analysis (refer documents Annexure I to Annexure VII following NABL protocols as per ISO/IEC 17025:2017).

- Data analysis part starts from Step 5 to Step 7, For detail explanation refer **Ground Water Quality data analysis Report (GWQDA-Report)**

3. Collection and Sample Preservation

The protocol for new groundwater quality monitoring framework is illustrated in Table 1 and 2. Criteria for Special Purpose Monitoring or Criteria for selection of Special purpose/New Hotspot monitoring should be in accordance to Figure 1. Ground Water Monitoring and analysis should be done as per protocol illustrated in Table 1.

Table 1: Sampling frequency and parameters for analysis

Type of Water Quality Monitoring	Sampling frequency	Parameters for analysis
Background Monitoring (All WQ Stations)	**Once every 5 years** **(PRE-MONSOON SEASON)**	**i) 15 major parameters** pH, EC, Ca^{2+}, Mg^{2+}, TH, Na^{+}, K^{+},F^{-}, CO_3^{2-}, HC Cl^{-}, NO_3^{-}, SiO_2, PO_4^{3-} **ii) minimum 5 trace elements** Fe, As, U plus any two-trace metal as per need of the respective region.
Trend Monitoring Minimum 25% of WQ stations (All locations where constituents exceed the permissible limit of IS 100500:2012 drinking water standards need to be study before selection of Trend Monitoring)	**Every Year** **(BOTH PRE AND POST-MONSOON SEASON)**	
Special Purpose Monitoring/ New Hotspot monitoring	**Only under special studies** **(**One time study, duration: region's need based) **(BOTH PRE AND POST-MONSOON SEASON)** Detailed sampling on a grid of 2 km x 2 km (From area falling within a radius of 5 km from locations from where the Contaminants like Arsenic, Uranium, Lead, Cadmium, Chromium, Selenium etc.)	

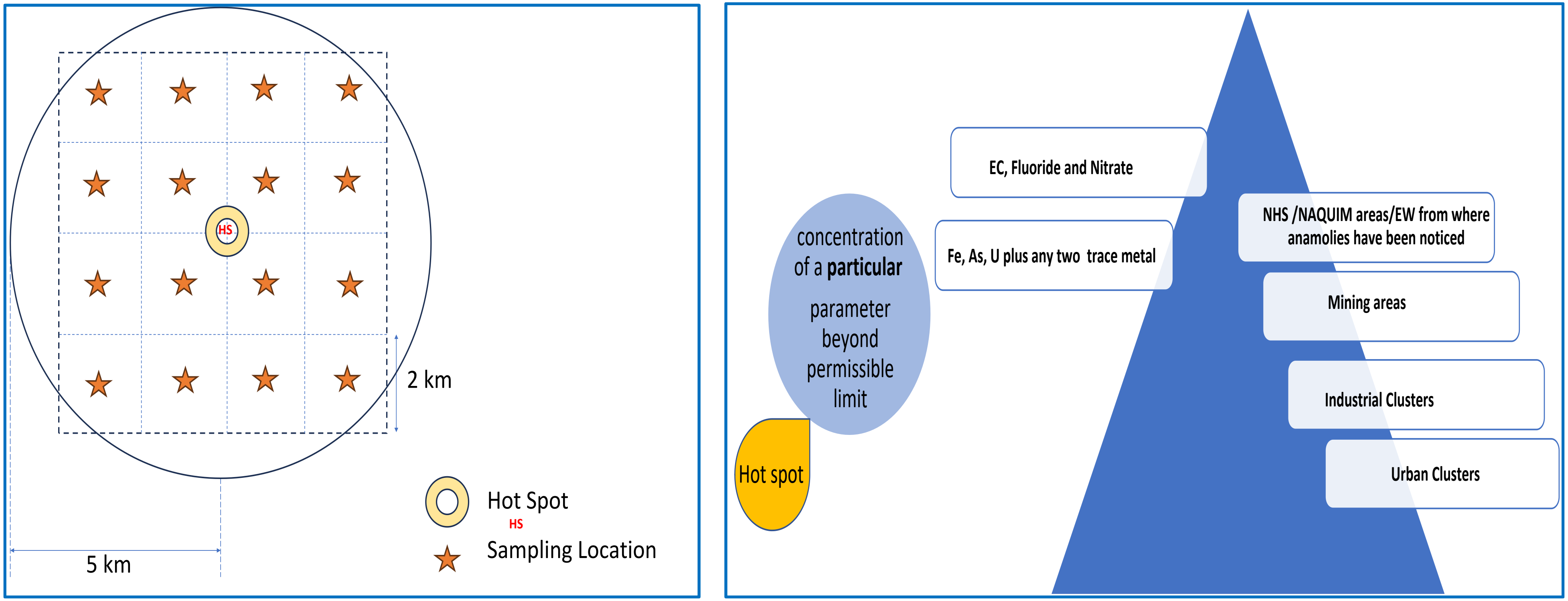


Figure 1: Criteria for Special Purpose Monitoring/New Hotspot monitoring

- **All the existing and new monitoring stations form the Background Monitoring.**
- **Stations/Areas which show anomalous concentration of any basic/trace/geogenic/anthropogenic contaminants more than the permissible limit should be monitored regularly and termed as Trend Monitoring Wells.**
- **In New Hotspot monitoring special focus should be taken up in areas where new geogenic contamination in ground water has been reported or anthropogenic influence has changed the ground water quality**

Table 2: Criteria for selection of new Ground Water Quality Monitoring Stations

S. No.	Thematic Area	No of water quality monitoring stations recommended
1	Urban Areas	One (1) Groundwater Quality GWQ monitoring stations in every 5 sq km
2	Agricultural belts with intensive application of chemical fertilizers	One (1) GWQ monitoring stations every 50 sq km area
3	Industrial areas	WQ Monitoring station in 1 x 1 Km grid.
4	Mining Areas	WQ Monitoring station in 1 x 1 Km grid.
5	Major Landfill sites	To establish well(s) within 100 m. from the landfill sites both in the upstream downstream side.
6	Sites where surface water quality is being monitored by CWC or CPCB	One (1) GWQ monitoring stations for Groundwater quality
7	Salt water intrusion	Monitoring stations are needed to be established along and across the coast li
8	Recharge Site/Special intervention Areas	To establish well(s) both in the upstream and downstream side and within 10 such sites.

3.1 Ground Water Sampling and preservation techniques

The sample collector should take utmost care while collecting, storing and handling the samples to the laboratory. The Laboratory should further maintain the recommended conditions and follow the parameter wise timeline for analysis as per Table 3.

Table 3. Summary of Sampling and Handling Requirements

Determination	Container	Minimum Sample Size, mL	Preservation	Maximum Storage Recommended	Analysis Standard Method
Field parameters (pH, EC, Temp etc.)				• Analyze immediately	APHA, 2021, 24th Edition/ IS standard IS 3025
Basic Parameters	PE	1000		• All basic parameters must be analysed within 3 months	
Heavy metals	PE (A)	500, 1000 (using AAS) 60 (using ICPMS)	For dissolved metals filter immediately, add HNO_3 to pH<2	• 6 months	

PE = Polyethylene or equivalent

PE(A) = Polyethylene acid wash

Note: Ground Water samples should be transported to Regional Chemical Laboratory as soon as possible, preferably within 48 hours. Sample should be refrigerated below 6°C for Temperature sensitive constituents.

Note: **Important information on the sample bottle/container should include**

1. Sample code number   2. Location
2. Source and type of sample   4. Date of sampling
5. Preservation carried out on the sample   6. Field Officer Name

Table 4. Sample submission format

Sl No	Details of Ground Water Quality Monitoring Stations																						
												Field parameters					No. of samples submitted to analyze						
	Well No.	State / UT	District	Block/ Taluka	Village	Station Name/ Location	Longitude (DD)	Latitude (DD)	Source of Sample	Depth of Sample	Sampling Date	Temp (°C)	pH	EC (µS/cm)	DO (mg/l) (Optional for Pollution/Special study)	ORP (mV) (Optional for Pollution/Special study)	Basic	Basic (Refrigerated sample)	Fe+As	Heavy Metal	U	Isotope	Any other

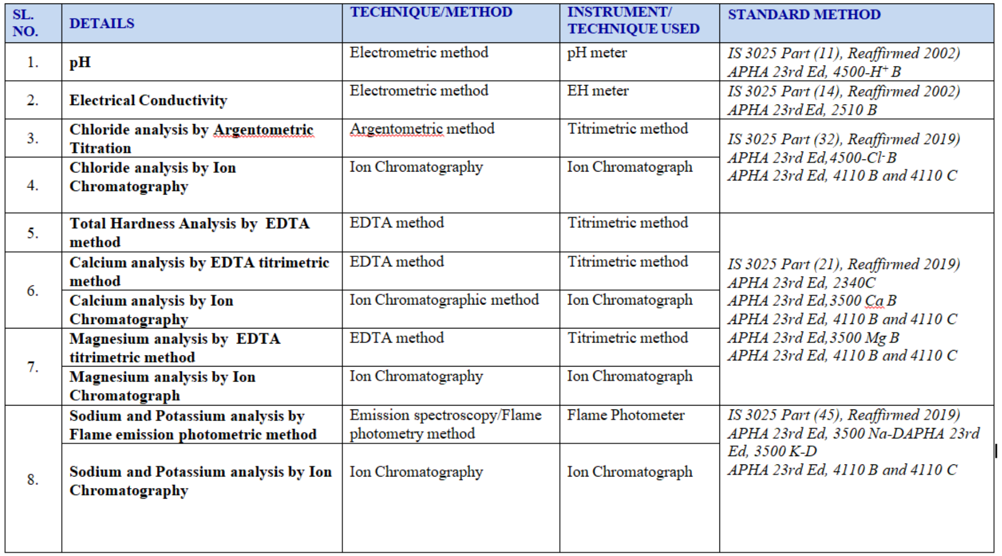
The above sample submission format (excel sheet) should be submitted in hard as well as in soft copy while submitting the ground water samples to Regional Chemical laboratory.

Geographical coordinates of a station must be accurate for its location.

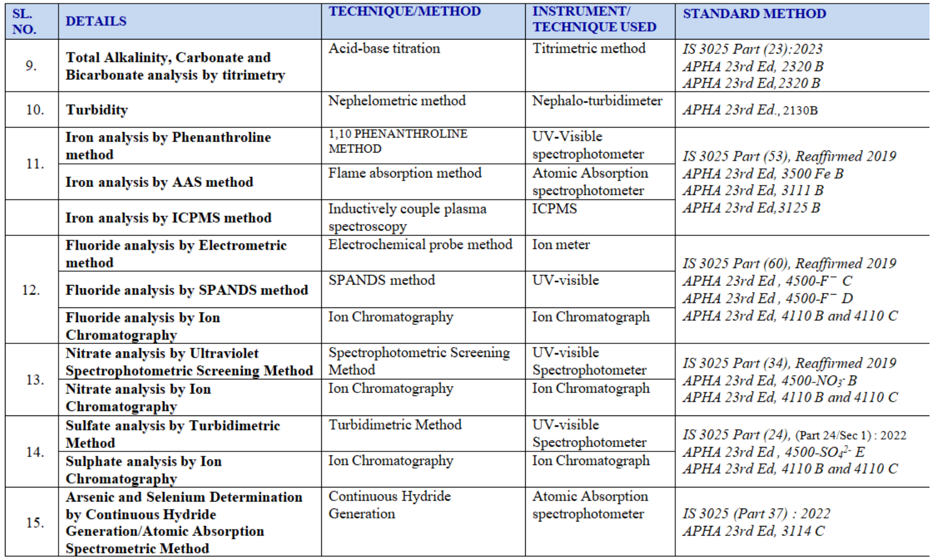
4. Water Sample Analysis

Laboratory analysis of the samples for various basic parameter, trace elements and uranium as per the standard method illustrated in Table 5.

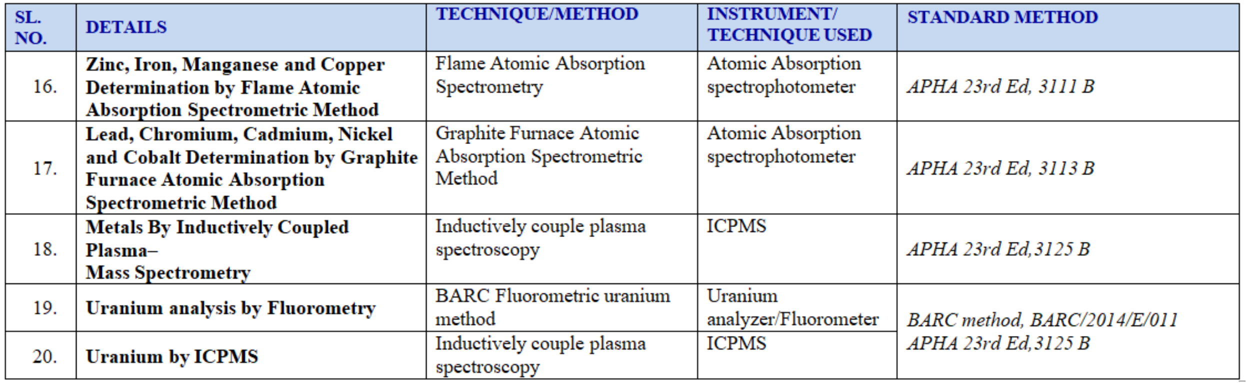
Table 5. Specifications of standard methods used for various parameters.



SL. NO.	DETAILS	TECHNIQUE/METHOD	INSTRUMENT/ TECHNIQUE USED	STANDARD METHOD
1.	**pH**	Electrometric method	pH meter	*IS 3025 Part (11), Reaffirmed 2002)* *APHA 23rd Ed, 4500-H$^+$ B*
2.	**Electrical Conductivity**	Electrometric method	EH meter	*IS 3025 Part (14), Reaffirmed 2002)* *APHA 23rd Ed, 2510 B*
3.	**Chloride analysis by Argentometric Titration**	Argentometric method	Titrimetric method	*IS 3025 Part (32), Reaffirmed 2019)* *APHA 23rd Ed,4500-Cl$^-$ B* *APHA 23rd Ed, 4110 B and 4110 C*
4.	**Chloride analysis by Ion Chromatography**	Ion Chromatography	Ion Chromatograph	
5.	**Total Hardness Analysis by EDTA method**	EDTA method	Titrimetric method	*IS 3025 Part (21), Reaffirmed 2019)* *APHA 23rd Ed, 2340C* *APHA 23rd Ed,3500 Ca B* *APHA 23rd Ed, 4110 B and 4110 C* *APHA 23rd Ed,3500 Mg B* *APHA 23rd Ed, 4110 B and 4110 C*
6.	**Calcium analysis by EDTA titrimetric method**	EDTA method	Titrimetric method	
	Calcium analysis by Ion Chromatography	Ion Chromatographic method	Ion Chromatograph	
7.	**Magnesium analysis by EDTA titrimetric method**	EDTA method	Titrimetric method	
	Magnesium analysis by Ion Chromatograph	Ion Chromatography	Ion Chromatograph	
8.	**Sodium and Potassium analysis by Flame emission photometric method**	Emission spectroscopy/Flame photometry method	Flame Photometer	*IS 3025 Part (45), Reaffirmed 2019)* *APHA 23rd Ed, 3500 Na-DAPHA 23rd Ed, 3500 K-D* *APHA 23rd Ed, 4110 B and 4110 C*
	Sodium and Potassium analysis by Ion Chromatography	Ion Chromatography	Ion Chromatograph	



SL. NO.	DETAILS	TECHNIQUE/METHOD	INSTRUMENT/ TECHNIQUE USED	STANDARD METHOD
9.	**Total Alkalinity, Carbonate and Bicarbonate analysis by titrimetry**	Acid-base titration	Titrimetric method	*IS 3025 Part (23):2023* *APHA 23rd Ed, 2320 B* *APHA 23rd Ed,2320 B*
10.	**Turbidity**	Nephelometric method	Nephalo-turbidimeter	*APHA 23rd Ed.*, 2130B
11.	**Iron analysis by Phenanthroline method**	1,10 PHENANTHROLINE METHOD	UV-Visible spectrophotometer	*IS 3025 Part (53), Reaffirmed 2019* *APHA 23rd Ed, 3500 Fe B* *APHA 23rd Ed, 3111 B* *APHA 23rd Ed,3125 B*
	Iron analysis by AAS method	Flame absorption method	Atomic Absorption spectrophotometer	
	Iron analysis by ICPMS method	Inductively couple plasma spectroscopy	ICPMS	
12.	**Fluoride analysis by Electrometric method**	Electrochemical probe method	Ion meter	*IS 3025 Part (60), Reaffirmed 2019* *APHA 23rd Ed , 4500-F$^-$ C* *APHA 23rd Ed , 4500-F$^-$ D* *APHA 23rd Ed, 4110 B and 4110 C*
	Fluoride analysis by SPANDS method	SPANDS method	UV-visible	
	Fluoride analysis by Ion Chromatography	Ion Chromatography	Ion Chromatograph	
13.	**Nitrate analysis by Ultraviolet Spectrophotometric Screening Method**	Spectrophotometric Screening Method	UV-visible Spectrophotometer	*IS 3025 Part (34), Reaffirmed 2019* *APHA 23rd Ed, 4500-NO$_3^-$ B* *APHA 23rd Ed, 4110 B and 4110 C*
	Nitrate analysis by Ion Chromatography	Ion Chromatography	Ion Chromatograph	
14.	**Sulfate analysis by Turbidimetric Method**	Turbidimetric Method	UV-visible Spectrophotometer	*IS 3025 Part (24),* (Part 24/Sec 1) : 2022 *APHA 23rd Ed , 4500-SO$_4^{2-}$ E* *APHA 23rd Ed, 4110 B and 4110 C*
	Sulphate analysis by Ion Chromatography	Ion Chromatography	Ion Chromatograph	
15.	**Arsenic and Selenium Determination by Continuous Hydride Generation/Atomic Absorption Spectrometric Method**	Continuous Hydride Generation	Atomic Absorption spectrophotometer	*IS 3025 (Part 37) : 2022* *APHA 23rd Ed, 3114 C*



SL. NO.	DETAILS	TECHNIQUE/METHOD	INSTRUMENT/ TECHNIQUE USED	STANDARD METHOD
16.	**Zinc, Iron, Manganese and Copper Determination by Flame Atomic Absorption Spectrometric Method**	Flame Atomic Absorption Spectrometry	Atomic Absorption spectrophotometer	*APHA 23rd Ed, 3111 B*
17.	**Lead, Chromium, Cadmium, Nickel and Cobalt Determination by Graphite Furnace Atomic Absorption Spectrometric Method**	Graphite Furnace Atomic Absorption Spectrometric Method	Atomic Absorption spectrophotometer	*APHA 23rd Ed, 3113 B*
18.	**Metals By Inductively Coupled Plasma–Mass Spectrometry**	Inductively couple plasma spectroscopy	ICPMS	*APHA 23rd Ed,3125 B*
19.	**Uranium analysis by Fluorometry**	BARC Fluorometric uranium method	Uranium analyzer/Fluorometer	*BARC method, BARC/2014/E/011* *APHA 23rd Ed,3125 B*
20.	**Uranium by ICPMS**	Inductively couple plasma spectroscopy	ICPMS	

5. Data Quality Control

Groundwater quality data validation is an essential step in ensuring the reliability and accuracy of the data. Detail QC & QA as per ISO/IEC 17025:2017 protocol for accreditation of Water testing Lab by NABL are illustrated in ***Annexure II to VII and Ground Water Quality Data Analysis Report.***

One of the mandatory steps to follow is as follows

Charge Balance Error

$$\%\text{balance error} = \frac{\Sigma\text{cat ions} - \Sigma\text{anions}}{\Sigma\text{cat ions} + \Sigma\text{anions}} * 100$$

Error ± 5% for GW & SW
Not applicable for very concentrated and very dilute solutions

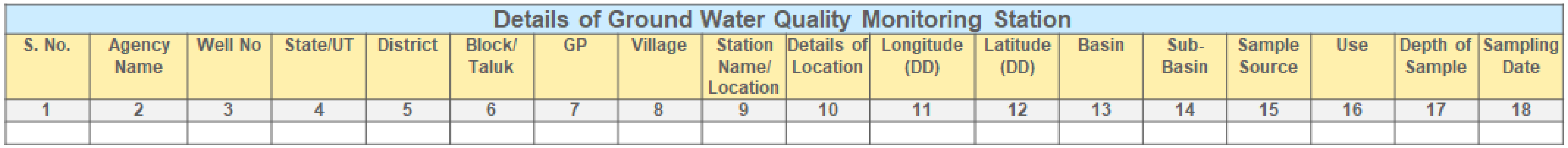
TDS (mg/l) ~ (0.65) x EC (µS/cm)
For Freshwater

- **It is recommended to take the value of constant as 0.65 in all regions for maintaining uniformity of data.**
- **ECB of 2% is inevitable in almost all laboratories. ECB%≤ 5% for groundwater but not applicable for very concentrated and very dilute solutions. ECB may go upto 10% for very low and very high concentrations.**
- **Flag Data: Flag any data that does not meet the quality control criteria and document the reason for flagging. The sample should be re-sampled/re-analysed to ensure the accuracy and validation of data.**

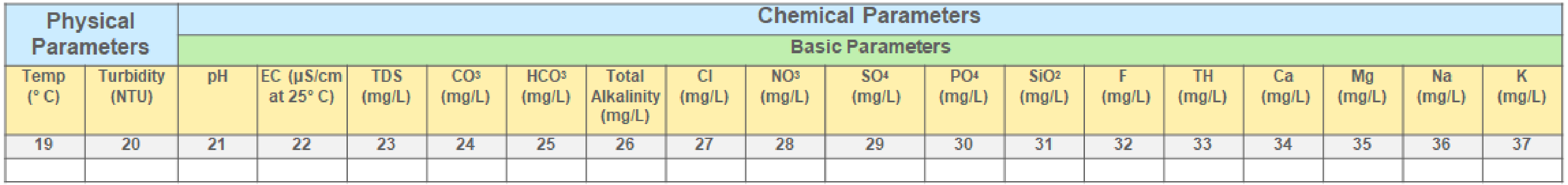
6. Pre-processing of Data

Convert the ground water quality data into a suitable format for analysis which is illustrated in Table 6. The same format will used to share data with Central Pollution Control Board (CPCB).

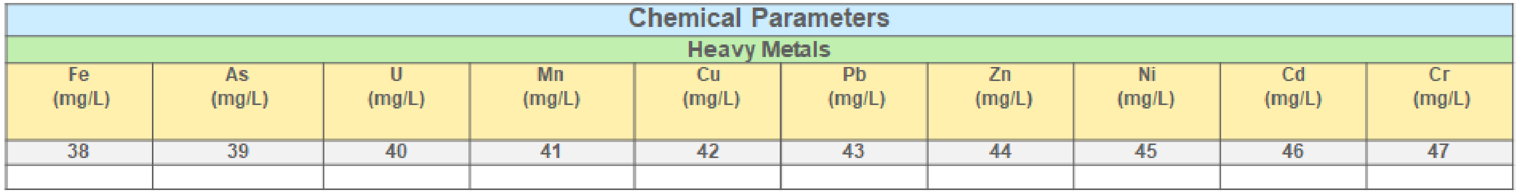
Table 6. Format for Water quality data sharing (Common excel format CGWB-CPCB)



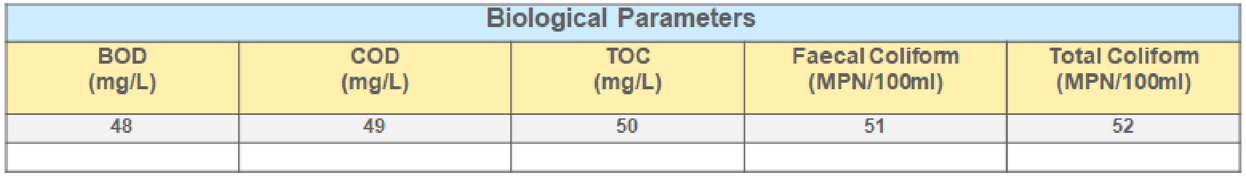
Details of Ground Water Quality Monitoring Station																	
S. No.	Agency Name	Well No	State/UT	District	Block/ Taluk	GP	Village	Station Name/ Location	Details of Location	Longitude (DD)	Latitude (DD)	Basin	Sub-Basin	Sample Source	Use	Depth of Sample	Sampling Date
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18



Physical Parameters		Chemical Parameters																	
		Basic Parameters																
Temp (° C)	Turbidity (NTU)	pH	EC (µS/cm at 25° C)	TDS (mg/L)	CO_3 (mg/L)	HCO_3 (mg/L)	Total Alkalinity (mg/L)	Cl (mg/L)	NO_3 (mg/L)	SO_4 (mg/L)	PO_4 (mg/L)	SiO_2 (mg/L)	F (mg/L)	TH (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37



Chemical Parameters									
Heavy Metals									
Fe (mg/L)	As (mg/L)	U (mg/L)	Mn (mg/L)	Cu (mg/L)	Pb (mg/L)	Zn (mg/L)	Ni (mg/L)	Cd (mg/L)	Cr (mg/L)
38	39	40	41	42	43	44	45	46	47



Biological Parameters				
BOD (mg/L)	COD (mg/L)	TOC (mg/L)	Faecal Coliform (MPN/100ml)	Total Coliform (MPN/100ml)
48	49	50	51	52

Checking of Coordinates: Geographical coordinates of a station must lie within the country boundary.

7. Data Analysis, Interpretation and Reporting

The specific groundwater data analyses are to be conducted depending on the water quality information desired or the specific questions about water quality being asked. Water quality concerns are wide and varied, but probably the most commonly asked questions are:

The Laboratory should make sure that the data analysis and interpretation performed by it is able to answer these questions clearly for effective management plans.

1. What is the water quality at any specific location or area?
2. What are the water quality trends in the region? Is the quality improving or getting worse?
3. How do specific water quality parameters relate with one another at given sites?
4. What are the total mass loadings of materials moving in and out of water systems and what sources and quantities do these originate?
5. Are sampling frequencies adequate, and are sampling stations suitably located to represent water quality conditions in an area?

7.1 Groundwater quality data analysis for Technical Reports

7.1.1 Data interpretation for drinking purposes

Comparing the data with national water quality standards - gives an insight into the scale of a particular data set (e.g., if the data show that a specific groundwater sample contains a higher concentration of pollutant than is allowed by a national drinking water standard -BIS drinking water specification, most people would assume that it may not be safe to drink this water).

(a) Statistical analysis

Analyze the data using appropriate statistical methods and tools such as descriptive statistics such as mean, median, mode, standard deviation, and range to describe the data set. Interpret the results to determine whether groundwater quality is within acceptable limits/permissible limits per BIS standards. If not, identify areas of concern and potential sources of contamination in consultation with field officers and by examining field conditions. Groundwater quality data comparing with national and international standards as illustrated in *Figure 3* *(Dutta et al., 2022)* *of GWQDA-Report may be referred*. An example of Statistical analysis is given below.

Paramters	**Unit**	**Post-Monsoon**				**Pre-Monsoon**				**Prescribed limits**	
		Min	**Mean**	**Max**	**SD**	**Min**	**Mean**	**Max**	**SD**	**BIS**	**WHO**

(b) Graphical analysis

Graphical representation of Ground Water Quality data is listed below:

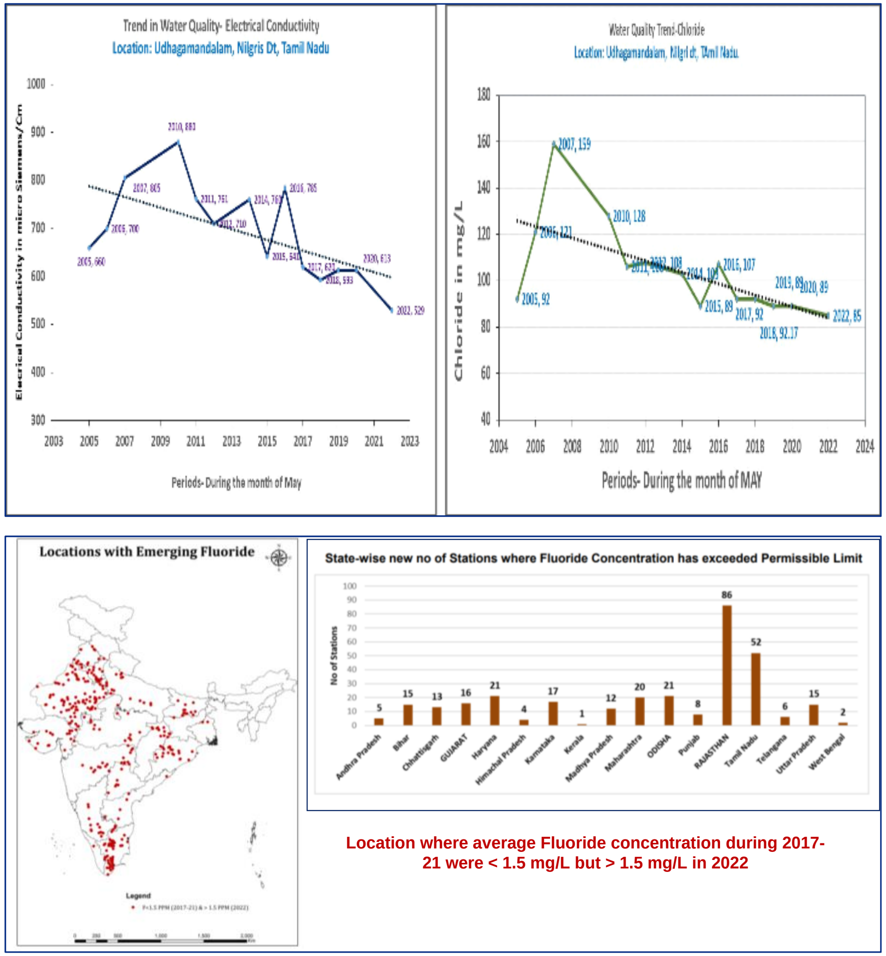
(i) Spatial Analysis

This type of analysis is essential because it helps to identify areas that may be at higher risk of contamination, as well as the sources and causes of contamination. Geographical Information System (GIS) tools may be used to map and visualize the distribution of various parameters geographically. Some examples of graphs showing Spatial analysis could be referred from *Datta et al., (2021); Barman et al., (2022); Figure* 4.**(GWQDA-Report).**

- **Contour map should be prepared for EC and Cl.**
- **Point map for As, F, U, Cd, etc.**

(ii) Trends Analysis

The **trend analysis for 5 or 10 years period using district or block-wise water quality data** is to be carried out and included in the water quality report. More than 10 year long- term trend analysis can be done subjected to availability of suitable data. Based on trend analysis, the reasons for ground water contamination may be assessed and shared with authorities for corrective action and adjustment of management strategies accordingly. Some examples of graphs showing trends analysis could be referred from the examples below.



Location where average Fluoride concentration during 2017-21 were < 1.5 mg/L but > 1.5 mg/L in 2022

Figure 2. (Up) Figure showing time series analysis for Electrical Conductivity and Chloride at Udhagamandalam, Nilgiris Dt, Tamil Nadu; (Down) trends analysis of Fluoride distribution

Year	Total Number of samples analysed	No. of districts affected by Fluoride	No. of locations affected by Fluoride	% of locations affected by Fluoride (F >1.5mg/l)
2017	13225	207	736	**5.57**
2018	13229	212	862	**6.52**
2019	12475	226	899	**7.21**
2020	6366	131	449	**7.05**
2021	8482	142	450	**5.31**
2022	15507	392	1048	**6.76**

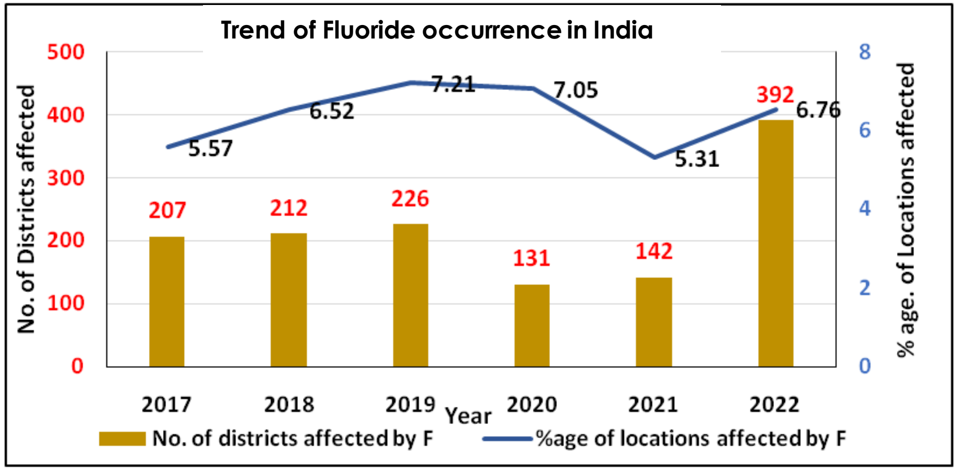


Figure 3. Example of Table and figure showing trend analysis of Fluoride of India

7.1.2 Data interpretation for irrigation purposes

Suitability of ground water for irrigation purpose is evaluated based on chemical characteristics indicative of their potential to create soil condition hazardous to crop growth and yield. Various indices are used for assessment and classification of ground water into different categories. Some of the widely used criteria are discussed below. The data obtained from various indices can be illustrated in ***Table 7 of GWQDA-Report.***

(a) U S Salinity diagram

U S Salinity diagram (Figure 4) can be used to quickly determine the viability of water for irrigation purposes. For detail explanation refers **GWQDA-Report**.

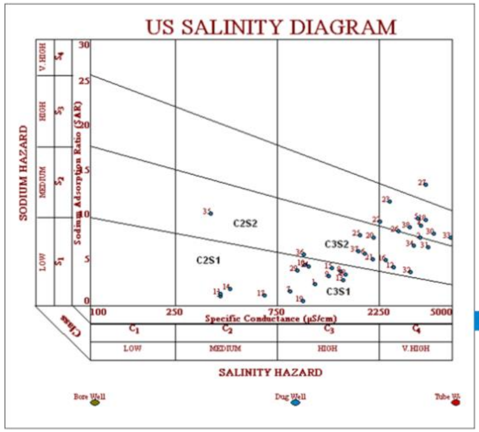
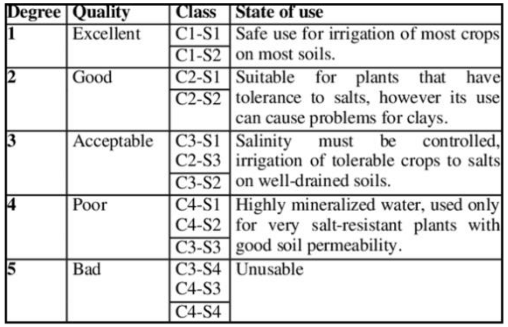
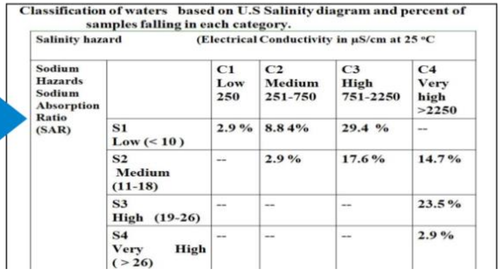


Figure showing US Salinity Diagram



Degree	Quality	Class	State of use
1	Excellent	C1-S1 C1-S2	Safe use for irrigation of most crops on most soils.
2	Good	C2-S1 C2-S2	Suitable for plants that have tolerance to salts, however its use can cause problems for clays.
3	Acceptable	C3-S1 C2-S3 C3-S2	Salinity must be controlled, irrigation of tolerable crops to salts on well-drained soils.
4	Poor	C4-S1 C4-S2 C3-S3	Highly mineralized water, used only for very salt-resistant plants with good soil permeability.
5	Bad	C3-S4 C4-S3 C4-S4	Unusable



Classification of waters based on U.S Salinity diagram and percent of samples falling in each category.

Salinity hazard		(Electrical Conductivity in μS/cm at 25 °C			
Sodium Hazards Sodium Absorption Ratio (SAR)		C1 Low 250	C2 Medium 251-750	C3 High 751-2250	C4 Very high >2250
	S1 Low (< 10)	2.9 %	8.8 4%	29.4 %	--
	S2 Medium (11-18)	--	2.9 %	17.6 %	14.7 %
	S3 High (19-26)	--	--	--	23.5 %
	S4 Very High (> 26)	--	--	--	2.9 %

Figure 4: Figure showing U S Salinity diagram

Several water quality indices should be calculated which indicate the suitability of water for different uses

- ***a.*** *Percent s*odium Absorption Ration (SAR)
- **b.** Percent Sodium for irrigation suitability
- **c.** Kelly's index (KI)
- **d.** Residual Sodium Carbonate – for irrigation suitability
- **e.** Chloride – bicarbonate ratio

(b) Wilcox Plot

Wilcox classified groundwater for irrigation purposes based on percent sodium and EC. For detail explanation refers **GWQDA-Report**. The water quality data of a well for the period of 1992 to 2006 was plotted on Wilcox plot for the classification of groundwater samples with respect to percent sodium and EC is shown in Figure 10.

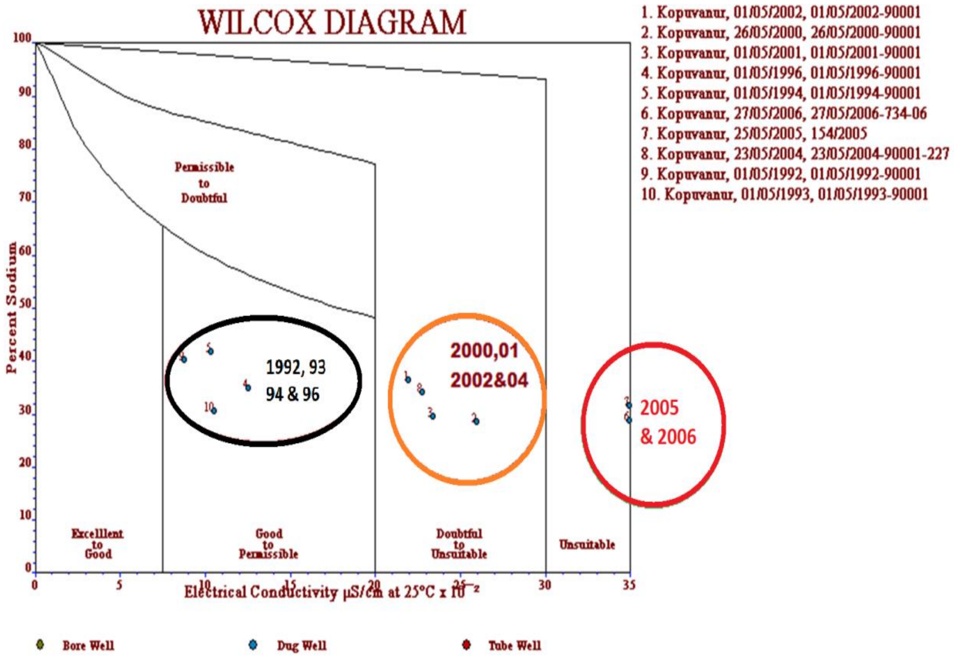


Figure 5. Figure showing classification of groundwater with respect to percent sodium and EC (Wilcox Diagram)

Table 7. Showing Classification of ground water samples for irrigation purposes.

Parameters	Range	Classification	Number of samples Pre-Monsoon	Post -monsoon
Total Dissolved Solid (TDS) (mg/L)	<1000	Non-saline	600	599
	1000-3000	Slightly saline	2	2
	3000-10000	Moderately saline	0	0
	>10000	Very saline	0	1
Salinity hazard (EC) (µS/cm)	<250	Excellent	279	394
	250-750	Good	267	184
	750-2000	Permissible	54	22
	2000-3000	Doubtful	0	1
	>3000	Unsuitable	0	0
Alkalinity hazard (SAR)	<10	Excellent	602	598
	10--18	Good	0	1
	18-26	Doubtful	0	1
	>26	Unsuitable	0	2
Percent Sodium (%Na)	<20	Excellent	98	338
	20-40	Good	240	149
	40-60	Permissible	185	88
	60-80	Doubtful	76	22
	>80	Unsuitable	3	5
Kelly's Index (KI)	<1	Suitable	467	564
	>1	Unsuitable	135	38
Residual sodium carbonate (RSC)	<1.25	Suitable	539	566
	1.25-2.5	Marginally suitable	37	22
	>2.5	Unsuitable	26	14

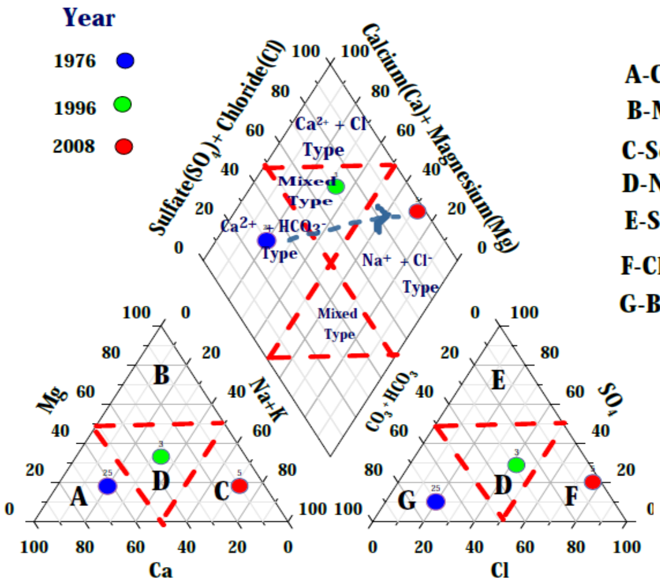
7.1.3. Groundwater quality data analysis for Hydrogeological Processes

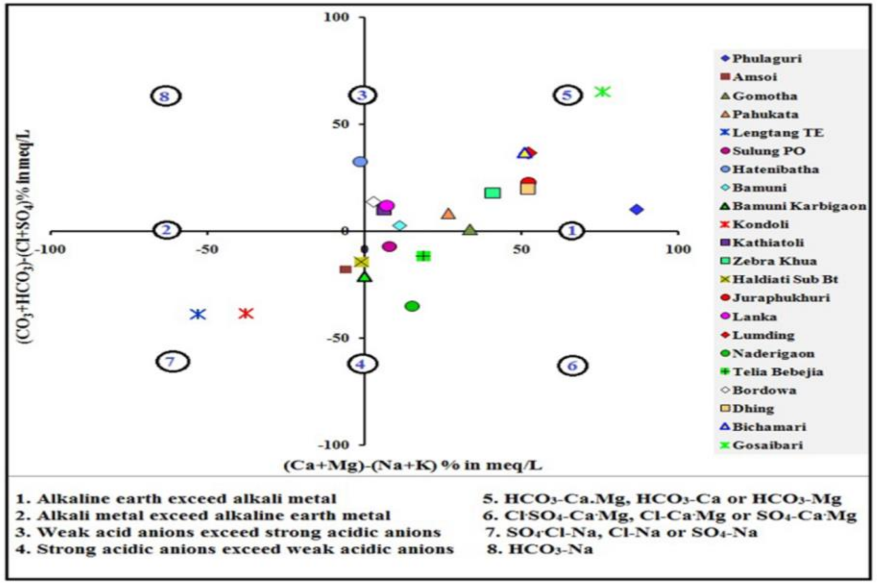
(a) Piper diagram

A trilinear diagram, Piper or Hill diagram, is used for identifying facies, as shown in Figure 6. The position of analysis of a water sample placed on a Piper plot can help reach a tentative conclusion as to the origin of groundwater. Piper plots can help us understand water type, precipitation, mixing and ion exchange in aquifer geochemistry. For detail explanation refers **GWQDA-Report**. Figure 6 shows the Piper plot of a groundwater sample from Vridachalam, Tamil Nadu, where the Water quality data of a well from 1986 to 2008 is plotted.

(b) Chadha Diagram

Another approach to investigating Groundwater facies assessment was introduced in the form of a modified Piper Diagram by D.K. Chadha, the former Chairman of CGWB (Chadha et al. in 1999). It's a simplified adaptation of the original Piper plot. The hydrogeochemical facies classification is then derived from the information presented in the Chadha diagram (Figure 7). *Refers **GWQDA-Report** for illustrated explanation.*





1. Alkaline earth exceed alkali metal
2. Alkali metal exceed alkaline earth metal
3. Weak acid anions exceed strong acidic anions
4. Strong acidic anions exceed weak acidic anions
5. HCO_3-Ca.Mg, HCO_3-Ca or HCO_3-Mg
6. Cl·SO_4-Ca·Mg, Cl-Ca·Mg or SO_4-Ca·Mg
7. SO_4·Cl-Na, Cl-Na or SO_4-Na
8. HCO_3-Na

Figure 6. Figure showing a trilinear diagram known as Piper or Hill diagram.

Figure 7. Figure showing Chadha Diagram (Barman et al., 2022)

(c) Schoeller diagram

Schoeller diagrams are used to show the relative concentrations of anions and cations typically expressed in milliequivalents per litre. Multiple samples from different wells may be plotted on a single diagram to distinguish similar patterns in the ratios of particular anions and cations. These patterns may be used to distinguish common or dissimilar source areas of water drawn from multiple wells. Figure 8 shows that shallow aquifer wells have different nitrate concentrations. For the same study area, nitrate concentration for the deeper aquifer is close to zero except for one well, which indicates that the deeper aquifer is not affected by nitrate. Still, the shallow aquifer is affected by nitrate due to anthropogenic activities

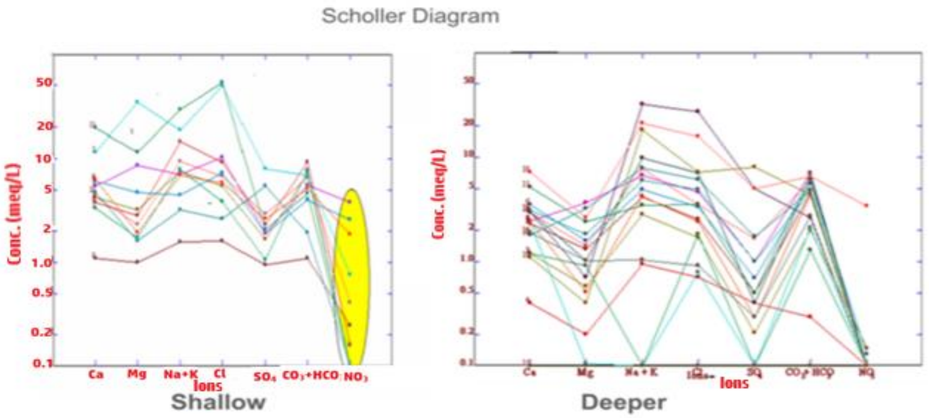


Figure 8: Relative concentrations of anions and cations in milliequivalents per liter for different aquifers of same area.

(d) Gibb's Plot

To further understand the hydrogeochemical procedures with reverence to atmospheric precipitation, rock–water interaction, and evaporation over the administration of geochemistry of groundwater, two diagrams called as 'Gibbs Plot' was introduced by R. J. Gibbs in 1970. In these plots the ratios for cations and anions are plotted against relative values of TDS for the groundwater samples. The relative clustering of the samples on the plot suggests dominance of evaporation or rock-water interaction phenomena. It also gives a clear idea about the influence of anthropogenic activities (like agricultural fertilizers, canal/river water mixing, etc.) on groundwater quality. A detailed explanation is explained in GWQDA-Report.

7.1.4 Water Quality Assessment

Water Quality Indices (WQI)

Water Quality Index (WQI) is a metric used to assess the overall quality of water based on multiple parameters. When analyzing groundwater quality data using WQI, the following steps are typically involved. Various WQI developed for surface water and other forms of water. However, no specific WQI developed for Ground water free from demerits. In this regard, a new WQI based on regional hydro-geological conditions may be a good option. Howbeit, weighted arithmetic WQI and CCME WQI can be employed for basic assessment and indexing. Example of weighted arithmetic WQI for assessment of ground water *(Datta et al., 2023; (Dutta et al., 2022)* **has been explained in GWQDA-Report.**

8. Data Compilation and Sharing

To ensure accurate and accessible information, compiling and sharing groundwater quality data is very crucial. The Ground Water Quality Analysis Report will be the annual compilation of ground water quality data of CGWB, which will be prepared on water year basis.

8.2 Data Compiling

Data reporting is necessary to ensure consistency in units, formatting, and data structures across different datasets. It may involve converting measurements to a standard unit system and standardizing data formats (e.g., CSV, Excel), e.g. Table 8 **(Annexure viii).**

8.2 Data Sharing

Once contamination of groundwater for any parameter is detected in any of the monitoring well (National level monitoring/Special purpose monitoring/Special studies) the following approach is to be adopted.

(a) *In the form of a Report*

The reports on State/UT or pan-India basis should be published in the month of September every year for the previous water year.

(b) *Online publication in CGWB web portal, India-WRIS portal (NWIC) etc.*

As per the directives from Ministry a common data format has been prepared for CGWB and CPCB for sharing and integration of ground water quality data as
shown in Table 6.

(c) *Sharing with Stakeholders*

This step involves sharing the compiled data with relevant stakeholders, such as local government agencies (PHED, JJM, WRD, DoDW&S etc.), water management organizations, researchers, and environmental NGOs. The report may be shared with District/State/UT administrations.

Sharing of Water Quality Report / Data

Report/ Data Sharing	Frequency (on water year basis)	Remarks
Pan-India Groundwater Quality Data / Report	September every year (for previous water year)	In Public domain
Trend analysis for 5-year and 10-year Quality data	September every year (for previous water year)	To be shared with Authorities for corrective action.
GW Quality Report	September every year (for previous water year)	In Public domain

The groundwater quality reports shall be shared with States/UTs, DoDW&S, and a copy shall be marked to the district administration.

The details of data collection points along with co-ordinates and utilization of the source is to be mentioned in the report.

Repeat sampling is to be done from the site where contaminants exceed BIS permissible limit.

Any information regarding groundwater contamination shall be brought into the public domain through the CGWB website and NWIC.

Annexures

Annexure I:	Collection and preservation of ground water sample
Annexure II:	SOP for water analysis
Annexure III:	Laboratory Procedure Manual
Annexure IV:	Work Instructions
Annexure V:	Quality Manual
Annexure VI:	Format
Annexure VII:	Measurement of Uncertainty
Annexure VIII:	Excel sheet as per CHQ format (Standard format for reporting)
Annexure IX:	Format for water quality data sharing (Common Excel format for CGWB-CPCB)

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COLLECTION AND PRESERVATION OF WATER SAMPLES (APHA, 23rd Edition) Annexure I

Table. Summary of Sampling and Handling Requirements (as per APHA, 2017)

Determination	**Container***	**Minimum Sample Size mL**	**Sample Type**	**Preservation**	**Maximum Storage Recommended**	**Regulatory#**
Acidity	P, G(B), FP	100	Grab	Cool, ≤6°C	24 h	14 d
Temperature	P, G, FP		Grab	Analyze immediately	0.25 h	0.25 h
Turbidity	P, G, FP	100	Grab, Composite	Analyze same day; store in dark up to 24 h, Cool, ≤6°C	24 h	48 h
Alkalinity	P, G, FP	200	Grab	Cool, ≤6°C	24 h	14 d
BOD	P, G, FP	1000	Grab, Composite	Cool, ≤6°C	6 h	48 h
Boron	F, P (PTFE) or quartz	1000	Grab, Composite	HNO3 to pH<2	28 d	6 months
Bromide	P, G, FP	100	Grab, Composite	None required	28 d	28 d
Carbon, organic, total	G(B), P, FP	100	Grab, Composite	Analyze immediately, or cool ≤6°C and add HCl, H_3PO_4, or H_2SO_4 to pH<2	7 d	28 d
Chloride	P, G, FP	50	Grab, Composite	None required	N.S.	28 d
Specific conductance	P, G, FP	500	Grab, Composite	Cool, ≤6°C	28 d	28 d
Fluoride	P	100	Grab, Composite	None required	28 d	28 d
Hardness	P, G, FP	100	Grab, Composite	Add HNO_3 or H_2SO_4 to pH<2	6 months	6 months
Metals	P(A), G(A), FP (A)	1000	Grab, Composite	For dissolved metals filter immediately, add HNO_3 to pH<2	6 months	6 months

COLLECTION AND PRESERVATION OF WATER SAMPLES (APHA, 23rd Edition)

Annexure I

Determination	Container*	Minimum Sample Size mL	Sample Type	Preservation	Maximum Storage Recommended	Regulatory#
Chromium (VI)	P(A), G(A), FP (A	250	Grab	Cool, ≤6°C, pH 9.3–9.7, ammonium sulfate buffer preservative as specified in method 3500-Cr to extend to 28 d HT	28 d	28 d
Nitrate	P, G, FP	100	Grab, Composite	Analyze as soon as possible; Cool, ≤6°C	48 h	48 h (14 d for chlorinated samples
Nitrate + nitrite	P, G, FP	200	Composite	Add H2SO4 to pH<2, Cool, ≤6°C	1–2 d	28 d
Dissolved Oxygen	G, BOD bottle	300	Grab			
(i) Electrode				Analyze immediately	0.25 h	0.25 h
(ii) Winkler				Titration may be delayed after acidification	8 h	8 h
pH	P, G	50	Grab	Analyze immediately	0.25 h	0.25 h
Phosphate	G(A)	100	Grab	For dissolved phosphate filter immediately; Cool, ≤6°C	48 h	48 h as per EPA manual for DW
Silica	F, P (PTFE) or quartz	200	Grab, Composite	Cool, ≤6°C, do not freeze	28 d	28 d
Solids##	P, G	200	Grab, Composite	Cool, ≤6°C,	7 d	2–7 d; see cited reference
Sulfate	P, G, FP	100	Grab, Composite	Cool, ≤6°C	28 d	28 d

COLLECTION AND PRESERVATION OF WATER SAMPLES (APHA, 23rd Edition) Annexure I

*P = plastic (polyethylene or equivalent); G = glass; G(A) or P(A) = rinsed with 1 + 1 HNO_3; G(B) = glass, borosilicate; G(S) = glass, rinsed with organic solvents, or baked; FP = fluoropolymer [polytetrafluoroethylene (PTFE, Teflon) or other fluoropolymer].

U.S. Environmental Protection Agency, 1992, Rules and Regulation, 40 CFR Parts 100-149.

U.S. Environmental Protection Agency, 2007, 40 CFR Parts 136, Table II.

N.S. = not stated in cited reference; stat = no storage allowed; analyse immediately (within 15 min).

Some drinking water (DW) and treated wastewater (WW) matrices may be subject to positive interference as a result of preservation. If such interference is demonstrable, samples should be analyzed as soon as possible without preservation.

Annexure II

STANDARD OPERATIONAL PROCEDURES

OF

क्षेत्रीय रासायनिक प्रयोगशाला
केन्द्रीय भूमि जल बोर्ड, उत्तरपूर्वी क्षेत्र,
गुवाहाटी REGIONAL CHEMICAL
LABORATORYCGWB. NER,
GUWAHATI

Specification, Standard (method) or Technique used APHA 23rd Ed. (2017)

CONTENTS

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6.	Magnesium by EDTA titrimetric method	APHA 23rd Ed,3500 Mg B	**23**
7.	Sodium and Potassium Flame emission photometric method	APHA 23rd Ed, 3500 Na-D APHA 23rd Ed, 3500 K-D	**24-25**
8.	Total Alkalinity, Carbonate and Bicarbonate	APHA 23rd Ed, 2320 B APHA 23rd Ed,2320 B	**26-27**
9.	Iron by Phenanthroline method	APHA 23rd Ed, 3500 Fe B	**28-31**
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12.	Sulfate by Turbidimetric Method	APHA 23rd Ed, 4500-SO_4^{2-} E	**38-40**

Chloride Analysis by Argentometric Titration

1. General Discussion

a. ***Principle:*** In a neutral or slightly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before red silver chromate is formed.

b. ***Interferences:*** Substances in amounts normally found in potable waters will not interfere. Bromide, iodide, and cyanide register as equivalent chloride concentrations. Sulfide, thiosulfate, and sulfite ions interfere but can be removed by treatment with hydrogen peroxide, Orthophosphate in excess of 25mg/L interfere by precipitating as silver phosphate. Iron in excess of 10mg/L interferes by masking the end point.

2. Apparatus

a. Erlenmeyer flask, 250-ml.

b. Burette, 50-ml.

3. Reagents

a. Potassium chromate indicator solution: Dissolve 50g K_2CrO_4 in a little distilled water. Add $AgNO_3$ solution until a definite red precipitate is formed. Let stand 12 h. filter, and dilute to 1 L with distilled water.

b. Standard silver nitrate titrant, 0.0141M (0.0141N): Dissolve 2.395 g $AgNO_3$ in distilled water and dilute to 1000 ml. Standardise against NaCl 1.00 mL= 500µg Cl^-. Store in a brown bottle.

c. Standard sodium chloride, 0.0141M (0.0141N: dissolve 824.0 mg NaCl (dried at 140^0C) in distilled water and dilute to 1000 mL; 1.00 mL = 500µg Cl^-.

d. Special reagents for removal of interference:

1. Aluminum hydroxide suspension: Dissolve 125g aluminum potassium sulfate or aluminum ammonium sulfate, $AlK(SO_4)_2 . 12H_2O$ or $AlNH_4(SO_4)_2 . 12H_2O$ in 1 L distilled water.

Warm to 60^0C and add 55 ml conc ammonium hydroxide (NH_4OH) slowly with stirring. Let stand about 1 h, transfer to a large bottle, and wash precipitate by successive additions, with thorough mixing and decanting with distilled water, until free from chloride. When freshly prepared, the suspension occupies a volume of approximately 1 L.

2. Phenolphthalein indicator solution.
3. Sodium hydroxide , NaOH, 1N
4. Sulfuric acid, H_2SO_4, 1N.
5. Hydrogen peroxide, H_2O_2, 30%.

4. Procedure

- Sample preparation: Use a 100 mL sample or a suitable portion diluted to 100 ml. If the sample is highly colored, add 3 mL $Al(OH)_3$ suspension, mix, let settle, and filter.
- If sulfide, sulfite, or thosulfate is present, add 1 mL H_2O_2 and stir for 1 min.
- Titration: Directly titrate samples in the pH range 7 to 10. Adjust sample pH to 7 to 10 with H_2SO_4 or NaOH if it is not at this range. For adjustment, preferably use a pH meter with a non-chloride-type reference electrode. (If only a chloride-type electrode is available, determine amount of acid or alkali needed for adjustment and discard this sample portion. Treat a separate portion with required acid or alkali and continue analysis). Add 1.0 mL K_2CrO_4 indicator solution. Titrate with standard $AgNO_3$ titrant to a pinkish yellow end point. Be consistent in end-point recognition.
- Standardize $AgNO_3$ titrant and establish reagent blank value by the titration method outlined above. A blank of 0.2 to 0.3 mL is usual.

5. Calculation

$$\mathbf{mg\ Cl^-/L} = \frac{(A-B)\times N\times 35450}{ml\ of\ Sample}$$

where:

A = mL titration for sample

B = mL titration for blank, and

C= mL normality of $AgNO_3$

$$\text{mg NaCl/L} = (\text{mg Cl}^-) \times 1.65$$

Measurement of pH

1. Principle

Measurement of pH is one of the most important and frequently used tests in water chemistry. pH as defined by Sorenson is –log $[H^+]$; it is the intensity factor of acidity. Pure water is very slightly ionized and at equilibrium the ion product is

$[H^+][OH^-] = K_w = 1.01 \times 10^{-7}$ at 25˚C

$[H^+] = [OH^-] = 1.005 \times 10^{-7}$

where:

$[H^+]$ = activity of Hydrogen ions, moles/L

$[OH^-]$ = activity of hydroxyl ions, moles/L

K_w = ion product of water.

2. General discussion

The basic principle of electronic pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and reference electrode. The hydrogen electrode consists of a platinum electrode across which hydrogen gas is bubbled at a pressure of 101 kPa.

Because single ion activities such as a $_{H^+}$ cannot be measured, pH is defined operationally on a potentiometric scale. The pH measuring is calibrated potentiometrically with an indicating (glass) electrode and reference electrode using National Institute of Standards and Technology (NIST) buffers having assigned values so that:

$$pH = -\log_{10} a_{H^+}$$

pH_B = assigned pH of NIST buffer

3. Apparatus

a. pH meter consisting of potentiometer, a glass electrode, a reference electrode, and a temperature compensating device. A circuit is completed through the potentiometer when the electrodes are immersed in the test solution.

b. Reference electrode consisting of a half cell that provides a constant electrode potential. Commonly used are calomel and silver: silver chloride electrodes. Either is available with several types of liquid junctions.

4. Procedure

a. Instrument Calibration

- Recommended solutions for short term storage of electrodes vary with type of electrode and manufacture, but generally have conductivity greater than 4000 µmhos/cm. Tap water is a better substitute than distilled water, but pH 4.1 buffer is best for single glass electrode and saturated KCl is preferred solution for a combination electrode. Keep electrodes wet by returning them to storage solution whenever pH meter is not in use.
- Before use remove electrodes from storage solution, rinse, blot dry with soft tissue, place in buffer solution, and set the iso-potential point. Select a second buffer within 2 pH units of sample pH and bring sample and pH to same temperature, which may be the room temperature, a fixed temperature such as 25ºC, or the temperature of a fresh sample. Remove electrode from the first buffer, rinse thoroughly with distilled water, blot dry, and immerse in second buffer and wait until the instrument calibrates itself in the pH of the used buffer.
- Remove electrodes from the second buffer, rinse thoroughly with distilled water and dry electrodes as indicated above. Immerse a third buffer below pH 10, approximately 3 pH units different from the second; the reading should be within 0.1 unit for the pH of the third buffer.

- ❖ The purpose of standardization is to adjust the response of the glass electrode to the instrument.

b. **Sample analysis:**

- ❖ Establish equilibrium between electrodes and sample by stirring sample to insure homogeneity; stir gently to minimize carbon dioxide entertainment. For buffered samples or those of high ionic strength, condition electrode after cleaning by dipping them into sample for 1 min. Blot dry, immerse in a fresh sample portion of the same sample, and read pH.
- ❖ With dilute, poorly buffered solutions, equilibrate electrodes by immersing in three or four successive portion of the sample. Take a fresh sample to measure pH.

Electrical Conductivity

1. General Discussion

Conductivity, k, is a measure of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions; on their total concentration, mobility, and valence, and on the temperature of measurement. Solutions of most inorganic compounds are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current very poorly, if at all.

a. Definitions and Units of Expression.

Conductance, G is defined as the reciprocal of resistance, R.

$$G = \frac{1}{R}$$

where the unit of *R* is ohm and *G* is ohm-1 (sometimes written mho). Conductance of solution is measured between two spatially fixed and chemically inert electrodes. To avoid polarization at the electrode surfaces the conductance measurement is made with an alternating current. The conductance of a solution, *G*, is directly proportional to the electrode surface area, *A*, cm^2, and inversely proportional to the distance between the electrodes, *L*, cm. The constant of proportionality, *k*, such that:

$$G = k\left(\frac{A}{L}\right)$$

is called "conductivity" (preferred to "specific conductance"). It is a characteristic property of the solution between the electrodes. The units of *k* are 1/ohm-cm or mho per centimeter. Conductivity is customarily reported in micromhos per centimeter (micro mho/cm).

In the International System of Units (SI) the reciprocal of the ohm is the siemens (S) and conductivity is reported as millisiemens per meter (mS/m); 1 milliS/m= 10 micro mhos/cm and 1 micro S/cm=1 micro mho/cm. To report results in SI units of milli S/m divide micro mhos/cm by 10.

To compare conductivities, values of k are reported relative to electrodes with A=1 cm^2 and L=1 cm. Absolute conductance, G, of standard potassium chloride solutions between electrodes of precise geometry have been measured; the corresponding standard conductivities, k, are shown in Table-I.

The equivalent conductivity, A, of a solution is the conductivity per unit of concentration. As the concentration is decreased towards zero, A approaches a constant, designated as A^0. With k in units of micromhos per centimeter it is necessary to convert concentration to units of equivalents per cubic centimeter; therefore:

$$A = 0.001\text{k/concentration}$$

where the unit of A, k, and concentration are mho-cm2/equivalent, µmho/cm, and equivalent/L, respectively. Equivalent conductivity, A, values for several concentrations of KClare listed to Table -I:

Table-I: Equivalent Conductivity A& Conductivity k of potassium chloride at25^{0}C

KCl Concentration M or equivalent/L	Equivalent Conductivity A mho-cm^2/equivalent	Conductivity, k, micro mho/cm
0	149.9	
0.0001	148.9	14.9
0.0005	147.7	73.9
0.001	146.9	146.9
0.005	143.6	717.5
0.01	141.2	1 412

0.02	138.2	2 765
0.05	133.3	6 667
0.1	128.9	12 890
0.2	124.0	24 800
0.5	117.3	58 670
1	111.9	111 900

* Based on the absolute ohm, the 1968 temperature standard, and the dm^3 volume standard. Values are accurate to ± 0.1% or 0.1 micro mho/cm, whichever is greater.

b. Measurement

Instrumental measurements: In the laboratory, conductance, G_s, (or resistance) of a standard KCl solution is measured and from the corresponding conductivity, k_s, (Table- I) a cell constant, c, cm^{-1}, is calculated.

$$C=\frac{k,}{Gs,}$$

Most conductivity meters do not display the actual solution conductance, *G*, or resistance, *R*; rather, they generally have a dial that permits the user to adjust the internal cell constant to match the conductivity, k_s, of standard. Once the cell constant has been determined, or set, the conductivity of an unknown solution, $k_u = CG_\mu$
will be displayed by the meter.

Distilled water produced in a laboratory generally has conductivity in the range 0.5 to 3 µ mhos/cm. The conductivity increases shortly after exposure to both air and the water container.

Estimate total dissolved solids (TDS in mg/L) in a sample by multiplying conductivity (in micromhos per centimeter) by an empirical factor. This factor may vary from 0.55 to 0.9, depending on the soluble components of the water and on the temperature of measurement.

Relatively high factors may be required for saline or boiler waters, whereas lower factors may apply where considerable hydroxide or free acid is present. Even though sample evaporation results in the change of bicarbonate to carbonate the empirical factor is derived for a comparatively constant water supply by dividing dissolved solids by conductivity. Approximate the milli equivalents per liter of either cations or anions in some water by multiplying conductivity in units of micro mhos per centimeter by 0.01.

2. Laboratory Method

A. Apparatus

a. Self contained conductivity instruments: Use an instrument capable of measuring conductivity with an error not exceeding 1% or 1 µ mho/cm, whichever is greater.

b. Thermometer, capable of being read to the nearest 0.1^{0}C and covering the range 15 to 50^{0}C. Many conductivity meters are equipped to read an automatic temperature sensor.

c. Conductivity cell:

1) Platinum-electrode type- Conductivity cells containing platinized electrodes are available in either pipet or immersion form. Cell choice depends on expected range of conductivity. Clean new cells, and platinize the electrodues before use, subsequently, clean and replatinize them whenever the readings become erratic, when a sharp end point cannot be obtained, or when inspection shows that any platinum black has flaked off.

2) To platinize, prepare a solution of 1 g chloroplatinic acid, $H_2PtCl_6.6H_2O$, and 12 mg lead acetate in 100 ml distilled water. A more concentrated solution reduce the time required to platinize electrodes and may be used when time is a factor, e.g. when the cell constant is 1.0/cm or more. Immerse electrodes in this solution and connect both to the negative terminal of a 1.5-V dry cell battery. Connect positive side of battery to a piece of platinum wire and dip wire into the solution. Use a current such that only a small quantity of gas is evolved. Continue electrolysis until both cell electrodes are coated with platinum black.

Save platinizing solution for subsequent use. Rinse electrodes thoroughly and when not in use keep immersed in distilled water.

3. Reagents

- Conductivity water: Any of several methods can be used to prepare reagent-grade water. The conductivity should be small compared to the value being measured.
- Standard potassium chloride solution, KCl, 0.01M: Dissolve 745.6 mg anhydrous KCl in conductivity water and dilute to 1000 ml in a class *A* volumetric flask at 25^0C. This is the standard reference solution, which at 25^0C has a conductivity of 1412 µ mhos/cm. It is satisfactory for most samples when the cell has a constant between 1 and 2 cm-1. For other cell constants, use stronger or weaker KCl solutions. Store in a glass –stopper borosilicate glass bottle.

4. Procedure

- Determination of cell constant: Rinse conductivity cell with at least three portions of 0.01 M KCl solution. Adjust temperature of a fourth portion to 25.0 ± 0.1^0C. If a conductivity meter displays resistance, R, ohms, measure resistance of this portion and note temperature. Compute cell constant C:

$C\ (cm^{-1}) = 0.001412)\ (R_{KCL})\ [1+0.019(t-25)]$

where : R_{KCL} = measured resistance, ohms, and

t= observed temperature, ^{0}C

Conductivity meters often indicate conductivity directly. Commercial probes commonly contain a temperature sensor. With such instruments, rinse probe three times with 0.0100 M KCl, as above. Adjust temperature compensation dial to 0.0191 C^{-1}. With probe in standard KCl solution, adjust meter to read 1412 µ mho/cm. This procedure automatically adjusts cell constant internal to the meter.

❖ Conductivity measurement: Rinse cell with one or more portions of sample. Adjust temperature of a final portion to about 250C. Measure sample resistance or conductivity and note temperature to ± 0.1^0C.

5. Calculation

The temperature coefficient of most waters is only approximately the same as that of standard KCl solution; the more the temperature of measurement deviates from 25^0C, the greater the uncertainty in applying the temperature correction. Report all conductivities at $25.^0$C.

When sample conductivity is measured without internal temperature compensation conductivity at 25^0C is:

$$k,\ \mu\ \text{mho/cm} = \frac{km}{1+0.019\ (t-25)}$$

where:

k_m = measured conductivity in units of µ mho/cm at t^0C, and other units are defined as above.

For instruments with automatic temperature compensation and readout directly in µ mho/cm or similar units, the readout automatically is corrected 25^0C. Report displayed conductivity in designated units.

❖ For instruments giving values in SI units,

1 mS/m = 10 µ mhos/cm, or conversely

1 µ mho/cm = 0.1 mS/m.

Total Hardness Analysis by EDTA Titrimetric Method

1. General Discussion:

a. ***Principle***: Ethylenediaminetetraacetic acid and its sodium salts (abbreviated EDTA) form a chelated soluble complex when added to a solution of certain metal cations. If a small amount of a dye such as Eriochrome Black T or Calmagite is added to an aqueous solution containing calcium and magnesium ions at a pH of 10.00 ± 0.1, the solution becomes wine red. If EDTA is added as a titrant, the calcium and magnesium will be complexed, and when all of the magnesium and calcium has been complexed the solution turns from wine red to blue, marking the end point of the titration. Magnesium ion must be present to yield a satisfactory end point. To insure this, a small amount of complexometrically neutral magnesium salt of EDTA is added to the buffer this automatically introduces sufficient magnesium and obviates the need for a blank correction.

The sharpness of the end point increases with increasing pH. However, the pH cannot be increased indefinitely because of the danger of precipitating calcium carbonate, $CaCO_3$, or magnesium hydroxide, $Mg(OH)_2$, and because the dye changes color at high pH values, The specified pH of 10.0 ± 0.1 is a satisfactory compromise. A limit of 5 min is set for the duration of the titration to minimize the tendency toward $CaCO_3$ precipitation.

b. **Interference:** Some metal ions interfere by causing fading or indistinct end points or by stoichiometric consumption of EDTA. Reduce this interference by adding certain inhibitors before titration. MgCDTA, selectively complexes heavy metals, releases magnesium into the sample, and may be used as a substitute for toxic or malodorous inhibitors. It is useful only when the magnesium substituted for heavy metals does not contribute significantly to the total hardness.

c. Titration precautions: Conduct titrations at or near normal room temperature. The color change becomes impractically slow as the sample approaches freezing temperature. Indicator decomposition becomes a problem in hot water.

The specified pH may produce an environment conducive to $CaCO_3$ precipitation. Although the titrant slowly rediscovers such precipitates, a drifting end point often yields low results. Completion of the titration within 5 min minimizes the tendency for $CaCO_3$ to precipitate. The following three methods also reduce precipitation loss:

1) Dilute sample with distilled water to reduce $CaCO_3$ concentration. This simple expedient has been incorporated in the procedure. If precipitation occurs at this dilution of 1 +1 use modification 2) or 3). Using too small a sample contributes a systematic error due to the buret-reading error.

2) If the approximate hardness is known or is determined by a preliminary titration, add 90% or more of titrant to sample before adjusting pH with buffer.

3) Acidify sample and stir for 2 min to expel CO_2 before pH adjustment. Determine alkalinity to indicate amount of acid to be added.

2. Reagents

a. Buffer solution

1) Dissolve 16.9 g ammonium chloride (NH_4Cl) in 143 mL concentrated ammonium hydroxide (NH_4OH). Add 1.25 g magnesium salt of EDTA (available commercially) and dilute to 250 mL with distilled water

2) If the magnesium salt of EDTA is unavailable, dissolve 1.179 g disodium salt of ethylenediaminetetraacetic acid dihydrate (analytical reagent grade) and 780 mg magnesium sulfate ($MgSO_4.7H_2O$) or 644 mg magnesium chloride ($MgCl_2.6H_2O$) in 50 mL distilled water. Add this solution to 16.9 g NH_4Cl and 143 mL conc NH_4OH with mixing and dilute to 250 ml with distilled water. To attain the highest accuracy, adjust to exact equivalence through appropriate addition of a small amount of EDTA or $MgSO_4$ or $MgCl_2$.

Store solution 1) or 2) in a plastic or borosilicate glass container for no longer than 1 month. Stopper tightly to prevent loss of ammonia (NH_3) or pickup of carbon dioxide (CO_2). Dispense buffer solution by means of a bulb-operated pipet. Discard buffer when 1 or 2 mL added to the sample fails to produce a pH of 10.0 ± 0.1 at the titration end point.

3) Satisfactory alternate 'odorless buffers' also are available commercially. They contain the magnesium salt of EDTA and have the advantage of being relatively odorless and more stable than the NH_4Cl-NH_4OH butter. They usually do not provide as good an end point as NH_4Cl-NH4OH because of slower reactions and they may be unsuitable when this method is automated. Prepare one of these buffers by mixing 55 mL concHCl with 400 mL 2-aminoethanol (free of aluminum and heavier metals). Add 5.0 g magnesium salf to EDTA and dilute to 1 L with distilled water.

MgCDTA: Magnesium salt of1, 2-cyclohexanediaminetetraacetic acid. Add 250 mg per 100 mL sample and dissolve completely before adding buffer solution. Use this complexing agent to avoid using toxic or odorous inhibitors when interfering substances are present in concentrations that affect the end point but will not contribute significantly to the hardness value.

b. Indicators

Many types of indicator solutions have been advocated and may be used if the analyst demonstrates that they yield accurate values. The prime difficulty with indicator solutions is deterioration with aging, giving indistinct end point. For example, alkaline solutions of Eriochrome Black T are sensitive to oxidants and aqueous or alocholic solutions are unstable. In general, use the least amount of indicator providing a sharp end point. It is the analyst's responsibility to determine individually the optimal indicator concentration.

1) Eriochrome Black T : Sodium salt of 1-(1-hydroxy-2-napohthylazo) -5-nitro-2-naphthol-4-sulfonic acid; Dissolve 0.56 g dye in 100 g 2,2',2" –nitrilotriethanol (also called triethanolamine) or 2-methoxymethanol) (also called ethylne glycol monomethyl ether). Add 2 drops per 50 mL solution to be titrated. Adjust volume if necessary.

2) Calmagite : 1-(1-hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid. This is stable in aqueous solution and produces the same color change as Eriochrome Black T, with a sharper end point. Dissolve 0.10 g Calmagite in 100 mL distilled water. Use 1 mL per 50 mL solution to be titrated. Adjust volume if necessary.

3) Indicators 1 and 2 can be used in dry powder form if care is taken to avoid excess indicator. Prepared dry mixtures of these indicators and an inert salt are available commercially.

If the end point color change of these indicators is not clear and sharp, it usually means that an appropriate complexing agent is required. If NaCN inhibitor does not sharpen the end point, , the indicator probably is at fault.

c. Standard EDTA titrant, 0.01M: Weight 3.723 g analytical reagent-grade disodium ethylenediaminetetraacetatedihydrate, also called (ethylenedinitrilo) tetraacetic acid disodium salt (EDTA). Dissolve in distilled water, and dilute to 1000 mL.Standardise against standard calcium solution.

Because the titrant extracts hardness-producing cations from soft-glass containers, store in polythylene (preferable) or borosilicate glass bottles. Compensate for gradual deterioration by periodic restandardization and by using a suitable correction factor.

d. Standard Calcium solution: Weigh 1.000 g anhydrous $CaCO_3$ powder (primary standard or special reagent low in heavy metals, alkalis, and magnesium) into a 500-mL erlenmeyer flask. Place a funnel in the flask neck and add, a little at a time, 1:1 HCl until all $CaCO_3$ has dissolved. Add 200 mL distilled water and boil for a few minutes to expel CO_2. Cool, add a few drops of methyl red indicator, and adjust to the intermediate orange color by adding 3N NH_4OH or 1:1 HCl, as required. Transfer quantitatively and dilute to 1000 mL with distilled water, 1 mL = 1.00 mg $CaCO_3$.

e. Sodium hydroxide, NaOH, 0.1N.

3. Procedure

- Pretreatment of polluted water and wastewater samples: Use nitric acid-sulfuric acid or nitric acid-perchloric acid digestion.
- Titration of sample: Select a sample volume that requires less than 15 mL EDTA titrant and complete titration within 5 min, measured from time of buffer addition.
- Dilute 25.0 mL sample to about 50 mL with distilled water in a porcelain casserole or other suitable vessel. Add 1 to 2 mL buffer solution. Usually 1 mL will be sufficient to give a pH of 10.0 to 10.1. The absence of a sharp end-point color change in the titration usually means that an inhibitor must be added at this point or that the indicator has deteriorate.
- Add 1 to 2 drops indicator solution or an appropriate amount of dry-powder indicator formulation. Add standard EDTA titrant slowly, with continuous stirring, until the last reddish tinge disappears. Add the last few drops at 3- to 5-s intervals. At the end point the solution normally is blue. Daylight or a daylight fluorescent lamp is recommended highly because ordinary incandescent lights tend to produce a reddish tinge in the blue at the end point.
- If sufficient sample is available and interference is absent, improve accuracy by increasing sample size.

4. Calculation:

$$\textbf{Hardness (EDTA) as mg CaCO3/L} = \frac{\textbf{A X B X 1000}}{\boldsymbol{ml\ of\ Sample}}$$

where:

A = mL titration for sample and

B = mg $CaCO_3$ equivalent to 1.00 mL EDTA titrant.

Calcium by EDTA Titrimetric Method

1. Principle

Many indicators such as ammonium purpurate, calcon etc. can form a complex with only calcium but not with magnesium at higher pH. Calcium forms a complex of pink colour with ammonium purpurate. As EDTA have a strong affinity towards calcium, therefore, when EDTA is added as a titrant, the former complex is broken and new complex between Ca^{+2} and EDTA of purple colour is formed.

2. Reagents

i) 0.01 N EDTA solution: Dissolve 1.8615 g of disodium salt of EDTA in 500 ml distilled water.

ii) 1 N sodium hydroxide: Dissolve 4 g of NaOH in 100 ml distilled water.

iii) Murexide indicator: Mix 0.2 g of ammonium purpurate with 100 g NaCl and grind.

3. Procedure

Take 50 ml sample in a conical flask. Add 2 ml of NaOH solution in the sample. Add 100-200 mg of murexide indicator; a pink colour develops. Titrate against EDTA solution until the colour changes from pink to purple.

4. Calculation

$$\mathbf{Calcium\ (mg/L)} = \frac{V \times 400.8}{ml\ of\ Sample}$$

Where, *V* = Volume of EDTA used

$$\textbf{Calcium Hardness as mg CaCO}_3\ /\textbf{L} = \frac{\textbf{A X B X 1000}}{\boldsymbol{ml\ of\ Sample}}$$

where:

A= Titrant for sample &

B= mg $CaCO_3$ equivalent to 1.00 ml EDTA titrant at the calcium indicator end point

Magnesium by EDTA Titrimetric Method

1. Principle

Calcium and magnesium form a complex of wine red colour with Eriochrome Black T indicator at pH 10.0. If EDTA is added as titrant, the complex between Eriochrome black T and Ca^{2+} and Mg^{2+} is broken down and a new complex of blue colour is formed. The value of Mg^{+2} can be obtained by substracting the value of calcium from the total of Ca^{2+} and Mg^{2+}.

2. Calculation

Magnesium (mg/L) = [Total hardness (as mg/L $CaCO_3$) – Calcium (as mg/L $CaCO_3$)] x 0.243.

Sodium and Potassium Flame Emission Photometric Method

1. Principle

Trace amounts of Sodium and Potassium can be determined by flame emission photometry. Sample is nebulized into a gas flame under carefully controlled, reproducible excitation condition.

2. Reagent and equipment

i) Flame photometer either direct-reading or internal standard type.

ii) Stock sodium solution: Dissolve 2.542 gm NaCl dried at 140^{o}C to constant weight and dilute to 1000 ml with water (1ml=1mg Na or 1000 ppm).

iii) Stock potassium solution: Dissolve 1.907 gm KCl dried at 110^{o}C and dilute to 1000 ml with water (1ml=1mg or 1000 ppm K).

a. Series preparation

Sl. No.	ml of stock	Diluted to (ml)	Concentration of Na mg/L
a)	10 ml	100	100
b)	5 ml	100	50
c)	2.5 ml	100	25
d)	1ml	100	10
e)	0.5	100	5

b. Series preparation

Sl. No.	ml of stock	Diluted to (ml)	Concentration of K mg/L
a)	10 ml	100	100
b)	5 ml	100	50
c)	2.5 ml	100	25
d)	1ml	100	10
e)	0.5	100	5

3. Method

Prepare a blank and calibration standard in the applicable ranges: 0 to 100 mg/L. Aspirate calibration standards to calibrate the instrument and determine the concentration of Na and K.

Total Alkalinity, Carbonate and Bicarbonate

a. Principle

Carbonate and bicarbonate can be estimated by titrating the sample with a strong acid (HCl or H_2SO_4) first to pH 8.3 using phenolphthalein as an indicator and then further to pH between 4.2 and 5.4 with methyl orange or mixed indicator. In first case, the value is called phenolphthalein alkalinity (PA) and in second case, it is total alkalinity (TA). Values of carbonates and bicarbonates can be computed from these two types of alkalinities.

b. Reagent

i) Standard H_2SO_4 (0.02 N): Take 1.11 ml of concentrated H_2SO_4 (36 N) with automatic pipette and dilute it to 2 L of distilled water.

ii) Phenolpthalein indicator (0.25 %): Dissolve 0.25 g powder of phenolpthalein in 100 ml of 62 % Ethanol.

iii) Methyl orange: Dissolve 0.5 ml of methyl orange in 100 ml of distilled water.

c. Method

- ❖ Pipette out 25 ml of water extract in a conical flask and add 2-3 drops of Phelopthalein indicator. Appearance of pink colour indicated presence of carbonate.
- ❖ If CO_3 is present add 0.02 N H_2SO_4 from a burette till the solution becomes colourless.
- ❖ Record the readings.
- ❖ Add few drops of methyl orange indicator and titrate till the solution changes from yellow to rose red.
- ❖ Record the readings. Repeat this procedure for three times to get concomitant readings.

d. Calculation

Calculation for Total Alkalinity

$$\mathbf{TA\ in\ mg\ CaCO_3/L =}$$

$$\frac{Volume\ of\ H_2SO_4\ X\ 1000}{ml\ of\ Sample}$$

Calculation for Phelopthalein Alkalinity

$$\textbf{PA in mg CaCO}_3\textbf{/L} = \frac{Volume\ of\ H_2SO_4\ (after\ using\ Phenopthalein\ Indicator X 1000}{ml\ of\ Sample}$$

Alkalinity relationship

Result of titration	Hydroxide alkalinity (as CaCO3)	Carbonate alkalinity (as CaCO3)	Bi Carbonate alkalinity (as CaCO3)
P=0	0	0	T
P<1/2 T	0	2P	T-2P
P=1/2 T	0	2P	0
P>1/2 T	2P-T	2(T-P)	0
P=T	T	0	0

Iron by Phenanthroline method

1. General Discussion

a. Principle: Iron is brought into solution, reduced to the ferrous state by boiling with acid and hydroxylamine, and treated with 1,10-phenanthroline at pH 3.2 to 3.3. Three molecules of phenanthroline chelate each atom of ferrous iron to form an orange-red complex. The colored solution obeys Beer's law; its intensity is independent of pH from 3 to 9. A pH between 2.9 and 3.5 ensures rapid color development in the presence of an excess of phenanthroline. Color standards are stable for at least 6 months.

b. Interference: Among the interfering substances are strong oxidizing agents, cyanide, nitrite, and phosphates (polyphosphates more so than orthophosphate), chromium, zinc in concentrations exceeding 10 times that of iron, cobalt and copper in excess of 5 mg/L, and nickel in excess of 2 mg/L. Bismuth, cadmium, mercury, molybdate, and silver precipitate phenanthroline. The initial boiling with acid converts polyphosphates to orthophosphate and removes cyanide and nitrite that otherwise would interfere. Adding excess hydroxylamine eliminates errors caused by excessive concentrations of strong oxidizing reagents.

2. Apparatus

a. Colorimetric equipment: One of the following is required:

UV-Visible Spectrophotometer, for use at 510 nm, providing a light path of 1 cm or longer.

b. Acid-washed glassware: Wash all glassware with conc hydrochloric acid (HCl) and rinse with reagent water before use to remove deposits of iron oxide.

c. Separatory funnels: 125-mL, Squibb form, with ground glass or TFE stopcocks and stoppers.

3. Reagents

Use reagents low in iron. Use reagent water in preparing standards and reagent solutions and in procedure. Store reagents in glass-stoppered bottles. The HCl and ammonium acetate solutions are stable indefinitely if tightly stoppered. The hydroxylamine, phenanthroline, and stock iron solutions are stable for several months. The standard iron solutions are not stable; prepare daily as needed by diluting the stock solution. Visual standards in nessler tubes are stable for several months if sealed and protected from light.

a. Hydrochloric acid (HCl), conc, containing less than 0.5 ppm iron.

b. Hydroxylamine solution: Dissolve 10 g $NH_2OH.HCl$ in 100 mL water.

c. Ammonium acetate buffer solution: Dissolve 250 g $NH_4C_2H_3O_2$ in 150 mL water. Add 700 mL conc (glacial) acetic acid. Because even a good grade of $NH_4C_2H_3O_2$ contains a significant amount of iron, prepare new reference standards with each buffer preparation.

d. Sodium acetate solution: Dissolve 200 g $NaC_2H_3O_2.3H_2O$ in 800 mL water.

e. Phenanthroline solution: Dissolve 100 mg 1,10-phenanthroline monohydrate, $C_{12}H_8N_2.H_2O$, 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.)

f. Potassium permanganate, 0.02M: Dissolve 0.316 g $KMnO_4$ in reagent water and dilute to 100 mL.

g. Stock iron solution: Iron standard of 1000 mg/L (traceable to NIST) is available and it is diluted to different concentrations to prepare the stock solutions.

4. Procedure

a. Total iron: Mix sample thoroughly and measure 50.0 mL into a 125-mL Erlenmeyer flask. If this sample volume contains more than 200 µg iron use a smaller accurately measured portion and dilute to 50.0 mL. Add 2 mL conc HCl and 1 mL $NH_2OH.HCl$ solution. Add a few glass beads and heat to boiling. To ensure dissolution of all the iron, continue boiling until volume is reduced to 15 to 20 mL. (If the sample is ashed, take up residue in 2 mL conc HCl and 5 mL water.) Cool to room temperature and transfer to a 50- or 100-mL volumetric flask or nessler tube. Add 10 mL $NH_4C_2H_3O_2$ buffer solution and 4 mL phenanthroline solution, and dilute to mark with water. Mix thoroughly and allow a minimum of 10 min for maximum color development.

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

c. Ferrous iron: Determine ferrous iron at sampling site because of the possibility of change in the ferrous-ferric ratio with time in acid solutions. To determine ferrous iron only, acidify a separate sample with 2 mL conc HCl/100 mL sample at time of collection. Fill bottle directly from sampling source and stopper. Immediately withdraw a 50-mL portion of acidified sample and add 20 mL phenanthroline solution and 10 mL $NH_4C_2H_3O_2$ solution with vigorous stirring. Dilute to 100 mL and measure color intensity within 5 to 10 min. Do not expose to sunlight. (Color development is rapid in the presence of excess phenanthroline. The phenanthroline volume given is suitable for less than 50 µg total iron; if larger amounts are present, use a correspondingly larger volume of phenanthroline or a more concentrated reagent.) Calculate ferric iron by subtracting ferrous from total iron.

d. Color measurement: Prepare a series of standards by accurately pipetting calculated volumes of standard iron solutions into 125-mL Erlenmeyer flasks and diluting to 50 mL by adding measured volumes of water. Add 2 mL conc HCl and 1 mL $NH_2OH.HCl$ solution. Carry out the steps as above beginning with transfer to a 100-mL volumetric flask or nessler tube. For visual comparison, prepare a set of at least 10 standards, ranging from

1 to 100 µg Fe in the final 100-mL volume. Compare colors in 100-mL tall-form nessler tubes.

e. Add 1 mL $NH_2OH.HCl$ solution, 10 mL phenanthroline solution, and 10 mL $NaC_2H_3O_2$ solution. Dilute to 100 mL with water, mix thoroughly, and let stand for a minimum of 10 min. Measure absorbance at 510 nm using a 5-cm absorption cell for amounts of iron less than 100 g or 1-cm cell for quantities from 100 to 500 µg. As reference, use either water or a sample blank prepared by carrying the specified quantities of acids through the entire analytical procedure. If water is used as reference, correct sample absorbance by subtracting absorbance of a sample blank.

Fluoride by SPANDS method

1. General Discussion

a) Principle: The SPADNS colorimetric method is based on the reaction between fluoride and a zirconium-dye lake. Fluoride reacts with the dye lake, dissociating a portion of it into a colorless complex anion (ZrF_6^{2-}); and the dye. As the amount of fluoride increases, the color produced becomes progressively lighter. The reaction rate between fluoride and zirconium ions is influenced greatly by the acidity of the reaction mixture. If the proportion of acid in the reagent is increased, the reaction can be made almost instantaneous. Under such conditions, however, the effect of various ions differs from that in the conventional alizarin methods. The selection of dye for this rapid fluoride method is governed largely by the resulting tolerance to these ions.

b) Interference: Alkalinity, aluminium, chloride, color and turbidity, iron, hexametaphosphate, phosphate, sulphate are some of the common interferences in fluoride determination. Because these are neither linear in effect nor algebraically additive, mathematical compensation is impossible. Whenever any one of the substances is present in sufficient quantity to produce an error of 0.1 mg/L or whenever the total interfering effect is in doubt, distill the sample. Also distill colored or turbid samples. In some instances, sample dilution or adding appropriate amounts of interfering substances to the standards may be used to compensate for the interference effect. If alkalinity is the only significant interference, neutralize it with either hydrochloric or nitric acid. Chlorine interferes and provision for its removal is made.

2. Apparatus

Colorimetric equipment UV-Visible Spectrophotometer, for use at 570 nm, providing a light path of at least 1 cm.

3. Reagents

a. Stock fluoride solution: Fluoride solution of strength 10 mg/kg is available.

b. SPADNS solution: Dissolve 958 mg SPADNS, sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate, also called 4,5-dihydroxy-3-(parasulfophenylazo)-2,7- naphthalenedisulfonic acid trisodium salt, in distilled water and dilute to 500 mL. This solution is stable for at least 1 year if protected from direct sunlight.

c. Zirconyl-acid reagent: Dissolve 133 mg zirconyl chloride octahydrate, $ZrOCl_2.8H_2O$, in about 25 mL distilled water. Add 350 mL conc HCl and dilute to 500 mL with distilled water.

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

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

f. Sodium arsenite solution: Dissolve 5.0 g $NaAsO_2$ and dilute to 1 L with distilled water. (CAUTION: Toxic—avoid ingestion.)

4. Procedure

a. Preparation of standard curve: Prepare fluoride standards in the range of 0 to 1.40 mg F^-/L by diluting appropriate quantities of standard fluoride solution to 50 mL with distilled water. Pipet 5.00 mL each of SPADNS solution and zirconylacid reagent, or 10.00 mL mixed acid-zirconyl-SPADNS reagent, to each standard and mix well. Avoid contamination. Set photometer to zero absorbance with the reference solution and obtain absorbance readings of standards. Plot a curve of the milligrams fluoride-absorbance relationship. Prepare a new standard curve whenever a fresh reagent is made or a different standard temperature is desired. As an alternative to using a 0.500 absorbance) with the prepared 0 mg F^-/L standard.

b. Sample pretreatment: If the sample contains residual chlorine, remove it by adding 1 drop (0.05 mL) $NaAsO_2$ solution/ 0.1 mg residual chlorine and mix. (Sodium arsenite concentrations of 1300 mg/L produce an error of 0.1 mg/L at 1.0 mg F^-/L.)

c. Color development: Use a 50.0-mL sample or a portion diluted to 50 mL with distilled water. Adjust sample temperature to that used for the standard curve. Add 5.00 mL each of

b. SPADNS solution and zirconyl-acid reagent, or 10.00 mL acidzirconyl- SPADNS reagent; mix well and read absorbance, first setting the reference point of the photometer as above. If the absorbance falls beyond the range of the standard curve, repeat using a diluted sample.

5. Calculation

$$mg\ F^-/L = \frac{A}{ml\ sample} \times \frac{B}{C}$$

where: A=µg F^- determined from plotted curve,

B=final volume of diluted sample, mL, and

C= volume of diluted sample used for color development, mL

When the prepared 0 mg F/L standard is used to set the photometer, alternatively calculate fluoride concentration as follows:

$$mg\ F^-/L = \frac{A_0 - A_x}{A_0 - A_1}$$

where: A_0 =absorbance of the prepared 0 mg F^-/L standard,

A_x= absorbance of the prepared sample, and

A_1 =absorbance of a prepared 1.0 mg F^-/L standard.

Nitrate by Ultraviolet Spectrophotometric Screening Method

1. General Discussion

a. Principle: Use this technique only to screen samples containing low organic matter (i.e., uncontaminated natural waters and potable water supplies). The NO_3^- calibration curve follows Beer’s law up to 11 mg N/L. Measuring UV absorption at 220 nm enables analysts to determine NO_3^- rapidly. Be aware that dissolved organic matter also may absorb at 220 nm but NO_3^- does not absorb at 275 nm, so a second measurement can be made at 275 nm and used to correct the NO_3^- value, if needed. The extent of this empirical correction is related to the nature and concentration of the organic matter and may vary from one water to another, so this method is not recommended if a significant correction is required. That said, it may be useful in monitoring NO_3^- levels in a water body with a constant type of organic matter.

b. Interferences: Potential interferences include dissolved organic matter, surfactants, NO_2^-, hexavalent chromium [Cr(VI)], and various inorganic ions. Correction factors for organic matter absorbance can be established by the method of additions combined with analysis of the original NO_3^- content via another method. Sample filtration eliminates interference by suspended particles. Acidification with 1M hydrochloric acid (HCl) to pH <2 prevents interference from hydroxide or carbonate concentrations up to 1000 mg calcium carbonate ($CaCO_3$)/L.

2. Apparatus

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

3. Reagents

a. Reagent water: Use reagent water to prepare all solutions and dilutions.

b. Stock nitrate solution: Solution of nitrate with 10 mg/kg is available.

c. Intermediate nitrate solution: Dilute 100 mL stock NO_3^--N solution to 1000 mL with water; 1.00 mL=10.0 µg NO_3^--N. Preserve with 2 mL $CHCl_3$/L. Solution is stable for 6 months.

d. Hydrochloric acid solution, (~1M): Dilute 83 mL concentrated HCl to 1L with reagent water. Store in a glass or high density polyethylene (HDPE) bottle. Solution is stable for 1 year if kept closed.

4. Procedure

a. Treatment of sample: To 50 mL clear sample (filtered if necessary), add 1 mL 1M HCl solution and mix thoroughly.

b. Standards: Prepare NO_3^- calibration standards in the range 0 to 7 mg NO_3^--N/L by diluting to 50 mL the following volumes of intermediate NO_3^- solution: 0, 1.00, 2.00, 4.00, 7.00 . . . 35.0 mL. Other standard concentrations may also be used. Treat NO_3^--N standards in same manner as samples.

c. Spectrophotometric measurement: Read absorbance or transmittance against reagent water set at zero absorbance or 100% transmittance. Use a wavelength of 220 nm to obtain NO_3^--N reading and a wavelength of 275 nm to determine any interference due to dissolved organic matter.

5. Calculation

For samples and standards, subtract two times the absorbance reading at 275 nm from the reading at 220 nm to obtain absorbance due to NO_3^--N. If correction value is >10% of reading at 220 nm for a particular sample, then the NO_3^--N concentration is considered a rough estimate. Use an electronic spreadsheet, a calculator, or instrument software to find the slope and intercept of the calibration curve by least squares linear regression. Calculate the NO_3^--N concentration from the following equation:

$$\boldsymbol{C = \frac{A - I}{S}}$$

where: C = concentration,

A = absorbance,

I = intercept of the regression line, and

S= slope of the regression line.

Sulfate by Turbidimetric Method

1. General Discussion

a. *Principle:* Sulfate ion (SO_4^{2-}) is precipitated in an acetic acid medium with barium chloride ($BaCl_2$) so as to form barium sulfate ($BaSO_4$) crystals of uniform size. Light absorbance of the $BaSO_4$ suspension is measured by a photometer and the SO_4^{2-} concentration is determined by comparison of the reading with a standard curve.

b. *Interference:* Color or suspended matter in large amounts will interfere. Some suspended matter may be removed by filtration. Silica in excess of 500 mg/L will interfere, and in waters containing large quantities of organic material it may not be possible to precipitate $BaSO_4$ satisfactorily. In potable waters there are no ions other than SO_4^{2-} that will form insoluble compounds with barium under strongly acid conditions. Make determination at room temperature; variation over a range of 10°C will not cause appreciable error.

2. Apparatus

a. Magnetic stirrer: Use a constant stirring speed. It is convenient to incorporate a fixed resistance in series with the motor operating the magnetic stirrer to regulate stirring speed. Use magnets of identical shape and size. The exact speed of stirring is not critical, but keep it constant for each run of samples and standards and adjust it to prevent splashing.

b. Photometer:

Spectrophotometer, for use at 420 nm, providing a light path of 2.5 to 10 cm.

c. Stopwatch or electric timer.

d. Measuring spoon, capacity 0.2 to 0.3 mL.

3. Reagents

a. Buffer solution A: Dissolve 30 g magnesium chloride, $MgCl_2.6H_2O$, 5 g sodium acetate, $CH_3COONa.3H_2O$, 1.0 g potassium nitrate, KNO_3, and 20 mL acetic acid, CH_3COOH (99%), in 500 mL distilled water and make up to 1000 mL.

b. Buffer solution B (required when the sample SO_4^{2-} concentration is less than 10 mg/L): Dissolve 30 g $MgCl_2.6H_2O$, 5 g $CH_3COONa.3H_2O$, 1.0 g KNO_3, 0.111 g sodium sulfate, Na2SO4, and 20 mL acetic acid (99%) in 500 mL distilled water and make up to 1000 mL.

c. Barium chloride ($BaCl_2$), crystals, 20 to 30 mesh: In standardization, uniform turbidity is produced with this mesh range and the appropriate buffer.

d. Standard sulfate solution: Solution of 10 mg/kg of sulphate is available.

4. Procedure

a. Formation of barium sulfate turbidity: Measure 100 mL sample, or a suitable portion made up to 100 mL, into a 250-mL Erlenmeyer flask. Add 20 mL buffer solution and mix in stirring apparatus. While stirring, add a spoonful of $BaCl_2$ crystals and begin timing immediately. Stir for 60±2 s at constant speed.

b. Measurement of barium sulfate turbidity: After stirring period has ended, pour solution into absorption cell of photometer and measure turbidity at 5±0.5 min.

c. Preparation of calibration curve: Estimate SO_4^{2-} concentration in sample by comparing turbidity reading with a calibration curve prepared by carrying SO_4^{2-} standards through the entire procedure. Space standards at 5-mg/L increments in the 0-to 40-mg/L SO_4^{2-} range. Above 40 mg/L accuracy decreases and $BaSO_4$ suspensions lose stability. Check reliability of calibration

b. curve by running a standard with every three or four samples.

a. Correction for sample color and turbidity: Correct for sample color and turbidity by running blanks to which $BaCl_2$ is not added.

5. Calculation

$$mg\ SO_4^{2-}/L = \frac{mg\ SO_4^{2-} \times 1000}{ml\ sample}$$

Arsenic Determination by Continuous Hydride Generation/Atomic Absorption Spectrometric Method

1. General Discussion

This method is applicable for the determination of arsenic and selenium by conversion to their hydrides by sodium borohydride reagent and aspiration into an atomic absorption atomizer.

2. Principle

Arsenous acid, the As (III) oxidation states of arsenic is instantaneously converted by sodium borohydride reagent in acid solution to its volatile hydride. The hydride is then purged continuously by argon or nitrogen into an appropriate atomizer of an atomic absorption spectrometer and convert it into the gas-phase atoms. The sodium borohydride acts as a reducing agent, by rapidly generating elemental hydride in an appropriate reaction cell, thus minimizing the dilution of the hydride by the carrier gas and provide rapid, sensitive determination of arsenic.

CAUTION: Arsenic and its hydride is toxic. Handle with care.

At room temperature and at a pH of 1 or less of the solution, arsenic acid, the As(V) oxidation state of arsenic, is reduced relatively slowly by sodium borohydride to As(III), which is then instantaneously converted to arsine. The arsine atomic absorption peaks commonly are decreased by one-fourth to one-third for As(V) when compared to As(III). Determination of total arsenic requires that all inorganic arsenic compounds be in the As(III) state. Organic and inorganic forms of arsenic are first oxidized to As(V) by acid digestion. The As(V) then is quantitatively reduced to As(III) with sodium or potassium iodide before reaction with sodium borohydride.

3. Apparatus

a. Atomic absorption spectrometer equipped with air–acetylene flame and T- shaped quartz cell with mounting bracket, As electrodeless discharge lamp with power supply, background correction at measurement wavelengths, and appropriate strip-chart recorder.

b. Atomizer: T- Shaped Cylindrical quartz cell, 10 to 20 cm long, bracket-mountable above air–acetylene burner.

Note: The sensitivity of quartz cells deteriorates over several months of use. Sensitivity sometimes may be restored by treatment with 40% HF. Quartz atomization cells provide for the most sensitive arsenic and selenium hydride determinations. The quartz cell can be heated electrically or by an air–acetylene flame in an atomic absorption unit.

c. *Continuous hydride generator*: The basic unit is composed of two parts: a precision peristaltic pump, which is used to meter and mix reagents and sample solutions, and the gas–liquid separator. At the gas–liquid separator, a constant flow of argon strips out the hydrogen and metal hydride gases formed in the reaction and carries them to the heated quartz absorption cell which is supported by a metal bracket mounted on top of the regular air acetylene burner head. The spent liquid flows out of the separator via a constant level side drain to a waste bucket.

Check flow rates frequently to ensure a steady flow; an uneven flow in any tubing will cause an erratic signal. Remove tubing from pump rollers when not in use. Typical flow rates are: sample, 7 mL/min; acid, 1 mL/min; and borohydride reagent, 1 mL/min. Argon flow usually is pre-fixed, typically at 90 mL/min.

4. Reagents

a. Sodium borohydride reagent: Dissolve 8 g $NaBH_4$ in 200 mL 0.1N NaOH. Prepare fresh daily.

b. Potassium iodide prereductant solution: Dissolve 50 g KI in 500 mL water. Prepare fresh daily. Alternatively, use an equivalent NaI solution.

c. Nitric acid (HNO_3), conc.

d. Hydrochloric acid (HCl), conc.

e. Argon (or nitrogen), commercial grade.

f. *Standard As solution* is prepared from 1000 mg/L solution (traceable to NIST)

5. Procedure

a. Digestion techniques: Waters and wastewaters may contain varying amounts of organic arsenic compounds and inorganic compounds of As (III) and As(V). To measure total arsenic in these samples requires sample digestion to solubilize particulate forms, oxidize reduced forms of arsenic, and convert any organic compounds to inorganic ones.

b. Apparatus setup: Before using the hydride generation/analysis system, optimize operating parameters. Align quartz atomizers for maximum absorbance. Aspirate a blank until memory effects are removed. Establish purging gas flow, concentration and rate of addition of sodium borohydride reagent, solution volume, and stirring rate for optimum instrument response for the chemical species to be analyzed. Optimize quartz cell temperature. Rapid injection of sodium borohydride reagent will increase sensitivities, so injection rates should be both consistent and as rapid as the system will tolerate. Recommended wavelength is 193.7 for As.

c. Instrument calibration standards: Prepare at least three standards and a blank by transferring appropriate volumes of As standard solutions to 100-mL volumetric flasks and bring to volume with water containing the same acid concentration used for sample preservation (typically 2 to 5 mL conc HNO_3/L). Standards should be prepared to cover the linear range of the instrument used (generally from 1 to 20 µg/L). Prepare fresh daily.

In all cases, standards must be carried through the same digestion protocol as the samples to monitor digestion effectiveness.

d. Preparation of samples and standards for total recoverable arsenic: By Recoverable HNO_3/HCl: For this less rigorous digestion procedure, transfer a measured volume of well-mixed, acid preserved sample to a flask or beaker. Add 2 mL 1 + 1 HNO_3 and 10 mL 1 + 1 HCl and cover with a ribbed watch glass. Heat on a steam bath or hot plate until volume has been reduced to near 25 mL, making certain sample does not boil. Cool and filter to remove insoluble material or alternatively centrifuge or let settle overnight. Quantitatively transfer sample to volumetric flask, adjust volume to 100 mL, and mix.

e. Determination of arsenic with sodium borohydride: To 20 mL digested standard or sample in a beaker, add 2 mL conc HCl and mix. Add 2 mL KI prereductant solution, mix, and wait at least 30 min. Put the sample to the hydride pump set up attached with sodium borohydride reagent and 10% HCl. After the instrument absorbance has reached a maximum and returned to the baseline, remove beaker, rinse dispersion tube with water, and proceed to the next sample or standard. Check for presence of chemical interferences that suppress instrument response for arsine by treating a digested sample with 10 µg/L As (III) or As (V), as appropriate. Average recoveries should be not less than 90%.

Zinc, Iron, Manganese and Copper Determination by Flame Atomic Absorption Spectrometric Method

1. General Discussion

This method is applicable for the determination of Antimony, Bismuth, Cadmium, Calcium, Cesium, Chromium, Cobalt, Copper, Gold, Iridium, Iron, Lead, Lithium, Magnesium, Manganese, Nickel, Palladium, Platinum, Potassium, Rhodium, Ruthenium, Silver, Sodium, Strontium, Thallium, Tin and Zinc.

2. Principle

In flame atomic absorption spectrometry, a sample is aspirated into a flame and atomized. A light beam is directed through the flame, into a monochromator, and onto a detector that measures the amount of light absorbed by the atomized element in the flame. For some metals, atomic absorption exhibits superior sensitivity over flame emission. Because each metal has its own characteristic absorption wavelength, a source lamp composed of that element is used; this makes the method relatively free from spectral or radiation interferences. The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample over a limited concentration range. Most atomic absorption instruments also are equipped for operation in an emission mode, which may provide better linearity for some elements.

3. Apparatus

a. Atomic absorption spectrometer, consisting of a light source emitting the line spectrum of an element (hollow-cathode lamp or electrodeless discharge lamp), a device for vaporizing the sample (usually a flame), a means of isolating an absorption line (monochromator or filter and adjustable slit), and a photoelectric detector with its associated electronic amplifying and measuring equipment.

b. Burner: The most common type of burner is a premix, which introduces the spray into a condensing chamber for removal of large droplets. The burner may be fitted with a conventional head containing a single slot; a three-slot Boling head, which may be preferred for direct aspiration with an air-acetylene flame; or a special head for use with nitrous oxide and acetylene.

c. Readout: Most instruments are equipped with either a digital or null meter readout mechanism. Most modern instruments are equipped with microprocessors or stand-alone control computers capable of integrating absorption signals over time and linearizing the calibration curve at high concentrations.

d. Lamps: Use either a hollow-cathode lamp or an electrodeless discharge lamp (EDL). Use one lamp for each element being measured. Multi-element hollow-cathode lamps generally provide lower sensitivity than single-element lamps. EDLs take a longer time to warm up and stabilize.

e. Pressure-reducing valves: Maintain supplies of fuel and oxidant at pressures somewhat higher than the controlled operating pressure of the instrument by using suitable reducing valves. Use a separate reducing valve for each gas.

f. Vent: Place a vent about 15 to 30 cm above the burner to remove fumes and vapors from the flame. This precaution protects laboratory personnel from toxic vapors, protects the instrument from corrosive vapors, and prevents flame stability from being affected by room drafts. A damper or variable-speed blower is desirable for modulating air flow and preventing flame disturbance. Select blower size to provide the air flow recommended by the instrument manufacturer.

g. Hot plate.

h. Conical (Erlenmeyer) flasks, 125-mL, or Griffin beakers,

i. 150-mL, acid-washed and rinsed with water.

j. Volumetric flasks, 100-mL.

k. Watch glasses, ribbed and unribbed.

l. Safety shield.

m. Safety goggles.

4. Reagents

a. Air, cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or commercially bottled gas.

b. Acetylene, standard commercial grade. Acetone, which always is present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing a cylinder when its pressure has fallen to 689 kPa (100 psi) acetylene.

CAUTION: Acetylene gas represents an explosive hazard in the laboratory. Follow instrument manufacturer's directions in plumbing and using this gas. Do not allow gas contact with copper, brass with >65% copper, silver, or liquid mercury; do not use copper or brass tubing, regulators, or fittings with >65% copper content.

c. Metal-free water: Use metal-free water for preparing all reagents and calibration standards and as dilution water. Prepare metal-free water by deionizing tap water and/or by using one of the following processes, depending on the metal concentration in the sample: single distillation, redistillation, or sub-boiling. Always check deionized or distilled water to determine whether the element of interest is present in trace amounts. (NOTE: If the source water contains Hg or other volatile metals, single- or redistilled water may not be suitable for trace analysis because these metals distill over with the distilled water. In such cases, use sub-boiling to prepare metal-free water).

d. Nitric acid, HNO_3, conc, or trace-metals grade or ultrapure.

e. Standard Zn, Fe, Mn and Cu solutions are prepared from 1000 mg/L solution (traceable to NIST)

5. Procedure

a. Sample preparation: Required sample preparation depends on the metal form being measured

If dissolved or suspended metals are to be determined, filter sample at time of collection using a preconditioned plastic filtering device with either vacuum or pressure, containing a filter support of plastic or fluorocarbon, through a prewashed ungridded 0.4- to 0.45-m-pore-diammembrane filter (polycarbonate or cellulose esters). Before use filter a blank consisting of metal-free (deionized) water to ensure freedom from contamination. Precondition filter and filter device by rinsing with 50 mL deionized water. If the filter blank contains significant metals concentrations, soak membrane filters in approximately 0.5N HCl or 1N HNO_3 (recommended for electrothermal atomic absorption spectrometry and ICP–MS analyses) and rinse with deionized water before use. NOTE: Take care to avoid potential contamination during filtration of samples.

Before filtering, centrifuge highly turbid samples in acid-washed fluorocarbon or high-density plastic tubes to reduce loading on filters. Stirred, pressure filter units foul less readily than vacuum filters; filter at a pressure of 70 to 130 kPa. After filtration acidify filtrate to pH 2 with conc HNO_3 and store until analyses can be performed. If a precipitate form on acidification, digest acidified filtrate before analysis. Retain filter and digest it for direct determination of suspended metals.

If it is not possible to field-filter the sample without contaminating it, obtain sample in an “unpreserved” bottle as above and promptly cool to 4°C. Do not acid-preserve the sample. Then, without delay, filter sample under cleaner conditions in the laboratory.

Test pH of a portion of aqueous sample upon receipt in the laboratory to ensure that the sample has been properly filtered and acid-preserved.

NOTE: Different filters display different sorption and filtration characteristics; for trace analysis, test filter and filtration system to verify complete recovery of metals.

If suspended metals are to be determined, filter sample as above for dissolved metals, but do not centrifuge before filtration. Retain filter and digest it for direct determination of suspended metals. Record sample volume filtered and include a filter in determination of the blank.

CAUTION: Do not use perchloric acid to digest membrane filters.

If total or acid-extractable metals are to be determined, use protective equipment and transfer a measured volume (100 mL recommended) of well-mixed, acid-preserved sample appropriate for the expected metals concentrations to a flask or beaker. In a hood, add 5 mL conc HNO_3. If a beaker is used, cover with a ribbed watch glass to minimize contamination. Boiling chips, glass beads, or Hengar granules may be added to aid boiling and minimize spatter when high concentration levels (> 10 mg/L) are being determined. Bring to a reflux temperature of approximately 95°C to achieve a slow boil and evaporate on a hot plate to the lowest volume possible (about 10 to 20 mL) before precipitation occurs. Continue heating and adding conc HNO_3 as necessary until digestion is complete as shown by a light-colored, clear solution. Do not let sample dry during digestion.

Wash down flask or beaker walls and watch glass cover (if used) with metal-free water. Filter if necessary, using TFE or glass fiber filters. Transfer filtrate to a 100-mL volumetric flask with two portions of reagent water, adding these rinsing to the volumetric flask. Cool, dilute to mark, and mix thoroughly. Take portions of this solution for required metal determinations.

b. Instrument calibration standards: Prepare at least three standards and a blank by transferring appropriate volumes of metal standard solutions to 100-mL volumetric flasks and bring to volume with water containing the same acid concentration used for sample preservation (typically 2 to 5 mL conc $HCL/HNO_3/L$). Standards should be prepared to cover the linear range of the instrument used (generally from 1 to 20 µg/L). Prepare fresh daily. In all cases, standards must be carried through the same digestion protocol as the samples to monitor digestion effectiveness.

c. Instrument operation: Install a hollow-cathode lamp for the desired metal in the instrument and roughly set the wavelength dial Set slit width according to manufacturer's suggested setting for the element being measured. Turn on instrument, apply to the hollow-cathode lamp the current suggested by the manufacturer, and let instrument warm up until energy source stabilizes, generally about 10 to 20 min. Readjust current as necessary after warmup. Optimize wavelength by adjusting wavelength dial until optimum energy gain is obtained. Align lamp in accordance with manufacturer’s instructions.

Install suitable burner head and adjust burner head position. Turn on air and adjust flow rate to that specified by manufacturer to give maximum sensitivity for the metal being measured. Turn on acetylene, adjust flow rate to value specified, and ignite flame. Let flame stabilize for a few minutes. Aspirate a blank consisting of deionized water containingthe same concentration of acid in standards and samples. Zero the instrument. Aspirate a standard solution and adjust aspiration rate of the nebulizer to obtain maximum sensitivity. Adjust burner both vertically and horizontally to obtain maximum response. Aspirate blank again and rezero the instrument. Aspirate a standard near the middle of the linear range. Record absorbance of this standard when freshly prepared and with a new hollow-cathode lamp. Refer to these data on subsequent determinations of the same element to check consistency of instrument setup and aging of hollow-cathode lamp and standard. The instrument now is ready to operate. When analyses are finished, extinguish flame by turning off first acetylene and then air.

d. Standardization: Select at least three concentrations of each standard metal solution to bracket the expected metal concentration of a sample. Aspirate blank and zero the instrument. Then aspirate each standard in turn into flame and record absorbance.

Prepare a calibration curve by plotting on linear graph paper absorbance of standards versus their concentrations. For instruments equipped with direct concentration readout, this step is unnecessary.

e. Analysis of samples: Rinse nebulizer by aspirating water containing 1.5 mL conc HNO3/L. Aspirate blank and zero instrument. Aspirate sample and determine its absorbance.

6. Calculations

Calculate concentration of each metal ion, in micrograms per liter for trace elements, and in milligrams per liter for more common metals, by referring to the appropriate calibration curve prepared. Alternatively, read concentration directly from the instrument readout if the instrument is so equipped. If the sample has been diluted, multiply by the appropriate dilution factor.

Lead, Chromium, Cadmium, Nickel and Cobalt Determination by Graphite Furnace Atomic Absorption Spectrometric Method

1. General Discussion

This method is suitable for determination of micro quantities of aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, silver, and tin.

2. Principle

Electrothermal atomic absorption spectroscopy is based on the same principle as direct flame atomization but an electrically heated atomizer or graphite furnace replaces the standard burner head. A discrete sample volume is dispensed into the graphite sample tube (or cup). Typically, determinations are made by heating the sample in three or more stages. First, a low current heats the tube to dry the sample. The second, or charring, stage destroys organic matter and volatilizes other matrix components at an intermediate temperature. Finally, a high current heats the tube to incandescence and, in an inert atmosphere, atomizes the element being determined. Additional stages frequently are added to aid in drying and charring, and to clean and cool the tube between samples. The resultant ground-state atomic vapor absorbs monochromatic radiation from the source. A photoelectric detector measures the intensity of transmitted radiation. The inverse of the transmittance is related logarithmically to the absorbance, which is directly proportional to the number density of vaporized ground-state atoms (the Beer-Lambert law) over a limited concentration range.

3. Apparatus

a. Atomic absorption spectrometer, consisting of a light source emitting the line spectrum of an element (hollow-cathode lamp or electrodeless discharge lamp), a device for vaporizing the sample (usually a flame), a means of isolating an absorption line (monochromator or filter and adjustable slit), and a photoelectric detector with its associated electronic amplifying and measuring equipment.

b. Lamps: Use either a hollow-cathode lamp or an electrodeless discharge lamp (EDL). Use one lamp for each element being measured. Multi-element hollow-cathode lamps generally provide lower sensitivity than single-element lamps. EDLs take a longer time to warm up and stabilize.

c. Graphite furnace: Use an electrically heated device with electronic control circuitry designed to carry a graphite tube or cup through a heating program that provides sufficient thermal energy to atomize the elements of interest. Furnace heat controllers with only three heating steps are adequate only for fresh waters with low dissolved solids content. For salt waters, brines, and other complex matrices, use a furnace controller with up to seven individually programmed heating steps. Fit the furnace into the sample compartment of the spectrometer in place of the conventional burner assembly. Use argon as a purge gas to minimize oxidation of the furnace tube and to prevent the formation of metallic oxides. Use graphite tubes with platforms to minimize interferences and to improve sensitivity.

d. Readout: Most instruments are equipped with either a digital or null meter readout mechanism. Most modern instruments are equipped with microprocessors or stand-alone control computers capable of integrating absorption signals over time and linearizing the calibration curve at high concentrations.

e. Sample dispensers: Use microliter pipets (5 to 100 L) or an automatic sampling device designed for the specific instrument.

f. Vent: Place a vent about 15 to 30 cm above the burner to remove fumes and vapors from the flame. This precaution protects laboratory personnel from toxic vapors, protects the instrument from corrosive vapors, and prevents flame stability from being affected by room drafts. A damper or variable-speed blower is desirable for modulating air flow and preventing flame disturbance. Select blower size to provide the air flow recommended by the instrument manufacturer.

g. Cooling water supply: Cool with tap water flowing at 1 to 4 L/min or use a recirculating cooling device.

h. Membrane filter apparatus: Use an all-glass filtering device and 0.45-m or smaller-pore-diameter membrane filters.

i. Hot plate.

j. Conical (Erlenmeyer) flasks, 125-mL, or Griffin beakers,

k. 150-mL, acid-washed and rinsed with water.

l. Volumetric flasks, 100-mL.

m. Watch glasses, ribbed and unribbed.
n. Safety shield.
o. Safety goggles.

4. Reagents

a. Metal-free water: Use metal-free water for preparing all reagents and calibration standards and as dilution water. Prepare metal-free water by deionizing tap water and/or by using one of the following processes, depending on the metal concentration in the sample: single distillation, redistillation, or sub-boiling. Always check deionized or distilled water to determine whether the element of interest is present in trace amounts. (NOTE: If the source water contains Hg or other volatile metals, single- or redistilled water may not be suitable for trace analysis because these metals distill over with the distilled water. In such cases, use sub-boiling to prepare metal-free water).

b. Nitric acid (HNO3), 1+1 and conc.

c. Standard Pb, Cr, Cd, Ni and Co solutions are prepared from 1000 mg/L solution (traceable to NIST).

5. Procedure

a. Use protective equipment and transfer a measured volume (100 mL recommended) of well-mixed, acid-preserved sample appropriate for the expected metals concentrations to a flask or beaker. In a hood, add 5 mL conc HNO_3. If a beaker is used, cover with a ribbed watch glass to minimize contamination. Boiling chips, glass beads, or Hengar granules may be added to aid boiling and minimize spatter when high concentration levels (> 10 mg/L) are being determined. Bring to a reflux temperature of approximately 95°C to achieve a slow boil and evaporate on a hot plate to the lowest volume possible (about 10 to 20 mL) before precipitation occurs. Continue heating and adding conc HNO_3 as necessary until digestion is complete as shown by a light-colored, clear solution. Do not let sample dry during digestion.

b. Wash down flask or beaker walls and watch glass cover (if used) with metal-free water. Filter if necessary, using TFE or glass fiber filters. Transfer filtrate to a 100-mL volumetric flask with two portions of reagent water, adding these rinsing to the volumetric flask. Cool, dilute to mark, and mix thoroughly. Take portions of this solution for required metal determinations.

c. Instrument calibration standards: Prepare at least three standards and a blank by transferring appropriate volumes of metal standard solutions to 100-mL volumetric flasks and bring to volume with water containing the same acid concentration used for sample preservation (typically 2 to 5 mL conc HNO3/L). Standards should be prepared to cover the linear range of the instrument used (generally from 1 to 20 µg/L). Prepare fresh daily. In all cases, standards must be carried through the same digestion protocol as the samples to monitor digestion effectiveness.

d. Instrument operation: Mount and align furnace device according to manufacturer's instructions. Turn on instrument and data collection system. Select appropriate light source and adjust to recommended electrical setting. Select proper wavelength and set all conditions according to manufacturer's instructions, including background correction. Background correction is important when elements are determined at short wavelengths or when sample has a high level of dissolved solids. Background correction normally is not necessary at wavelengths longer than 350 nm. If background correction above 350 nm is needed, deuterium arc background correction is not useful and other types must be used. Select proper inert- or sheath-gas flow. In some cases, it is desirable to interrupt the inert-gas flow during atomization. Such interruption results in increased sensitivity by increasing residence time of the atomic vapor in the optical path. Gas interruption also increases background absorption and intensifies interference effects, but modern background correction methods usually eliminate these problems. Consider advantages and disadvantages of this option for each matrix when optimizing analytical conditions. To optimize graphite furnace conditions, carefully adjust furnace temperature settings to maximize sensitivity and precision and to minimize interferences. Follow manufacturer’s instructions.

Use drying temperatures slightly above the solvent boiling point and provide enough time and temperature for complete evaporation without boiling or spattering.

Select atomization temperature by determining the lowest temperature providing maximum sensitivity without significantly eroding precision. Optimize by a series of successive determinations at various atomization temperatures using a standard solution giving an absorbance of 0.2 to 0.5.

The charring temperature must be high enough to maximize volatilization of interfering matrix components yet too low to volatilize the element of interest. With the drying and atomization temperatures set to their optimum values, analyze a standard solution at a series of charring temperatures in increasing increments of 50 to 100°C. When the optimum charring temperature is exceeded, there will be a significant drop in sensitivity. Plot charring temperature versus sample absorbance: the optimum charring temperature is the highest temperature without reduced sensitivity. Verify optimization with major changes in sample matrix.

f. Standardization: Select at least three concentrations of each standard metal solution to bracket the expected metal concentration of a sample. Aspirate blank and zero the instrument. Then aspirate each standard in turn into flame and record absorbance.

Prepare a calibration curve by plotting on linear graph paper absorbance of standards versus their concentrations. For instruments equipped with direct concentration readout, this step is unnecessary.

g. Analysis of samples: Rinse nebulizer by aspirating water containing 1.5 mL conc HNO_3/L. Aspirate blank and zero instrument. Aspirate sample and determine its absorbance.

7. Calculations

Calculate concentration of each metal ion, in micrograms per liter for trace elements, and in milligrams per liter for more common metals, by referring to the appropriate calibration curve prepared. Alternatively, read concentration directly from the instrument readout if the instrument is so equipped. If the sample has been diluted, multiply by the appropriate dilution factor.

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END OF THE DOCUMENT

CONTENTS

6.2P-01 PROCEDURE FOR PERSONNEL, TRAINING NEEDS AND TRAINING CONDUCT

1.0 PURPOSE

This procedure is intended to ensure continuing competence and skill of personnel of Laboratory.

2.0 SCOPE

The procedure is specified to cover all the personnel of the laboratory to update the competence and skills of personnel's through training (in-house and outside).

3.0 RESPONSIBILITY

TM : Planning for training needs of Laboratory Personnel.

QM : To arrange training in-house and outside (if required).

4.0 REFERENCE

Laboratory Quality Manual doc No. CGWB/QM/01, NABL - 103

5.0 PROCEDURE REQUIREMENTS

5.1 Personnel

Personnel are employed as per Recruitment Rules of Central Ground Water Board, Ministry of Water Resources, River Development & Ganga Rejuvenation and approved by DOPT by following Central Civil Services Rules of Government of India, which includes requisite Qualification and Experience as per designation in view of work to be done by the person who is being appointed. Personnel are appointed for handling of samples, job performance, supervision and management of the laboratory as per sanctioned number of posts. Personnel competency record is maintained and responsibilities of key official are mentioned in the Quality Manual CGWB/QM/01.

5.2 Training

Training needs of personnel's are identified by Technical Manager of the laboratory and may be requested by individual through proper channel. Requested & identified training needs are forwarded to Quality Manager, who further forwards it to Regional Director/Chief Executive with his recommendation. Quality Manager prepares the final list on approval of Chief Executive. Yearly Training calendar is prepared by Quality Manager on the basis of above list.

After finalization of training plan, Quality Manager reviews and identifies that whether it is possible to conduct requisite training in-house or to send the persons outside. Quality Manager informs the concerned personnel to attend the training with training schedule, venue and title in case of in-house training and outside training.

5.2.1 In-house Training

In-house lectures / discussions on relevant subject are arranged from time to time. The details of in-house lectures / training programme are recorded.

5.2.2 Training (External / Outside)

Nomination for outside training are made by Regional Director (Chief Executive) /Quality Manager keeping in view, the usefulness of training for the laboratory personnel nominated with reference to yearly Training Plan of the laboratory.

Individual is informed by Regional Director (Chief Executive) /Quality Manager regarding the venue, date, training schedule. On the basis of above, individual will participate in the training.

Concerned official reports to Quality Manager with a brief report on training acquired. The training records are maintained.

6.0 Monitoring of Competence:

The competency of laboratory personnel is monitored by a written exam time to time and on the basis of PT participation.

7.0 RECORDS

1. Competence Chart for staff (Minimum Requirement),
2. Competence Evaluation Form,
3. Authorized Laboratory Staff,
4. Job description (Role, Responsibility & Authority matrix) ,
5. Training Calendar,
6. Training Record,
7. Training Evaluation Performa,

6.4P-01 PROCEDURE FOR HANDLING, TRANSPORT, STORAGE AND MAINTENANCE OF EQUIPMENT

1.0 PURPOSE

The purpose of this procedure is to maintain safe handling, transportation, storage, use, and planned maintenance of all laboratory equipment to ensure proper functioning and in order to prevent contamination or deterioration.

2.0 SCOPE

All Laboratory equipment are covered by this procedure.

3.0 RESPONSIBILITY

The Technical Manager is responsible for the implementation of this procedure.

4.0 PROCEDURE

4.1 List of Laboratory Equipment / instruments with all details is maintained.

4.2 The calibration calendar is prepared in the month of April for each year.

4.3 All the equipments are handled safely as per the manufacture's instructions during their use by all the laboratory personnel. Laboratory equipments are used by the authorized persons, and are used for testing purpose only.

4.4 All the laboratory equipment are stored and maintained in appropriate environment as per the manufacturer's instruction to protect their integrity.

4.5 Where appropriate, a preventive plan for maintenance is prepared as per the manufacturer's instructions.

4.6 Whenever practicable intermediate checks are carried out. Its record is maintained. The laboratory checks the analysis tests randomly with reference to known standards.

4.7 The major laboratory equipments/ instruments are calibrated from NPL or NABL Accredited calibration laboratory.

4.8 Some of the equipment are calibrated in-house.

4.9 Log books are maintained for the major equipment

4.10 In case of breakdown of the instrument / equipment the laboratory maintains its record.

5.0 RECORDS

1. List of Equipment,
2. Calibration calendar of Laboratory Equipment,
3. In-house Calibration Certificate,
4. Equipment Log book,
5. Breakdown Record of Equipment,
6. Instrument Authorization Records,
7. Preventive Maintenance Schedule,
8. Original Calibration Certificate File,

6.4 P-02 Procedures for Intermediate Checks of Equipment

1.0 PURPOSE

To lay down procedure for intermediate checks

2.0 SCOPE

This procedure is used for all essential intermediate checks as per the specified methods.

3.0 RESPONSIBILITY

The Technical Manager is responsible for the implementation of this procedure.

4.0 PROCEDURE

a) All the equipments are handled safely as per the manufacturer's instructions during their use by all the laboratory personnel. Only authorized laboratory personal are allowed to enter in the laboratory. Instruments are made password protected, wherever applicable, to avoid mishandling.

b) All the laboratory equipments are stored and maintained in appropriate environment as per the manufacturer's instruction to protect their integrity.

c) For the proper functioning, equipments are checked prior to use against Certified Reference Materials (CRMs) or standards specifically made for checking the functioning / calibration status of the equipments.

d) Intermediate checks are carried out by the concerned laboratory personnel as per specified methods. The maintenance and performance checks records are maintained in a logbook, log sheet, or electronically. The frequency of intermediate check shall be once in a month for all parameters under NABL scope. The range of accuracy for each parameters shall be + 2%.

e) NRWQL Laboratory is responsible for developing comparable maintenance schedules for equipment.

f) Preventative maintenance procedures, other than basic cleaning, for each equipment item performed internally, are developed unless they are already described elsewhere (e.g. the instrument manual).

g) The laboratory prepares the plan for periodic intermediate checking of the instruments.

h) Records of intermediate checks are maintained.

5.0 RECORDS

1. Intermediate Check Register,

6.4 P-03 Procedure for Verification of Calibration Certificate of Equipment

1.0 PURPOSE

The purpose of this procedure is to verify the calibration certificate to ensure that NABL accredited calibration agency/organization convey accurately all information pertaining to the testing so that the certificate may be used with maximum benefit by all concerned. The calibration certificate must contain or refer to all the information necessary to justify the test results.

2.0 SCOPE

All laboratory equipments and glassware are covered by this procedure.

3.0 RESPONSIBILITY

The Technical Manager is responsible for the implementation of this procedure.

4.0 PROCEDURE

For equipment returned after calibration, the calibration certificates are reviewed for the following information to ensure the adequacy of the calibration status. The Calibration certificate shall include at least the following information:

a) The title “Certificate of Calibration.”

b) Name and address of the laboratory and the place where the measurements took place, if it is different than that of the laboratory premises.

c) A unique identification of the calibration certificate (e.g. the issue number) and into each page an identification element, in order to ensure that the page is recognized as part of the calibration certificate, and also a clear identification of the end of the certificate.

d) The name and the address of the client /customer, the identification of the method and the instrumentation used (type of instrument and serial number/code).

e) The description, status and the identity of the calibrated item.

f) The date of receipt of the item when it is critical for the validity and the application of the results and the date of calibration.

g) The calibration results and where necessary the units.

h) The name, position and the signature of the person(s) who are in charge to grant the calibration certificate

i) Environmental Conditions including Temperature & Relative Humidity, under which the calibration was carried out

j) Expanded Uncertainty of Measurement at 95% Confidence Level

k) A statement indicating how traceability to national standards has been achieved

l) Accreditation logo.

m) Original Calibration Certificate File is maintained.

n) Date of Calibration, Due Date of Calibration and Least Count are well recorded in the certificate.

o) Whenever any lack of vital information is noticed, the calibrating laboratory is contacted to provide the information and the same is recorded after receiving it from the calibration service provider.

p) The format of certification of certificate is updated after every calibration.

5.0 RECORDS

1. Verification of Calibration Certificate

Annexure III

6.5 P-01 PROCEDURE FOR MEASUREMENT AND MAINTAIN MATRLOGICAL TRACEABILITY

1.0 GENERAL

The laboratory has an established program and procedure for the calibration of its equipments/ instruments and standards before putting it to use, in-house as well as from NABL accredited laboratories, for which the record is maintained.

In-house the instruments are calibrated by the method given in the respective manual of the instrument and using standard solution prepared from CRM's.

2.0 SPECIFIC REQUIREMENTS

2.1 Calibration

Laboratory has scope of testing of River water sample only. Lab gets its major equipments/ instruments calibrated from NABL accredited calibration laboratories.

2.2 Testing

2.2.1 For testing of water samples laboratory applies standard methods for measuring and testing equipments with measuring function. Testing procedures also include the determination of uncertainty due to relative contribution of various components used in the testing methods.

2.2.2. For traceability of measurements to SI units confidence in measurements is established by using CRM's.

3.0 REFERENCE STANDARDS AND REFERENCE MATERIALS

3.1 Reference Standards

The laboratory is in practice to prepare working standards which are standardized with CRM's and also used for in-house calibration of instruments.

3.2 Reference Material

The laboratory has purchased CRM's to be used for standardization of working standard solutions.

3.3 Intermediate Checks

The laboratory is in practice to do intermediate checks to maintain confidence in calibration/ standardization status of the instruments/ working solution. Checks are also done before and after any adjustment.

3.4 Transport and Storage

The reference standard and reference materials are used only in the laboratory and are stored safely at proper place and where necessary these are kept in the refrigerator.

4.0 RECORDS

1. Records of CRMs,
2. Calibration calendar of Laboratory Equipment,
3. List of Laboratory Equipment,

6.6 P-01 PROCEDURE FOR USING EXTERNALLY PROVIDED PRODUCTS AND SERVICES

1.0 PURPOSE

The purpose of this procedure is to ensure that all chemicals, consumables & services are purchased as per the specifications, so that the quality of the test results is not affected.

2.0 SCOPE

This Procedure is applicable for the effective procurement of consumables, supplies & services which effects the quality of testing work.

3.0 RESPONSIBILITY

Responsibilities of each laboratory personnel according to organization chart.

Regional Director/Chief Executive is overall responsible.

Technical Manager/QM is responsible for the finalization of specifications as per the test methods requirement and for procurement request placement, monitoring, inspection as one of the member of inspection committee and storage.

4.0 REFERENCE

Laboratory Quality Manual CGWB/QM/01

5.0 PROCEDURE REQUIREMENTS

The Laboratory purchases the following supplies:

- Standard / Reference Chemicals
- Equipment
- Glass wares
- Other Laboratory Consumable items
- The purchases are being made as per the specifications given by the laboratory to the Stores section. The Procurement is made after taking the approval of Regional Director. After procurement, inspection/ verification of the purchased material is done by a committee formed by the Regional Director. After verification/inspection, the material is handed over to Chemical laboratory. It is ensured that procured supplies comply with specified requirements. The relevant records are maintained.

6.0 SERVICES

The laboratory is taking the following services

- **Testing services –**
- Proficiency Testing services: 6.6F-01
- Calibration services: 6.6F-02
- Equipment maintenance services (CMC) : 6.6F-03
- Sampling /testing services: 6.6F-04
- Purchase orders verified wherever required, before issue by the Technical Manager for the data / specifications describing the serv=ices and supplies ordered.
- Description of data / specification may include type, class, precise identification, specifications, other technical data and the management system requirements etc.

7.0 STORAGE & ISSUANCE SUPPLIES

- All the purchased supplies are being stored in such a way that the integrity and specifications of all the consumables is not changed. These are being stored in almirahs/racks in safe environment with lock & key system. Store is handled under the supervision of Technical Manager/QM. Stock position of all the materials is always entered in stock register while depositing and issuing the materials.
- Identified Quantity of minimum samples is always maintained in the store.
- The laboratory is providing, monitoring and maintaining the environmental conditions, wherever required.

8.0 SUPPLIER SELECTION AND PERFORMANCE EVALUATION

- The suppliers supplying material / services are included in the approved supplier list based on their previous performance.
- New suppliers are selected on the basis of past experience, reputed brand name, approved or accredited quality system, evaluation of sample, evaluation of capability for quality, supply, price & payment terms etc.
- The suppliers, as identified, are evaluated once in a year based on the quality and delivery. (4.6F-06).
- Suppliers are rated based on their quality and delivery rating and decision regarding continuation of them is taken by the Technical Manager based on their performance, as under :
  75%-100% Continued
  75%- 50% Continued but asked to improve the performance
  below 50% are discontinued.

9.0 RECORD:

1. Proposal for the purchases and services,
2. Incoming Material Inspection Form,
3. Stock Register (Chemical/glassware/plastic ware/T&P,

4. List of Approved Supplier,
5. Laboratory Purchase File,
6. Supplier Evaluation Form,

7.1 P-01 PROCEDURE FOR REVIEW OF REQUESTS, TENDER AND CONTRACTS

1.0 PURPOSE:

To ensure that the requirements of technical officer are clearly understood and agreed for undertaking and completion of water sample analysis prior to sample receipt.

2.0 SCOPE:

This procedure is applicable to all the testing works carried out in the laboratory.

3.0 RESPONSIBILITY:

The overall responsibility for implementing of this procedure lies with the QM.

4.0 REFERENCE:

Laboratory Quality Manual Doc. No. **CGWB/QM/01**.

5.0 PROCEDURE REQUIRMENT

The request for analysis covers following aspects:

a) Requirements & methods of testing are adequately defined, documented and understood by laboratory people.

b) Laboratories have technical capability in view of proper equipments, trained manpower or operations and supervision of tests to be conducted.

c) Test method selected for testing and sampling is appropriate and capable to meet the requirements of technical officer.

d) Changes in the request (Analytical Request) from either side are reviewed in case it is required and the same, whether accepted or not accepted, are communicated to all the concerned personnels.

5.1 Samples

Technical Manager is authorized to review the Analytical Request Form for the following factors:

a) Type of Analysis

b) Sampling and Preservation

c) Date of Collection

d) Volume of Sample

e) Reporting Methodology of Test Results

f) Any other point concerning with technical officer’s requirement.

6.0 RECORD:

1. Analytical Request Form,
2. Sample Receipt File

7.4 P-01 PROCEDURE FOR RECEIPT, STORAGE AND HANDLING OF SAMPLES

1.0 PURPOSE

1.1 To adopt systematic procedure for receipt storage and handling of samples.

2.0 RESPONSIBILITIES

2.1 Technical Manager is responsible for safe handling & storage of samples till they are transferred to testing laboratory.

2.2 Technical Manager is responsible for storage & handling, testing till its disposal.

3.0 PROCEDURE

3.1 On sample Receipt, Technical Manager collects all the details of the samples from the technical officer regarding purpose, location, testing parameters, site treatment if any and ensures that the sample has been collected and sealed properly. He also puts Lab Id. and puts up the related file/Register to Quality Manager for allotment of testing work to analyst.

3.2 At testing laboratory, the Technical/Quality Manager checks the details/identity of samples before allotting them to analyst for testing.

3.2.1 The technical manager ensures that the analyst keeps the records of data in detail on data calculation sheet/Register.

3.2.2 After the tests are completed the technical manager ensures that the remnants of sample are stored safely at proper place for retention and disposal as per procedure.

4.0 RECORDS

1. Sample Receipt file
2. Analytical Data Calculation sheet/Register
3. Receipt of sample (Register)

7.7P-02 Procedure for Ensuring the validity Test Results

1.0 PURPOSE

To exercise adequate level of quality control for quality assurance of test results provided to technical officer. Quality Assurance shall be established in the Test results in following areas -

- use of CRM
- Intermediate Checks of equipment,
- Inter laboratory Comparison Programme
- Participation in PT programme
- Retesting of retained items
- Replicate Testing

2.0 SCOPE

The entire tests are under the scope of Accreditation.

3.0 RESPONSIBILITY

The Technical Manager and the Quality Manager.

4.0 PROCEDURE

4.1 Quality Control of test is done under supervision of Technical Manager of the section of the laboratory conducting the quality control.

4.2 Quality Manager prepares a Quality Control Programme in consultation with Technical Manager.

The programme shall have at least following common to all laboratories

Reference

Use of Certified Reference Material and or Secondary Reference Material at regular intervals by Chemical Laboratory.

Calibration of Equipment and Reference Standard:

Laboratory maintains the frequency of calibration of the equipment including reference standard and schedule is maintained as per programme of the calibration of equipment Records of the calibration are maintained in the file along with calibration status in format.

Intermediate Checks

Intermediate checks of the instrument or equipment whenever required are done at regular interval by reference standard. Records are maintained in the Instruments Check Register.

Inter Laboratory Comparison Programme:

Quality assurance is ensured by participation in inter laboratory testing by sending the samples to NABL accredited laboratories. While conducting Inter Laboratory Testing, samples are selected from homogeneous nature of material. Enough material is procured and prepared for testing four times. Quality Manager puts identification number on the samples. Sample is tested first in Chemical Laboratory. All the selected parameters shall be done on the same sample or on different samples selected for different parameters. After tests are completed at the laboratory, samples are sent to 4-5 or more other NABL accredited laboratories, subject to availability, without disclosing the test results found in the laboratory.

On receipt of the results from laboratories, the test results are compared and records are maintained by Quality Manager. Z-score is evaluated where ever possible. Laboratory conducts standard type test again on the sample and may find out the root cause of deviation. Records of inter laboratory comparison of testing are maintained by Technical Manager in file as given at the end of this procedure. Inter Laboratory Comparison Programme is planned and conducted in a manner to ensure coverage of entire scope at least once in four years.

Replicate Testing

Periodic replicate test are conducted on retained items as and when required, using same or different method, where available and possible by different persons or by same person under the supervision of Quality Manager.

Retesting of Retained Items

For Assurance of test results, correlation of different characteristics of items are done by Technical Manager, if any discrepancy is observed, some parameters, which are feasible, are rechecked on retained item under different code. Confidentiality in Code No. is maintained by Quality Manager. 2% of retained items shall be covered for retesting.

Participation in Proficiency Testing

The laboratory shall participate in Proficiency testing for the item under the scope of accreditation whenever any source (Nodal Laboratory) is available. The laboratory shall be in contact with NABL for the availability of source. After evaluation of Z- score by nodal laboratory/NABL, if found more than ± 2, Technical Manager & Quality Manager will review necessary resources of testing for further improvement to achieve z score less than 2. If z-score is away from ±3, then effective Internal Quality Control is reviewed in the Review Meeting to employ better resources to achieve the goal. Separate file is maintained, marked as proficiency testing, by Quality Manager.

5.0 RECORDS

1. Replicate Testing / Retesting of Retained sample,
2. Inter-Laboratory Comparison / PT Program,
3. ILC/PT Calendar,
4. CRM or Quality Control Material Results

7.9 P-01 PROCEDURE FOR RESOLUTION OF COMPLAINTS

1.0 PURPOSE

1.1 To take effective action on the complaints received on any activity of the Laboratory.

2.0 RESPONSIBILITY AND PROCEDURE

2.1 Any complaint is received by Quality Manager.

2.2 Quality Manager scrutinizes the complaint and register it in format 7.9F-01, the acknowledgement of the same is sent to the complainant 7.9 F-02.

2.3 The scrutiny is done so as to identify the complaint with Laboratory Personnel of the following-

a) Documentation

b) Quality of Testing

2.4 In case of 2.3(a) above, full investigation is carried out by Quality Manager and he/she takes the action on the outcome.

2.5 In case of 2.3(b) above, the complaint is referred to Technical Manager who conducts the investigation.

2.6 The Technical Manager after investigating the case, including re-testing of samples, if necessary, sends a reply indicating the investigation made along with his findings to Quality Manager for his examination and taking action. In case the investigation leads to amendment of a test report, a revised test report is sent along with the the reply of Technical Manager to Quality Manager who takes appropriate action in the matter.

2.7 The complainants are informed about the final outcome.

2.8 The action taken is verified by a special audit or during the next internal audit.

3.0 RECORDS

1. Complaint File,
2. Complaints acknowledgment card,

7.10 P-01 PROCEDURE FOR CONTROL OF NON-CONFORMING TESTING WORK

1.0 PURPOSE

1.1 To take action when the work does not conform to the requirements of technical officer and established policies and procedures of laboratory.

2.0 RESPONSIBILITY AND PROCEDURE

The laboratory has a policy and a procedure that is implemented when any aspect(s) of its testing or the results do not conform to the agreed requirements of the technical officer. The procedure involves the following steps:-

2.1 Any concerned person can bring in the non-conformance and inform the Quality Manager.

2.2 Quality Manager, with the help of other laboratory personnel carries out the investigation so as to identify the non-conforming work and the action to be taken for correction.

2.3 Quality Manager asks the related personnel for remedial measures to be taken along with decision on the acceptability of the non-conforming work.

2.4 Depending on the decision of Quality Manager, the test report issued is called back from the customer. The same is re-issued to the customer after the correction.

3. 0 OTHER ACTIONS

3.1 In order that non-conformance does not reoccur, the procedure for corrective and preventive actions, **8.7 P-01** is followed immediately.

3.2 Report on non-conforming testing work, if any, is included in the agenda of Management Review Meeting by the Quality Manager.

3.3 Audit is arranged in the area to ensure that Non - conformance does not re-occur.

4. 0 RECORDS

1. Non-conforming testing work analysis and corrective Action

8.3 P-01 PROCEDURE FOR CONTROL OF MANAGEMENT SYSTEM DOCUMENTS

1.0 PURPOSE

1.1 To streamline preparation, issue and control of new document and to make the amendments if necessary to the existing documents.

2.0 RESPONSIBILITIES

2.1 The responsibilities of preparation, approval, issue & review of the various types of documents shall be as follows:

S. No.	Nature Of Document	Level	Responsibility of		
			Preparation	Approval	Review & Issue
1.	Quality Manual	I	QM	RD	QM
2.	Quality Procedures	II	QM	QM	QM
3.	Standard operating Procedure	III	TM	QM	QM
4.	Work Instruction.	IV	TM	QM	QM
5.	Forms & Formats	IV	TM	QM	QM

Quality manager shall review the document (Quality Manual, Quality Procedures, Standard Operating Procedures, Work Instructions, Records & formats) and other documents. After Every two year from the effective date, document shall be reviewed. In case any need arise, document shall be reviewed. After reviewing, stamp of "REVIEWED ON" put along the date.

3.0 PROCEDURE

Activity		Responsibility
3.1	**Preparation of Document**	
3.1.1	Identification of need of new document/ Inadequacy in an existing document.	Lab Personnel
3.1.2	Informing Quality Manager	Lab Personnel
3.1.3	Verification if necessary,	QM/Tech. Manager
3.1.4	Preparation of draft document	As per 2.1 above
3.1.5	Circulation of the draft document to all concerned	QM/Tech. Manager
3.1.6	Completion of the comment and discussion with affective Section	QM/Tech. Manager

3.1.7	Modification of the documents (if necessary) and to put up for approval.	QM/Tech. Manager
3.1.8	In case, the approving authority has certain objections, then discussion with effected sections.	QM/Tech. Manager
3.1.9	Up-date the draft for approval	QM/Tech. Manager
3.2	**Issue of Document**	Quality Manager
3.2.1	Assign document number to approved document (Refer 8.3P-02)	QM/Tech. Manager
3.2.2	Quality Manager maintains an updated Master List of Documents (8.3F-02) both for internal documents (Quality Manual, Quality Procedure Manual, Work Instructions and Formats) and External documents (Indian Standards, NABL Guidelines, list of instrument, chemical and glassware). Updation of Master list is ensured at-least once six months by liaison with issuing bodies or website.	Quality Manager
3.2.3	Issuance of documents to Authorized personals Control Document Distribution Register	Quality Manager
3.2.4	To check receipt of the document and return of Superseded copy.	QM/Tech. Manager
3.2.5	To up-date the Master List of Documents	Quality Manager
3.2.6	To mark superseded copies as ‘Obsolete’ and to destroy them except one copy.	Quality Manager
3.2.7	To keep one copy of ‘Obsolete’ in safe custody.	Quality Manager
3.3	**Revision of documents & their issue.**	QM/Tech. Manager
3.3.1	Same procedure, as given in 3.1 & 3.2 above, shall be followed.	
3.4	**Document of External origin.**	QM/Tech. Manager
3.4.1	To keep the document up-dated through inter-action or their website with Standards Bodies /B.I.S. / International Bodies.	
3.4.2	To inform the concerned user of the lab of any amendment revisions in the document.	
3.5	**Document change**	QM/Tech. Manager

3.5.1 Changes to the documents are reviewed and approved by the same authority who performed the original review unless specifically designated otherwise.

3.5.2 All alterations are listed in the Amendment Record Sheet of the document.

3.5.3 Whenever a need arises for amendment in the quality management system documentation, an amendment is immediately conveyed through a handwritten note to all concerned. The concerned person is also verbally explained of the changes to be incorporated in the procedure(s) for immediate implementation. Quality manager issues such amendments after approval. The document is formally revised and issued within 15 days by Quality Manager.

3.5.4 Laboratory maintains NABL guidelines and Quality Systems documents (Quality Manual, Quality Procedure Manual, Work Instructions and Formats) as softcopy under custody of authorized person (QM). Quality Manager ensures updating of NABL guidelines through NABL website. Quality Manager informs to the concerned user of the lab of any amendment/revisions in the document. The laboratory has the policy that after 15 amendments in the documents, if good enough amendment in QPM the same will be revised and reissued.

Records:

1 Document Distribution of Control Registre,

2. Master List of Document,
3. Obsolete Documents,
4. List of Externally originated documents,

8.3P-02 PROCEDURE FOR NUMBERING OF DOCUMENTS

1.0 PURPOSE

1. To establish a uniform practice for numbering of the documents pertaining to Quality System Documentation.

2.0 DEFINITION

2.1 LEVEL I DOCUMENT - QUALITY MANUAL (QM)

Quality manual addresses itself to all the quality system elements. This manual contains the policies and methodologies for the operation of laboratory quality management system.

2.2 LEVEL II DOCUMENT - QUALITY PROCEDURE MANUAL (QP)

This document contains all the quality procedures adopted in the laboratory.

2.3 LEVEL III DOCUMENT – STANDARD OPERATING PROCEDURE MANUAL (SOP)

Standard Operating Procedures Manual prepared from standard methods of BIS and APHA are referred by technical staff for carrying out testing.

2.4 a. LEVEL IV DOCUMENT - WORK INSTRUCTION MANUAL (WI)

The Work Instructions give in detail the step-by-step instructions for handling of laboratory equipments/instruments.

b. LEVEL IV DOCUMENT - FORMATS MANUAL (F)

The record formats are maintained and referred in level I & level II documents constitute the level IV document.

3.0 RESPONSIBILITY

The following is given the responsibility for allotting the document numbers:

S. No.	Document Level	Responsibility
1.	I & II	Quality Manager
2.	III	Quality Manager
3.	IV	Quality Manager

4.0 PROCEDURE

4.1 Quality Manual

Example: Quality Manual, Section 6.3

6.3

It indicates the Para / section of quality manual as per ISO/IEC 17025:2017 clause no. 6.3. Similarly other sections are numbered with respect to clause nos. of ISO/IEC 17025:2017.

4.2 Quality Procedure Manual and Formats

The Level II, IV documents are referenced by 1 Numerical + 1 Alpha + 2 digit numerical. The 1 numerical indicates clause no., 1 Alpha character indicates either “P (for procedures)” or “F (for record formats), and last two digit number indicates the Sl. No. of document for that particular clause.
Example 4.3P-01

6.3 P - 01

Two digit running serial no. giving the s. no. for that particular clause.

Alpha character indicates procedure for clause 6.3.

Indicates the clause no. of ISO/ IEC 17025:2005, for which procedure 6.3P-01 is prepared.

4.3 Standard Operating Procedure

The compiled document has been numbered by 3 Alpha and single number code. The first 3 alpha characters (SOP) indicate-Standard Operating Procedure and single numerical indicate s. no. of Standard Operating Procedure.

Example:

SOP-01 = Standard Operating Procedure No. 01.

4.4 Work Instruction

The compiled document has been numbered by two Alpha and single number code. The first two alpha characters (WI) indicate-work instruction and single numerical indicate s. no. of Work Instruction. Example:

WI-01 = Work Instruction No. 01.

8.4 P-01 PROCEDURE FOR CONTROL OF RECORDS

1.0 PURPOSE

To maintain records including, Quality System and Technical Records to demonstrate compliance with the requirements and effective implementation of ISO/IEC 17025: 2017

2.0 SCOPE

a) Quality System.

b) Technical Records.

3.0 RESPONSIBILITY

The Quality Manager is responsible for the implementation of this procedure.

4.0 PROCEDURE

4.1 The Quality Manager maintains a list of all relevant records with clear identification along with their retention period and the person(s) responsible for maintaining the record.

4.2 Concerned function(s), where the records are generated or preserved, is(are) responsible for maintenance and storage of the records.

4.3 Observation data and calculation sheet are recorded in such a way that they are easily retrievable.

4.4 The records are stored at proper place in such a way that they are protected from damage and deterioration.

4.5 Analysis results available in computers are stored in the hard disk of the computer. The backups of important records are taken on regular basis.

4.6 Every year, respective record holder reviews the records. The expired records are destroyed and necessary records are kept for use.

4.7 In case of any mistake occurs in any technical records, each mistake is crossed out but not erased and correct value is entered alongside. All the alterations are signed by the person making the corrections.

5.0 RECORDS

1. List of Records with Retention period,

8.7 P-01 PROCEDURE FOR CORRECTIVE ACTION

1.0 PURPOSE

To initiate relevant corrective action when any non-conforming work or departure from policies and procedures of the quality system or technical operations is identified.

2.0 RESPONSIBILITY AND PROCEDURE

The laboratory has its policy and procedure to identify the problems/ non- conforming work (if any) with the management system or with the technical system. However, the procedure for corrective actions involves reviewing of the following activities:

a) Internal Quality Audit findings,

b) Technical officer's Complaints and Feedback,

c) Control of Non-conforming testing Work,

d) Management Review Meeting and discussion with staff, and

e) Procedure for purchasing of services and supplies.

2.1 After identification of the problem, investigation is done to determine the root cause(s).

2.2 Based on investigation made, corrective action(s) are decided and implemented to eliminate the problem, and to prevent its recurrence.

2.3 Corrective actions arising from the Internal Quality Audit are initiated through Internal Quality Audit Procedure 8.8 P-01.

2.4 The corrective actions arising from the technical officer's complaints and feedback are initiated through Procedure for Resolution of Complaints 7.9P-01

2.4 Corrective actions arising from the Non-conforming testing Work are initiated through Non-conforming testing work and corrective action Format.

2.5 Quality manager ensures that concerned person takes the corrective action(s) arising from the decisions taken during Management Review Meeting.

2.6 Whenever the non-conformance casts doubts about the laboratories compliance with its own policies and procedures or on its compliance with NABL or ISO /IEC 17025:2017, the laboratory will conduct additional internal audits of the appropriate section in the organization.

2.7 The Quality Manger monitors the effectiveness of the corrective action(s) taken and ensures that the required changes resulting from corrective actions or investigation are documented and implemented.

3.0 RECORDS

1. Officer’s Complaints,
2. Non-conforming Work analysis and Corrective Action,
3. Internal Audit Non-Conformance Report,
4. Management Review Meeting status report

8.8 P-01 PROCEDURE FOR INTERNAL AUDIT

1.0 PURPOSE

This procedure is required for ensuring to carry out the Internal Audits to find out the status on compliance of the Management System of the Laboratory.

2.0 SCOPE

This procedure is applicable to all the areas of the Laboratory.

3.0 RESPONSIBILITY

Quality Manager is responsible for the audit planning, making arrangement to conduct audit, selection of auditors and reporting audit summary including correctiveaction. Technical Manager is responsible for taking corrective action to close the non-confirming reports in his area.

4.0 REFERENCE

Laboratory Quality Manual Doc. No. CGWB/QM/01.

5.0 PROCEDURE REQUIREMENT

The Internal Audits are planned in April for all the activities of the laboratory and annual plan is prepared (8.8 F-01). Additional / unscheduled audits are also carried out additionally whenever there is large no. of Non Conformances in particular area. The existing Audit plan is revised for these additional audits. The additional/unscheduled Audits are planned by considering the following points.

- Importance of Area / Activities being audited,
- Management Concern,
- Officer’s Complaints / Feed Backs,
- Corrective / Preventive Action Plan / Report,
- Previous Audit Findings,
- Management Review Decisions,

Internal Audit is being conducted by trained and qualified auditors selected by the laboratory, who is independent of activity being audited. Internal audit may be conducted by in – house or by an approved external qualified auditor. Audit schedule indicating month, date and activities to be audited for laboratory is prepared in and circulated as internal audit notice by the Quality Manager.

This audit schedule is circulated to all concerned personnel of laboratory and to the auditors well in advance. The requirement of Management System as described in Laboratory Manual / Procedure Manual and other relevant document is to be verified for compliance.

To harmonize the audit process and to ensure that all the auditors conduct the audits in uniform manner and all the requirements of Management System are audited, Audit Check list is prepared. The Audit observations (positive compliances) are recorded in the audit check list.

Audit findings are recorded iand duly signed by auditor & the auditee by indicating corrective action proposed, corrective actions taken, corrective action acceptance and follow up actions. These are to be signed by Auditor / Audittee / QM at respective columns. One copy of NC form is given to auditee and the auditors give original form to the Quality Manager.

On closer of non-conformities on or before the due date, Quality Manager verifies the closing action of NC and makes entry of it in the NC form. If agreed, it is closed. Otherwise he will perform the follow up audit for the same to verify the corrective action taken. Records are maintained.

Audit findings are put up to the Chief Executive for his review and also discussed in the management review meeting. All the records are maintained by Quality Manager.

In case the internal audit cast doubts on the effectiveness of the operations or on the correctness / validity of test results, the procedure for corrective action is followed for necessary action and verification including informing to customer, if needed.

6.0 RECORDS:

1. Internal Audit Plan
2. Internal Audit Checklist
3. Internal Audit Non-Conformance Format
4. Internal Audit Non-Conformance Status Report

8.9 P-01 PROCEDURE FOR MANAGEMENT REVIEW

1.0 PURPOSE

Purpose of this procedure is to ensure the holding of periodic Management Review Meeting to find out the various requirements of the Laboratory Management System, its continuous suitability and effectiveness and to introduce necessary changes for improvements.

2.0 SCOPE

This procedure is applicable to all the areas where Management System has been implemented in the Laboratory.

3.0 RESPONSIBILITY

The overall responsibility for implementing of this procedure lies with the Quality Manager.

4.0 REFERENCE:

Laboratory Quality Manual Doc. No. CGWB/QM /01.

5.0 PROCEDURE REQUIRMENT

The effectiveness of the Management System in the laboratory is reviewed periodically, at least once in a year, by the Management Review Committee. The committee is headed by Regional Director/Chief Executive, as Chairman and includes Technical Manager, Quality Manager, scientific staff (ARO's, SRA's), any other personnel, specially invited by Chief Executive. The agenda for the Management Review Meeting (8.9F-01) is communicated to all members by Quality Manager. The aspects reviewed during the meeting are:

a) Continuing suitability of Quality Policy, objectives and other policies and procedures,

b) Input provided by committee members or any person of Laboratory regarding improvements,

c) Findings and status of Internal and External Audits,

d) Status of Corrective and Preventive Actions identified, and action taken,

e) Findings of inter laboratory comparison or proficiency tests scheduled by accreditation agencies / laboratory,

f) Work load and type of jobs received,

g) Suitability of Test Methods being used,

h) Feedback from Technical Oofficer, including complaints,

i) Training of Personnel,

j) Changes in volume and type of work,

k) Status of implementation of minutes of last Management Review Meeting,

l) Any other point(s).

Minutes of the meeting are recorded by Quality Manager with due date of completion and responsibility for completion of particular point as identified in the meeting. Minutes of the Management Review Meeting are circulated to all the committee members and monitored by Quality Manager for its implementation within agreed time frame. Chief Executive is being informed from time to time regarding progress in the implementation

6.0 RECORDS

1. Management Review Meeting Agenda
2. Management Review Meeting Status Report
3. Minutes of Management Review meeting

Annexure IV

क्षेत्रीय रासायनिक
प्रयोगशाला
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WORK INSTRUCTION MANUAL

Doc. No: WI-01A	Computation of uncertainty Measurement by calculation.	Clause No. 7.6
Rev. No: 0	Issue Date: 1/1/2020	Page No.: 1 of 3

1.0 Purpose

To describe the procedure for computing uncertainty measurement by 6 statistical calculation

2.0 Scope

The work instruction is application for evaluation of uncertainty Measurement by statistical analysis by series of observations.

3.0 Responsibility

Quality Manager/Technical Manager/Dy. QM/TM

4.0 Definition

Standard uncertainty of the result of a measurement when that result is obtained from the values of a number of other quantities , equal to the positive square root of a sum terms, the terms begin the variances or co variances of these other qualities weighted according to how the measurement result varies with changes in these quantities.

5.0 Method

Uncertainty estimation is simple in principal. The following two types summarize the tasks that need to be performed in order to obtain an estimate of the uncertainty associated with a measurement results.

5.1 Type A Evaluation of Standard Uncertainty

5.1.1 Type A evaluation of standard uncertainty applies the situation when several independent observations have been made for any of the input quantities under the same conditions of measurements.

5.1.2 Perform a series of test on same sample for at least 5 (Five) times minimum by using same standard method.

5.1.3 Calculate the mean value of all above observation by mathematical calculation or using calculator.

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5.1.4 From the mean value and series of individual value calculate median, variance and standard deviation by statistical calculation or by using scientific calculator, estimate standard deviation directly.

5.1.5 Calculate type 'A' uncertainty measurement by using following formula.

$$\text{Type A uncertainty Measurement} = \frac{\text{Standard deviation}}{\sqrt{\text{No. of times test performed}}}$$

5.1.6 Find out degree of freedom vi = n-1, where n= number of time test performed

5.2 TYPE B EVALUTION OF STANDARD UNCERTAINITY:

5.2.1 Type B evaluation of standard uncertainty is associated with an estimate of and input quantity by means other than statistical analysis of series of observations. It is scientifically judged based on all available information on possible variability like

- Uncertainty provided in master certificate of calibration
- Accuracy/Resolution of instruments
- Accuracy/Resolution of Balance, Thermometer
- Accuracy/Resolution of Glassware's
- Purity of reagents

As per test parameters, calculate the above possible variables, convert these factors into percentage and find out type B uncertainty for each test wise variables by judging statistically under Normal distribution A, B, Rectangular Distribution, Triangular Distribution or U shaped Distribution. Estimates these values by statistical calculation or determine by using calculator as Ub1, Ub2, Ub3, Ub4… ....etc.

5.3 Combined Standard Uncertainty

Estimate the combined standard uncertainty by using formula:

$$\sqrt{(Ua)^2 + (Ub1)^2 + (Ub2)^2 + (Ub3)^2 + (Ub4)^2 + ----}$$

Where Ua is type A uncertainty measurement

And Ub1, Ub2 and Ub4 ---------type B uncertainty measurement.

5.4 Effective Degree Of Freedom (Veff)

The effective degree of freedom of the combined standard uncertainty is estimated by using FORMULA.

$$\frac{\textbf{Combined Standard Uncertainty: }(UC)^4}{\frac{(Ua)^4}{n-1} + \frac{(Ub1)^4}{\infty} + \frac{(Ub2)^4}{\infty} + \frac{(Ub3)^4}{\infty} + \frac{(Ub4)^4}{\infty}}$$

From the estimated value of effective degree of freedom find the coverage factor at 95% confidence level by referring **Page no. 41 of NABL**

Expanded Uncertainty: This is calculated by using following formula

Expanded Uncertainty: Combined Uncertainty X K

K= Coverage factor 95% C.L.

Report: Report the result of Uncertainty Measurement as per accuracy of individual test method.

Participation in inter laboratory test comparisons are undertaken by a laboratory, to ascertain the quality of its results in general and to achieve.

- Checking overall laboratory testing performance.
- Checking an individual's testing performance from among laboratory staff.
- Establishing the effectiveness of test method.
- Determining one or more characteristics of a material or product to a particular degree of accuracy.

Proficiency testing Data obtained from different Laboratories on the two samples provided needs to be statistically analysis to carry out with in Laboratory and between Laboratories comparisons. This also helps in identifying outliers using Z- score.

Mean: Total of all the results divided by the number of results.

Median: The median is the middle value of the group (i.e.) half of the results are higher than it an half are lower. It is calculated from the sorted values (from lowest to highest). If n is an odd number, the Median is the singular central value, if "n" is even, it is the average of the two central values.

Standard Deviation: Mean indicates the location and standard deviation indicates dispersion around the Mean. The square of the standard deviation is known as the variance.

If X1,X2-------------Xn are 'n' observation, then the Mean is
X= X1+X2+ ---------- + X n/n=∑ x /n

For an ungrouped data with 'n' observations the standard deviation is given by

S= (sq e (X1-X) / n-1)^$^{o.5}$

Range (R): Difference between the highest value and the lowest value

Range Value = Max value- Min value

Inter Quartile Range: (IQR): It is the difference between the lower and upper quartiles. The lower quartile (Q1) is the value which a quartiles of the results lie. Similarly, the upper Quartile (Q3) is the value above which a quartiles of the results lie.

NIQR= IQR X 0.7413

Z-score

Z-score are normalized value gives a 'scores' to each result relative to the other members in the group, so a Z-score value close to Zero means That the results agrees well those from the other values.

Classical Z-score

$$Z=\frac{\text{Result-Mean}}{\text{Standard Deviation}}$$

Robust Z-score

$$Z=\frac{\text{Result-Mean}}{\text{Normalized IQR}}$$

The Statistical procedure uses Z-score to identify outlier's results. An outlier will be any result, which has an absolute Z-score value greater than 3.

Statistical Analysis:

- Each lab is provided two samples A&B are results of two samples:
- Summary table of Robust statistics for each sample:
  1. No of results
  2. Mean
  3. Median
  4. Normalized IQR
  5. Robust
  6. Minimum
  7. Maximum
  8. Range

- Calculation of between Z-scores and within Z-scores for each result.
- Identifications of outlier results.
- Interpretation.

WORK INSTRUCTION MANUAL

Doc. No: WI-04B	Doc Name: Z- Score Calculation	Clause No. 4.1
Rev. No: 0	Issue Date: 1/1/2020	Page No.: 3 of 3

Calculation of between Lab Z-score (ZB)

S= (A+B) S= (sq e (X1-X) / n-1)^$^{\circ.5=}$ Standardized sum of Laboratory

Find Median of S

Find Inter quartile Range (IQR) of S

Between Laboratory Z- Score (ZB)

$$ZB= \frac{S- Median (S)}{IQR (S) \times 0.7413}$$

Calculation of within Lab Z-score (ZWB)

D= Standardized difference between the two result for Laboratory.

i.e. D= (A-B) /2^°.5 = if (A) > (B)
= (B-A) /2^°.5 = if (A) < (B)

- Find Median of D and IQR of D
- Within Laboratory Z-Score (ZW)

$$ZB= \frac{D-Median (D)}{IQR (D) \times 0.7413}$$

- Z-score assign a score to each result relative to the other results in the group
- Z-score is a measure of how far the result is from the consensus value.
- Use Z score to identify outlier results.
- Outlier will be any result which has an absolute Z-score is greater than 3.

i.e. if $Z > 3$ result is too high
if $Z< 3$ result is too low

In general
$Z\leq 2$ = Satisfactory
$2<Z<3$ = Questionable
$Z\geq 3$ = Unsatisfactory

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Annexure IV

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WORK INSTRUCTION MANUAL

Doc. No: WI- 01C	Doc Name: **In – House Calibration of Thermometer**	Clause No. 6.4
Rev. No: 0	Issue Date: 1/1/2020	Page No.: 1 of 1

1. Appropriate Reference Thermometer calibrated by external approval accredited laboratory to be selected as against the In-use Thermometer to be calibrated/verified.
2. Condition of Thermometer (Reference & In-use) to be verified for any flaws in the glass, any broken in the memory column.
3. A constant temperature oil bath with the bath stability of (±) 0.02°C to be selected.
4. Both Thermometers are to be supported vertically in the constant temperature oil bath.
5. The Thermometer readings are viewed with a magnifying lens.
6. Thermometer should be gently and repeatedly tapped at right angles to its axis while noting the readings.
7. Keep both the Thermometers for 20 minutes in the Constant Temperature Oil Bath without any disturbances.
8. Observed the reading of both the Thermometers after reaching a steady state.
9. Repeat the procedure for another two constant temperatures.
10. Record the observed reading.
11. Correction, if any, with the reference to the Calibrated Thermometer Certificate, to be applied for the Thermometer in Calibration.
12. Report the reading after correction, if any, in the appropriate format.

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QUALITY MANAGER 1/1/2020 TECHNICAL MANAGER

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WORK INSTRUCTION MANUAL

Doc. No: WI-01D	Doc Name: In- House Calibration of Volumetric Glasswares	Clause No. 6.4
Rev. No: 0	Issue Date: 1/1/2020	Page No.: 1 of 1

Pipette: (0.1 ml to 100ml capacity)

Fill the pipette with Double distilled water and adjust to the mark, Run this water to a previously weighed bottle and take the weight in a calibrated Mettler Balance. Note the temperature of the water and record the volume of water by referring to the table given below.

Volume Flast: (25ml to 100ml capacity)

Measuring cylinder: (10ml to 50ml capacity)

Record the weight of clear and dry flask/cylinder. Transfer double distilled water into it through funnel ensuring that the water does not wet the sides of the flask/cylinder above the mark. Carefully remove the funnel and adjust the volume to the mark. Take the final weight of the flask/cylinder in a calibrated mettler balance. Note the temperature of the water and find out the volume of the water referring to the table given below:

Burette: (5 ml to 50 ml capacity)

Leakage test: Remove the stopcock from the burette. Degrease it and wet with distilled water. Reassemble the stopcock in the burette. Fill the burette and adjust to zero mark with distilled water. Allow it to stand for 20 minutes. If the meniscus is constant than the burette is said to be leakage proof.

Calibration: Fill the burette with the doubled distilled water and adjust it to zero mark. Take a previously weighed clean dry stoppered flask and place it below the burette and open stopcock till the desired calibration point is reached. Restopper and take the final weight in a calibrated mettler balance. Note the temperature of the water and find out the volume by referring to the tables given below:

Temp (°C)	Volume (ml)	Temp (°C)	Volume ml

Higher Capacity Glasswares

Other higher capacity volumetric glassware are verified by comparing the volume with respective 'A' class glasswares.

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WORK INSTRUCTION MANUAL

WORK INSTRUCTION

All the Officers of Regional Chemical Laboratory are informed to carry out the Laboratory work as per ISO/IEC17025:2017, QUALITY MANUAL of Chemical Laboratory, CGWB, NER including the laid down procedures, instructions, forms and format etc. for all the laboratory activities.

Special emphasis is to be taken for the followings as per NABL Guidelines-

1. Use/testing of CRM for all the parameters being analysed and proper entry should be ensured.
2. Calibration of instruments/apparatus timely being used in analysis and proper entry should be ensured.
3. Repeat and Retest for the parameters and proper entry should be ensured.
4. Intra & Inter laboratory comparision of samples and proper entry should be ensured.
5. Measurement of Uncertainity at each step of analysis when reagent, apparatus, method etc are being changed for every analytical parameter and proper entry should be ensured.
6. Environmental conditions to be maintained as per guidelines and proper entry should be ensured.
7. Records maintain as per NABL Guidelines and proper entry should be ensured.
8. Result with UID are to be send with authorized signatories i.e. either Quality Manager/Technical Manager.

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QUALITY MANAGER	1/1/2020	TECHNICAL MANAGER

Annexure V

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प्रयोगशाला केन्द्रीय
भूमि जल बोर्ड
उत्तरी क्षेत्र लखनऊ

क्वालिटी मैनुअल

आई.एस.ओ/आई.ई.सी/ 17025:2017

सी.जी.ब्ल्यू.बी/यि.आर/क्यू.एम/०१

QUALITY MANUAL
(ISO/IEC 17025:2017)
(CGWB/NR/QM/01)

REGIONAL CHEMICAL LABORATORY
CENTRAL GROUND WATER BOARD
NORTHERN REGION
BHUJAL BHAWAN,
LUCKNOW

Copy No. : Controlled / Uncontrolled

Issue No. : **01** Date : 03.01.2022

Holder Name :

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THIS QUALITY MANUAL IS RELEASED UNDER THE AUTHORITY OF

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AMENDMENT RECORD

Amendments are recorded in the amendment record sheet as below.

S. No.	Page No.	Section/ Clause/ Para/line (As applicable)	Date of Amendment	Amendment made	Reasons of Amendment	Signature of OIC Chem
1.	7/46	1.1	03.01.2022	APHA 23rd Edition	Change of APHA Edition	
2.	8/46	1.2	03.01.2022	Regional Director Signature	Change of Regional Director	
3.	17/46	5.5	03.01.2022	Name change of OIC	Change of OIC	
4.	33/46	7.8.6	03.03.2022	Deletion of 7.8.6.1 & 7.8.6.2	Correction made as per NABL L.A	

Annexure V

CONTENTS

1.0 INTRODUCTION

This document is the Quality Manual for the Regional Chemical Lab, CGWB, NR, Lucknow.

This document provides a detailed description of the organization and processes within the Certification Body (CB). It is primarily intended for the better understanding of the Quality Management System.

History of changes

Revision date	Brief summary of changes
08.07.2019	Complete document replacement to address introduction of ISO 17025:2017, therefore, no track changes

1.1 BACKGROUND

Central Ground Water Board was constituted as an Apex Organization at the national level in respect of matters relating to ground water exploration, assessment, development, scientific management and regulation of the country’s ground water resources. Presently it is headed by the Chairman and has four main wings namely Exploratory Drilling & Material Management (ED&MM); Sustainable Management & Liasion (SML); Survey Assessment & Monitoring (SAM) and Training & Technology Transfer (T&TT). Each wing is headed by a Member. The administrative and financial matters of the Board are being dealt with by the director (Administration) and Finance and Accounts Officer (FAO) respectively.

For undertaking the activities in different fields, it has 18 Regional Offices, each headed by Regional Director, and 11 State Unit Offices (SUO). The State Unit Offices have been established in those states, which have large geographical area for better management of field activities. There are 17 Divisional Offices to handle the exploratory drilling and related activities and each is headed by an Executive Engineers (EE).

Central Ground Water Board is monitoring ground water levels and ground water quality, which are the most important aspects of spatial and temporal variation of ground water regime. Thus, the accurate monitoring of the ground water levels and its quality, both in time and space, are the main pre-requisite for assessment, scientific development and planning of this vital resource. The changes in water quality and water levels are result of the development pattern of ground water resource for irrigation and drinking water needs.

The Central Ground Water Board has 16 well-equipped Regional Chemical Laboratories to carry out chemical analysis of major and minor inorganic constituents in water samples collected in-house. All Chemical Laboratories carry out Basic analysis, Heavy and Toxic elements analysis.

The Regional Chemical laboratory of NR, Lucknow is presently having all basic instruments and equipments required for physical & chemical analysis of ground water and industrial effluents. Chemical Data generated is used for monitoring and evaluating the ground water quality in compliance with National Standards for designated use, to study the impact of anthropogenic activities on ground water quality, to demarcate critical areas where water quality deterioration has been observed and areas vulnerable to quality deterioration and to assess point and non-point sources of ground water pollution for taking necessary action for management of ground water resources.

Laboratory has a team of highly qualified scientists with several years of experience in the field of ground water and is having sufficient literature on water Chemistry including Manuals for Methods of water analysis.

- It has successfully implemented ISO / IEC 17025:2017 management system.

1.1 SCOPE OF CHEMICAL LAB

Scope of NABL Accreditation includes the testing of the following-

S. No.	Product(s) / Material of test	Specific tests performed	* Test Method / Standard against which tests are performed	Range of Testing/ Limits of detection
	Water(G. W)			
1.		Arsenic	APHA 23rd Ed. 3125 B ICP-MS Method: 2017	0.001 mg/l to 2 mg/l
2.		Bicarbonate	APHA 23rd Ed. 2320 B Titration Method: 2017	6.1 mg/L to 100 mg/L
3.		Calcium Hardness	APHA 23rd Ed. 3500-Ca B EDTA Titrimetric Method: 2017	2 mg/L to 10000 mg/l
4.		Carbonate	APHA 23rd Ed. 2320 B Titration Method: 2017	3 mg/L to 100 mg/L
5.		Chloride	APHA 23rd Ed. 2320 B Titration Method: 2017	3.5 mg/L to 10000 mg/L
6.		Chromium	APHA 23rd Ed. 3125 B ICP-MS Method: 2017	0.001 mg/L to 2 mg/L
7.		Conductivity at 25 Deg. C	APHA 23rd Ed. 2510 B Laboratory Method: 2017	5 micromho/cm to 10000 micromho/cm
8.		Copper	APHA 23rd Ed. 3111 B Air-Acetylene Flame Method: 2017	0.02 mg/L to 2 mg/L
9.		Fluoride	USGS Zirconium-eriochrome Cyanine R Method: 1989	0.1 mg/l to 3 mg/l
10.		Iron	APHA 23rd Ed. 3125 B ICP-MS Method: 2017	0.05 mg/L to 5 mg/L
11.		Lead	APHA 23rd Ed. 3125 B ICP-MS Method: 2017	0.001 mg/L to 2 mg/L
12.		Magnesium Hardness	APHA 23rd Ed. 3500-Mg B Calculation Method: 2017	1.2 mg/L to 10000 mg/L
13.		Manganese	APHA 23rd Ed. 3125 B ICP-MS Method: 2017	0.05 mg/L to 5 mg/L
14.		Nitrate	APHA 23rd Ed. 4500-NO3 B Ultraviolet Spectrophotometric Method: 2017	5 mg/L to 45 mg/L
15.		pH	APHA 23rd Ed. 4500-H B Electrometric Method: 2017	1 to 14
16.		Phosphate	APHA 23rd Ed. 4500-P E Ascorbic Acid Method: 2017	0.2 mg/L to 5 mg/L
17.		Potassium	APHA 23rd Ed. 3500-K B Flame Photometric Method: 2017	1 mg/L to 1000 mg/L
18.		Silica	APHA 23rd Ed. 4500-SiO2 C Molybdosilicate Method: 2017	5 mg/L to 50 mg/L
19.		Sodium	APHA 23rd Ed. 3500-Na B Flame Photometric Method: 2017	2 mg/L to 1000 mg/L
20.		Sulphate	APHA 23rd Ed. 4500-SO4 E Turbidimetric Method: 2017	5 mg/L to 100 mg/L
21.		Total Hardness	APHA 23rd Ed. 2340 C EDTA Titrimetric Method: 2017	5 mg/L to 10000 mg/L
22.		Uranium	APHA 23rd Ed. 3125 B ICP-MS Method: 2017	0.002 mg/L to 2 mg/L
23.		Zinc	APHA 23rd Ed. 3125 B ICP-MS Method: 2017	0.05 mg/L to 5 mg/L

Annexure V

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भूमिजल बोर्ड,
उत्तरी क्षेत्र

1.2 QUALITY POLICY AND OBJECTIVES

Quality Policy:

Laboratory is committed to provide analytical data testing services on in house basis to concerned officer with high degree of confidence through accurate and reliable testing methods and continual improvement in the system by implementing ISO/IEC-17025: 2017 with commitment to impartiality. Laboratory ensures that its entire staff is familiar with Management System. Lab gives emphasis to produce reliable and accurate Test Results.

Quality Objectives:

- To constantly strive for excellence in all laboratory activities by implementing the adequate quality standards.
- Regularly participate in ILC/PT Program. We will ensure that there is no outlier in any parameter in two consecutive PT Program.
- To provide quality services within time period desired by Technical Officer as per policy of CGWB.
- To ensure that not more than three complaints regarding accuracy of test results and service to the Technical officer are received in a year.

To achieve these objectives the laboratory has implemented a detailed management system. It is responsibility of all staff to familiarize themselves with the contents of management system and comply with them at all times.

(**Regional Director)**

Date:

2.0 NORMATIVE REFERENCES

In developing this QM the following documents have been taken in to consideration.

ISO/IEC 17025-2017

3.0 TERMS AND DEFINITIONS

For the purpose of this document, the terms and definitions given in ISO/IEC 17025-2017 apply and following Abbreviations apply.

Abbreviation	=	**Full Form**
AO	=	Administrative Officer
APHA	=	American Public Health Association
CEO	=	Chief Executive Officer
CGWB	=	Central Ground Water Board
CRM	=	Certified Reference Material
Doc.	=	Document
F	=	File
FR	=	Format / File
HOO	=	Head of Office
IEC	=	International Electro-technical Commission
ILC	=	Inter-Laboratory Comparison
IS	=	Indian Standard
ISO	=	International Organization for Standardization
MRM	=	Management Review Meeting
NC	=	Non-Conformity
OIC Chemical	=	Officer in Charge, Chemical Laboratory
PT	=	Proficiency Testing
QM	=	Quality Manager / Quality Manual
QP	=	Quality Procedure Manual
RD	=	Regional Director
TM	=	Technical Manager
WI	=	Work Instruction

4.0 GENERAL REQUIREMENTS

4.1 IMPARTIALITY

4.1.1 The Chemical Laboratory is a part of CGWB and works under the control of Regional Director but works independently under supervision of Officer in charge (Chemical). The organizational arrangement is such that other sections (departments) do not adversely influence the compliance with the requirements of International Standards.

4.1.2 Laboratory management is committed to impartiality (Quality Policy). All personnel within lab avoid involvement in any activities that would diminish confidence in lab's competence, impartiality, judgment or operational integrity.

4.1.3 The laboratory personnel are regular Government employees and their salary is not linked with the work done. The laboratory personnel are dedicated workers and are free from any undue internal and external pressures, which may influence the quality of laboratory work.

4.1.4 Dedicated test areas with requisite infrastructure and resources are provided so that staff can deliver in an effective manner. Such events as falsifying test data, altering test and results, not fully completing test activities, alternating test methods using non-standard techniques, etc. are not tolerated at NR, Chemical Lab.

4.1.5 If a situation does occur, the person involved or who is knowledgeable about such an activities has the responsibility to report the information to the OIC Chem as soon as possible. If the OIC Chem is involved, the information shall be reported to the RD, CGWB, NR, Lucknow.

The OIC Chem has the responsibility of notifying the ISO 17025:2017 accreditation organization when such an incident occurs.

Reference:

- ISO 17025:2017
- Lab procedure manual 2019

4.2 CONFIDENTIALITY

4.2.1 The laboratory is bound by the CCS Conduct Rules to observe professional secrecy with regard to all information related to the activities of Central Ground Water Board including procedures for protecting hard copy and the electronic storage and transmission of results.

4.2.2 The lab is part of Central Govt. Organisation and all its customers are internal technical officers. Information is placed in public domain as per govt. rules. Customers' “confidential information” if any (i.e. laboratory test results or other recorded information) will be provided only on directions of RD.

4.2.3 Information from sources other than customer is not shared with concerned officer unless otherwise specified by source in written. Registration of samples received from customers wherever information is to be retained confidentially, details are maintained in relevant records.

4.2.4 The laboratory personnel are qualified and trained personnel. Laboratory personnel adhere to code of conduct, discipline rules as per CCS rules.

Reference

-ISO 17025:2017

-Lab procedure manual 2019

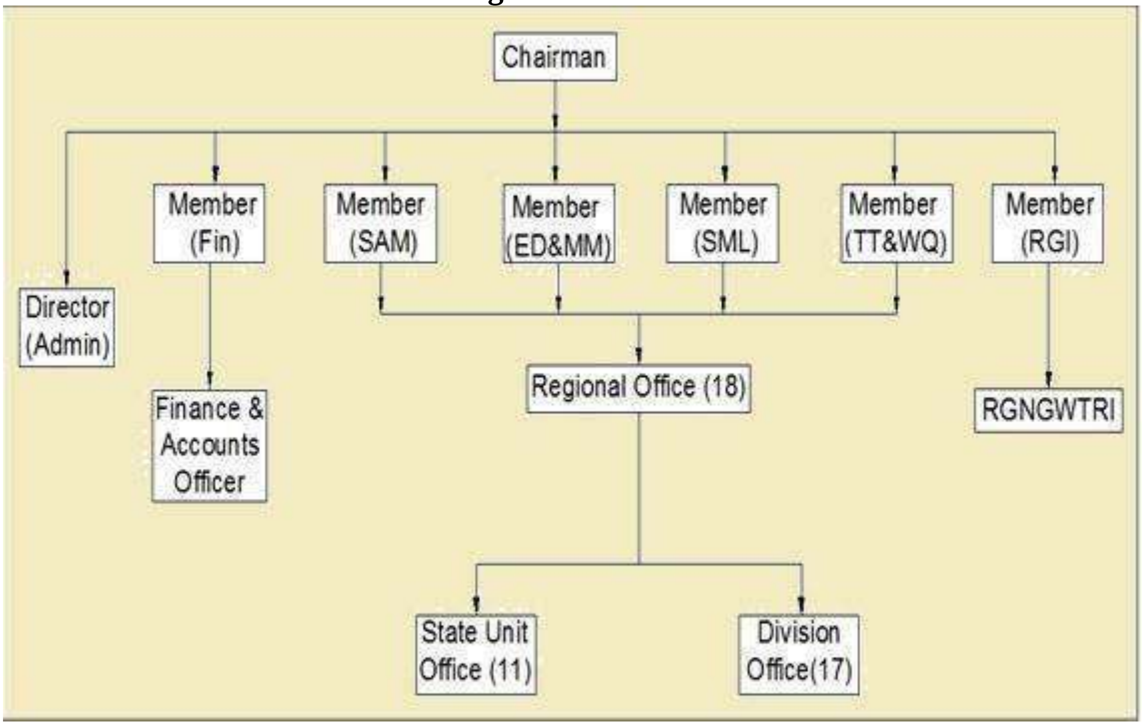
5.0 STRUCTURAL REQUIREMENTS

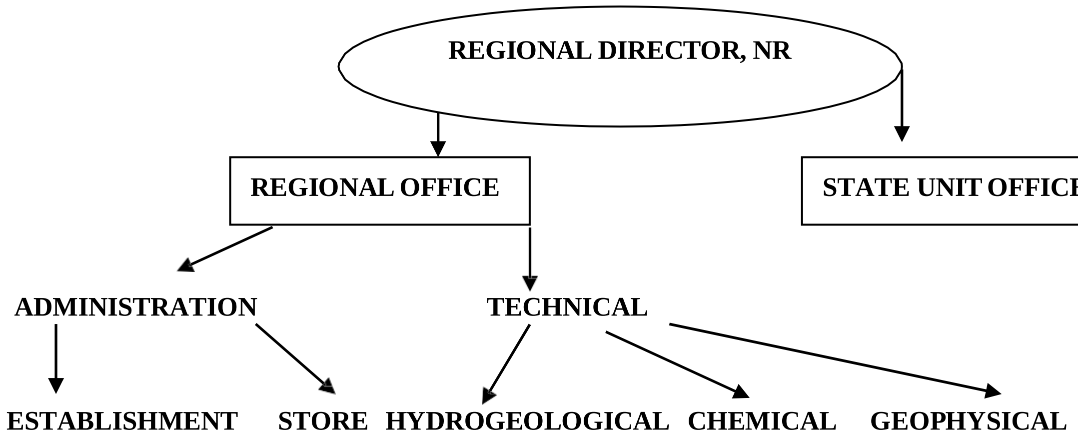
5.1 Legal Identity

Name:		CENTRAL GROUND WATER BOARD
Address:		Central Ground Water Board Bhujal Bhawan, Northern region Lucknow -226021
Status	:	National Apex Organization for Ground Water Ministry of Jal Shakti Deptt of Water Resources, RD & GR, Govt. of India
Established	:	Constituted in 1972
Mobile / Stationary	:	Stationary

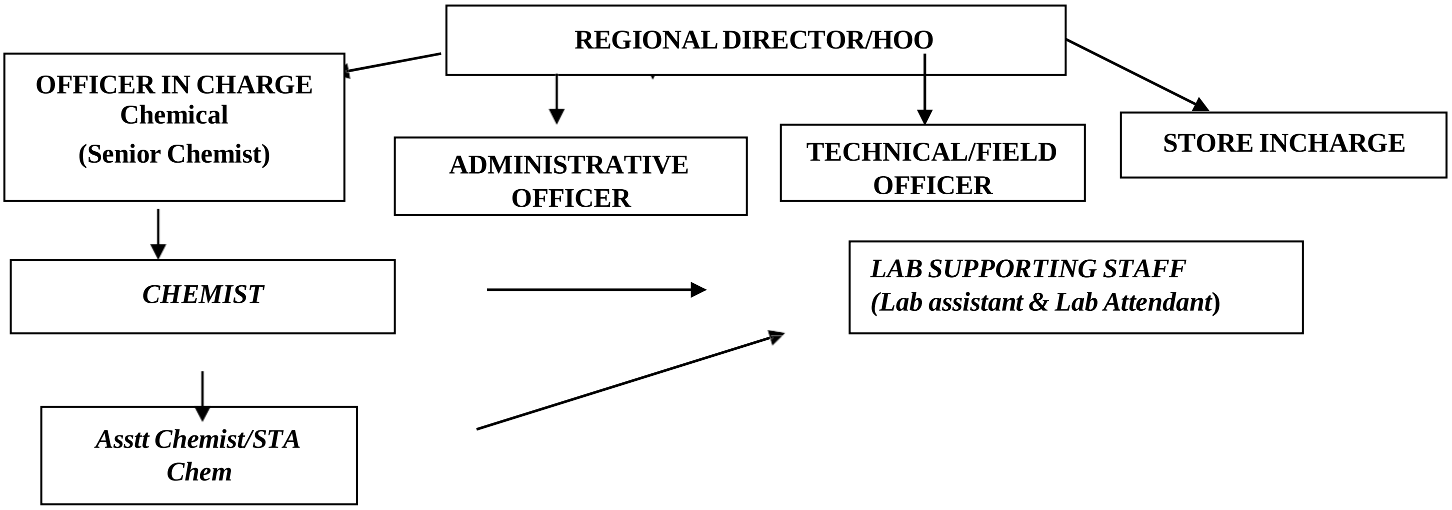
5.2 The laboratory is part of the Central Ground Water Board, Ministry of Jal Shakti, Deptt of Water Resources, RD & GR, Govt. of India.

Organization Chart





REGIONAL CHEMICAL LABORATORY



The OIC Chem provides required supervision and arrange for training to laboratory staff with regard to all the tests performed in the laboratory with the approval of Regional Director.

The laboratory's technical management consists of highly qualified and experienced staff and they are responsible for all technical operations and provision of resources needed to ensure quality laboratory operations.

5.3 The lab activities for testing of Groundwater samples conform to ISO 17025:2017.Regional Director ensures through official letters/circulars that appropriate communication between various levels and functions is maintained in matters related to the processes of management systems and their effectiveness and records are maintained under the supervision of OIC Chem.

5.4 The Chemical Laboratory is a part of Regional office of Central Ground Water Board, which is headed by Regional Director/HOO. The top management ensures that appropriate communication processes are established within the laboratory for implementation of the management system, and that communication takes place regarding the effectiveness of the management system. The Laboratory provides testing services in the field of ground water at permanent site (own building) at the above address.

5.5 The Regional Director/HOO ensures that the integrity of the management system is maintained when changes to the management system are implemented.

Regional Director/HOO:

The major duties of Regional Director are:

- He is the in-charge of the Regional Office including Chemical Laboratory and is responsible for providing adequate resources to enable effective implementation of the management system in the laboratory and chair management review meetings. He is responsible for over-all compliance of the Laboratory to this quality manual
- Reviews & approves Technical Reports.
- Gives administrative and financial approval for purchase chemical equipments, chemicals, glass apparatus and miscellaneous items related to optimum functioning of a laboratory
- Reviews and approves correspondence/interaction with NABL.
- Approves the training of personnel

- Review of requests, tenders and contracts.

Administrative Officer / DDO

The major functions of Administration Officer are:

- Arrange housekeeping of laboratory
- Arrangement of funds/payments

Technical/Field Officers

- Collection of water samples
- Preparation of Technical Reports

Store Officer

- Purchasing of services and supplies and keep recording.
- Bring out quotation for all purchasing.
- Approval of vendors.

OIC Chemical:

The major duties of OIC Chem. are:

- Design, Develop, and implement the Management system.
- Maintenance and issue of Management system, Documents and their distribution.
- Make interaction with NABL with approval of RD/HOO.
- Preparation of quality management documents - Quality Manual and Quality Procedure.
- Arrangement of management review meetings.
- Review Formats.
- Arrangement of Internal Audit
- Sample allocation to Analyst
- Approval of Test reports.
- Provide Training opportunity to Lab. Personnel
- Initiation for Corrective and Preventive actions.
- Authorize personnel for specific job.
- To co-ordinate proper functioning of staff.

The OIC Chem has direct access to RD who has the authority to make decisions in regard to Chemical Lab.

Chemist

The major functions of Chemist are:

- Preparation of Standard Operating Procedures, work instructions and Format.
- Implementation of Technical system.
- Arrange Calibration of laboratory equipment and in-house Calibration of instruments.
- Receiving of test samples, allotment of ID and maintain their record
- Initiate allotment of test work to the analyst by OIC Chem.
- Initiation of Corrective and Preventive actions.
- Maintain accuracy & quality in Testing as per standard & established procedures
- Update the calibration record.
- Maintenance of Laboratory equipments & intermediate checks
- Approval of Test reports.
- Supervision of Technical work.

Asstt Chemist/STA Chem/ Analyst

Some of major functions are:

- Reporting to Chemist / OIC Chem.
- Testing as per standard & established procedures.
- Standardization of standard solutions/ reagents and maintain the record.
- Monitoring & recording of environmental conditions.
- Preparation of Test Results.
- Checking Quality of Distilled water.
- Maintenance of Laboratory equipments & intermediate checks
- Receiving enquires/complaints from Field Officers and forward it to the OIC Chem
- Keep record of results of tested samples.

Lab Supporting Staff

a) Lab Assistant / Lab Attendant

- Preparation of Sample Reagent Solution, reagent grade water and maintenance of stock solution.
- Receiving water samples in the lab and maintenance of records of water samples.

- Maintenance of equipment, chemical and glassware records under supervision of Chemist.
- Any other work assigned by Chemist/chemist/analyst.

b) Lab Attendant

- Preparation of deionised/demineralised/distilled water.
- Cleaning up of glassware in lab and dusting of instruments/equipment/work tables.
- Any other work assigned by technical manager/chemist/analyst

Dr. S.K. Srivastava, Sr. Chemist (Scientist-D) has been nominated as the OIC Chem of the laboratory. In addition to other duties and responsibilities, he has defined responsibility and authority for ensuring that the management system as per ISO/IEC 17025: 2017 is implemented and followed at all times. **Sh. Karam Singh, Chemist (Scientist-B)** has been nominated to look after Technical work.

The laboratory functions under the supervision and guidance of Regional Director who is Head of Department. The laboratory has established, implemented and maintained a management system appropriate to the scope of its activities in a formal documented Management System. The laboratory has documented its policies, system, procedures and instructions to the extent necessary to assure the quality of the test results in above stated documents. The OIC Chem ensures that documentation system is communicated to, understood by, available to, and implemented by the appropriate personnel.

5.6 The laboratory has well-qualified, experienced, and trained personnel to carry out both managerial and technical functions with needed authority and resources. They are authorized to identify any occurrence of departure from testing procedures and to initiate actions to prevent/minimize such departures. Employees care free to express concerns through proper channel to top Management, need for further improvement if any and ensuring the effectiveness of lab activities.

Laboratory continuously make efforts for the improvement of the management system through quality policy and quality objectives, Proficiency Testing, Inter- laboratory/Analytical Quality Comparison, effective Internal Audits, Replicate Testing and other Quality control activities.

5.7 Lab ensures that

a) Communication regarding effectiveness of management system and customer requirements are met through internal audits, management review meetings, customer feed back.

b) RD/HOO ensures integrity of management system is maintained when changes are planned and implemented through official communications.

6.0 RESOURCE REQUIREMENTS

6.1 GENERAL

The laboratory has well-qualified, experienced, and trained personnel, equipment, facilities to carry out both managerial and technical functions with needed authority and resources. They are authorized to identify any occurrence of departure from testing procedures and to initiate actions to prevent/minimize such departures.

6.2 PERSONNEL

6.2.1 The Chemical Laboratory is a part of CGWB and works under the control of Regional Director but works independently under supervision of Officer in charge (Chem). The organizational arrangement is such that other sections (departments) do not adversely influence the compliance with the requirements of International Standards.

The laboratory ensures that its personnel are dedicated workers and are free from any undue internal and external pressures, which may influence the quality of laboratory work. The laboratory personnel are regular Government employees and their salary is not linked with the work done. Thelaboratory does not use any contracted personnel for testing activities.

Dedicated test areas with requisite infrastructure and resources are provided so that staff can deliver in an effective manner. Employees care free to express concerns through proper channel to top Management.

Trained personnel perform all laboratory tests under the direct supervision of the OIC Chem. The test results are carefully reviewed and approved by OIC Chem.

6.2.2 It is the policy of the Organization under which the laboratory functions, to employ personnel, as per the recruiting rules approved by DOPT regarding education, qualification, experience and skills. The laboratory personnel are regular Government employees governed by CCS rules. The Organization has formulated norms with respect to education, training, and skills of the laboratory personnel and maintained in Competence Chart (Lab procedure manual 2019).

6.2.3 The laboratory has well-qualified, experienced, and trained personnel to carry out both managerial and technical functions with needed authority and resources. They are authorized to identify any occurrence of departure from testing procedures and to initiate actions to prevent/minimize such departures. OIC Chem through in house meetings/official letters/circulars ensures that the laboratory personnel are aware of the relevance and importance of their activities and how they contribute to achieve the objective of management system.

6.2.4 The laboratory functions under the supervision and guidance of Regional Director who is Head of Department. The laboratory has established, implemented and maintained a management system appropriate to the scope of its activities in a formal documented Management System. The laboratory has documented its policies, system, procedures and instructions to the extent necessary to assure the quality of the test results in above stated documents. The OIC Chem ensures that documentation system is communicated to, understood by, available to, and implemented by the appropriate personnel. The lab management is aware of meeting with field officers as well as regulatory requirements and meetings are conducted with approval from RD.

6.2.5. It is the policy of the Organization under which the laboratory functions,

a) To employ personnel, as per the recruiting rules approved by DOPT.

b) The Organization has formulated norms with respect to education, training, and skills of the laboratory personnel and maintained in Competence Chart (Lab procedure manual 2019).

c) Periodic in house training is carried out and effectiveness of training is evaluated. Records are maintained.

d) The lab has procedure and retains records of training, supervision, authorization and monitoring of lab personnel. OIC Chem through in house meetings/official letters/circulars ensures that the laboratory personnel are aware of the relevance and importance of their activities and how they contribute to achieve the objective of management system. The laboratory does not use any contracted personnel for testing activities.

e) OIC Chem specifies personnel to perform specific job depending upon qualification, experience and training.

f) Appropriate Training records, feedback and evaluation records are maintained (Training Records - Lab procedure manual 2019)

6.2.6 OIC Chem authorizes personnel to perform specific activities including:

a) Lab is in practice of using Standard methods for analysis.

b) Analysis of results, statements of conformity and opinions / interpretations;

c) Report, review and authorize results.

Reference: Procedure for Personnel, Training Needs & Training Conduct. - Lab procedure manual 2019

6.3 LABORATORY FACILITIES AND ENVIRONMENTAL CONDITIONS

6.3.1 It is the policy of the laboratory to provide appropriate laboratory facilities including accommodation and environmental conditions required for particular test so as to facilitate correct performance of the tests.

It is ensured that environmental conditions do not invalidate the results or adversely affect the quality of measurement. The technical requirements of environmental conditions that can affect the test results are documented.

6.3.2 The technical requirements of environmental conditions that can affect the test results are documented.

6.3.3 The laboratory monitors, controls, and records all environmental conditions required for the tests at its permanent premises and tests are stopped when the environmental conditions jeopardize the results of tests (Lab procedure manual 2019).

6.3.4 Only laboratory personnel are allowed access in the laboratory.

a) If any of our outsider wants to visit the laboratory, he is allowed with the permission of RD/OIC Chem.

b) The laboratory monitors, controls, and records all environmental conditions sufficient space is provided in the laboratory for smooth working.

c) There are no incompatible activities carried out in the Laboratory.

6.3.5 Lab does not conduct lab activities at site or outside its control.

Reference:

Procedure for Maintenance of Facilities and Environmental Conditions, - **(**Lab procedure manual 2019)

6.4 EQUIPMENT

6.4.1 The laboratory has access to all equipment/instruments required for the correct performance of the testing. It is ensured that all laboratory equipment used for testing and sampling which has significant effects on the test result are calibrated / checked before placing into the service and they are capable of achieving accuracy required for specific test. Calibration Programme has been established and implemented for all the equipment

6.4.2 In case lab needs to use equipment outside its permanent control, it is ensured that all requirements of International Standards are met.

6.4.3 The equipment is maintained to ensure proper functioning and operated under proper environmental conditions, transport, storage to prevent contamination or deterioration. All laboratory equipment is used by experienced trained personnel only. Up-to-date instructions on the use and maintenance of equipment are available at the point of use.

6.4.4 Equipment and test instruments are used for the testing/calibration after the verification of serviceability and integrity. Equipment is calibrated/ checked after the installation prior to use to ensure its suitability for the purpose.

6.4.5 The equipment used for measurement is capable of achieving measurement accuracy and/or MU required to produce valid result.

6.4.6 The laboratory has implemented a calibration schedule for key quantities of values where these properties have a significant effect on the results of its laboratory equipments used for testing and are calibrated from NABL Accredited laboratories for establishing traceability through an unbroken chain to International System of Units (SI). Laboratory has taken relative contribution of the calibration of instruments in developing their total uncertainty of the test result.

6.4.7 Calibration Programme has been established and implemented for all the equipment. It is reviewed and adjusted whenever necessary to maintain confidence in status of calibration.

6.4.8 It is ensured that equipment, requiring calibration are identified and labeled to indicate the calibration status (indicating date of last calibration and next calibration due on).

6.4.9 Whenever mishandling damages any equipment, overloading, or the accuracy of the measurement result is doubtful, it is taken out of service and clearly labeled till it is corrected. The previous test result is re-validated and the effect of the defect or departure from the specified limit on the previous results are analyzed through Section 7.10 of this manual

6.4.10 Intermediate calibration are done is accordance with the established procedure whenever required to maintain the confidence in the calibration status.

6.4.11 Correction factors, arising out of calibration of master equipments / Lab equipments (if any) are taken into consideration while conducting the testing. It is ensured that correction factors of master equipments remain updated.

6.4.12 Equipment is protected from unintended adjustment through passwords or other appropriate means.

6.4.13 The Chemist maintains records of equipment significant to the test. The record includes the following-

a) The identification of the item(s) of equipment.
b) The manufacturer’s name and serial number or other unique identification,
c) Checks that equipment complies with specifications.
d) The current location
e) Calibration/adjustment details like date, results, calibration certificates/reports, acceptance criteria and the due date of calibration;
f) Dates, results and copies of reports and / or certificates of all Tests, adjustments, acceptance criteria, and the due date of next Testing;
g) Maintenance plan if required and maintenance record.
h) Any damage, malfunction, modification or repair of equipment.

Reference:

Procedure for Maintenance Equipment, **(**Lab procedure manual 2019)

6.5 METEOROLOGICAL TRACEABILITY

6.5.1 Metrological traceability of measurement results is established and maintained by means of documented unbroken chain of calibrations, each contributing to measurement uncertainty linking them to appropriate reference.

6.5.2 The lab ensures

a) All equipments used for testing are calibrated from NABL Accredited laboratories for establishing traceability through an unbroken chain to International System of Division of the Units (SI).

b) All the Certified reference materials used by the laboratory are traceable to SI units of measurement or International or National Standard

c) Direct realization of SI units ensured by comparison directly/indirectly with national/international standards.

6.5.3 Laboratory has taken relative contribution of the calibration of instruments in developing their total uncertainty of the test result. For traceability of measurement to SI units confidence in measurement is established through the use of appropriate measurement standards such as Certified Reference Material.

Reference:

Procedure for Maintaining Metrological Traceability, - **(**Lab procedure manual 2019)

6.6 EXTERNALLY PROVIDED PRODUCTS AND SERVICES

6.6.1 Laboratory does not sub-contract any work in the field of testing. The laboratory has established policies and maintained a procedure (Lab procedure manual 2019) for the selection and purchasing of services and supplies it uses that affect the quality of tests.

The lab ensures that only CRMs are used reference standards and equipment is calibrated from NABL accreditated lab. PT services are also taken from NABL accreditated service providers.

6.6.2 The lab has procedure and retains records for:

a) All laboratory equipment is calibrated only from NABL accredited laboratories. Only standard Certified Reference Materials (CRMs), Reference Materials (RMs), other chemicals and consumables meeting the IS codes of practice & APHA / product of good companies with reliable quality are purchased.

b) Procedures for these purchases, reception and storage of reagents and laboratory consumable materials relevant for test and calibration have been documented and are in practice (Lab procedure manual 2019). Purchases are inspected & verified by Store Section before handing over to chemical laboratory. It is ensured that the purchased supplies comply with the specified requirement(s). Relevant records are maintained.

c) Documents relating to purchase of items related to the laboratory use are maintained by Store Officer. The purchasing document(s) are reviewed and approved for technical content prior to issue to lab by officers nominated by Regional Director.

d) Lists of approved supplier of supplies, equipments, and calibration laboratories are maintained.

Laboratory has implemented a procedure for performance evaluation of suppliers of critical consumables, which affect the quality of testing.

6.6.3 Requirements are communicated to external provider through defined govt. procedures and protocols for products/services to be provided as per specifications/acceptance criteria.

Reference:

Procedure for Externally Provided Products and Services, (Lab procedure manual 2019)

7.0 PROCESS REQUIREMENTS

7.1 REVIEW OF REQUESTS, TENDERS AND CONTRACTS

7.1.1 The laboratory has established and maintains a procedure for the review of request for analysis. The Lab in-charge ensures that-

a) The requirements are adequately defined, documented and understood.

b) The laboratory has the capability to meet these requirements.

c) At present, the laboratory does not sub-contract any work in the field of testing.

d) The appropriate test method is selected capable to meet customer requirements.

7.1.2 The laboratory uses only recognized APHA and USGS for testing. It is ensured that valid editions of standards are in practice.

7.1.3 Standard methods are followed for analysis where concentration of parameters under scope are given in mg/l.

7.1.4 Differences if any, are resolved before test activities commence. Record of request for Analysis and of any significant discussion with the Field Officer related to the sample are maintained.

7.1.5 The lab will inform Field Officer in case of any delay or deviation in the performing of the test.

7.1.6 Whenever any testing parameter needs to be amended after work has commenced, the same is communicated to all concerned personnel.

7.1.7 The customers of the CGWB Laboratory are mainly officers/officials of CGWB itself or from other state/central government organizations. CGWB, NR Laboratory is open to serve its customers for their legitimate request. It assists them by possible means in their presence or in the presence of their representative for witnessing the test on directions from RD. In doing so the Procedure of confidentiality is maintained for customers.

7.1.8 Records of request for Analysis and also record of significant discussion with the Field Officer related to the sample is maintained.

Reference:

1. Procedure for Review of Requests, Tenders and Contracts, - Lab procedure manual 2019

7.2 SELECTION, VERIFICATION AND VALIDATION OF METHODS

7.2.1 Selection and Verification of Method

7.2.1.1 Well-documented procedures are provided for all types of tests carried out by the laboratory, which includes, handling, transport, storage (if any) of item to be tested. Procedures for estimation of uncertainty in measurement have been established and are in practice.

7.2.1.2 Documented instructions on the use of equipments, handling, and testing of items are made available, where absence of such instructions could affect the test results. All relevant standards, manuals, manufacturer’s instructions, and reference data relevant to the work are regularly updated and made available at the point of use.

7.2.1.3 The laboratory uses only recognized APHA for testing. It is ensured by keeping close liaison with issuing authorities that valid editions of standards are in practice.

7.2.1.4 The Laboratory performs the testing of items to meet the customer requirement by using the appropriate test methods preferably the international and national standards, unless specified by the customer otherwise. The laboratory does not use any laboratory-developed methods.

7.2.1.5 The laboratory uses only recognized APHA methods for testing verified by planned ILC/PT exercise.

7.2.1.6 At present lab is not practicing any Laboratory Developed Method, therefore this clause is not applicable to the management system of the laboratory

7.2.1.7 No Deviations from the documented procedures and test methods are permitted.

7.2.2 Validation of Methods

Since lab is not using any Laboratory Developed Method and Non Standard Methods, therefore this clause is not applicable.

Reference:

1. APHA, 23rd Edition

7.3 SAMPLING

At present laboratory is not in practice of sampling therefore this clause is not applicable to the management system of the laboratory.

7.4 HANDLING OF TEST ITEM

7.4.1 The Laboratory has a documented procedure for receipt, handling, protection, storage, retention and/or disposal of the test items. The lab receives ground water samples in bulk during the month of May-June to monitor the water quality of Ground water monitoring stations as per the policy of the organization. These samples are stored in air conditioned environment.

The laboratory has system and appropriate facilities for avoiding deterioration, loss, or damage to the test sample during storage and handling. When sample have to be stored or conditioned under specified environmental conditions, these conditions are maintained, monitored, and recorded.

7.4.2 Every test item received at the laboratory is identified with a unique code number in accordance with the documented procedure, which is maintained till the life of the item so as to facilitate the physical identification and the reference to the relevant records. All listed in the sample register as well as sample file.

7.4.3 Upon receipt of sample in the laboratory, any departures or abnormalities from normal or specified conditions are recorded with check list. If there is any doubt as to the suitability of a sample for testing / does not conform to the description provided / when the test requirement(s) are not specified in sufficient details, clarification is asked from technical officer before proceeding and relevant records are maintained. The laboratory includes a disclaimer in the report indicating that results may be compromised.

7.4.4 The laboratory has appropriate facilities for avoiding deterioration, loss, or damage to the test sample during storage and handling. When sample have to be stored or conditioned under specified environmental conditions, these conditions are maintained, monitored, and recorded.

Reference:

Procedure for Handling Of Test Items, - **(**Lab procedure manual 2019)

7.5 TECHNICAL RECORDS

7.5.1 Technical records of original observations, derived data, and sufficient information to establish an audit trail, calibration record of all relevant equipments, staff records, a copy of each test are retained for a defined period. The records also include the identification of personnel responsible for performance of each test, and approval of test results.

Observations, data, and calculations are recorded at the time they are made and are identifiable to the specific task.

7.5.2 Whenever mistakes occur in recording the data, each mistake is crossed out not erased, made illegible or deleted, and the correct value is entered alongside with date of alteration. All such alterations are signed and initialed by the person responsible for the correction. Both original and amended data and files are retained.

Reference:

1. Procedure for Control of Records - Lab procedure manual 2019

7.6 EVALUATION OF MEASUREMENT UNCERTIANITY

7.6.1 Lab identifies the contribution to measurement uncertainty. When evaluating the uncertainty measurements, all important uncertainty components in the given situation are taken into account using appropriate method of analysis.

7.6.2 Lab is not performing calibration, therefore this clause not applicable.

7.6.3 Standard methods and procedures are followed as per APHA, that specify limits to the values of major sources of MU.

Reference:

Procedure for Evaluation of Measurement Uncertainty, - Lab procedure manual 2019

7.7 ENSURING THE VALIDITY OF THE RESULTS

7.7.1 The Laboratory has a documented procedure for monitoring the validity of tests undertaken through inter-laboratory testing and, replicates testing. The results of testing are recorded in order to detect the trends of testing processes. Such results are analyzed using the statistical techniques, wherever possible. This monitoring includes the following:

a) Regular use of certified reference materials and/or internal quality control using secondary reference material.

b) Intermediate checks.

c) Participation in intra-laboratory comparison or proficiency testing programs

d) Replicate testing.

e) Retesting of retained items.

f) Review of reported results.

g) Correlation of result for different characteristics of an item.

7.7.2 The lab monitors its performance by comparison with results of other labs where available and appropriate. The activity is planned and reviewed and includes

a) Participation in inter-laboratory comparison and/or

b) Participation proficiency testing programs

7.7.3 Quality control data is to be analyzed to improve lab activities & where they are found outside predefined criteria, planned action is taken to correct the problem & to prevent incorrect result from being reported.

Reference:

Procedure for Ensuring the Validity of the Test Results, - Lab procedure manual 2019

7.8 REPORTING OF RESULTS

7.8.1 **General**:

7.8.1.1 Results are reviewed and authorized prior to release.

7.8.1.2 The results of each test or series of tests carried out by the laboratory are reported accurately, clearly, unambiguously, and objectively, and in accordance with any instruction in any specific Testing method. The results are reported in a Test report is a comprehensive document, which includes all the information related to the water sample

7.8.1.3 The results are reported in a Test report is a comprehensive document, which includes all the information related to the water sample

7.8.2 **Common Requirements of Test Report**:

7.8.2.1 Each test report is being generated in the defined format, which includes the following information:

a) Title-Test report.
b) Name and address of the Laboratory where test has been carried out.
c) Unique identification of the test report Lab number,
d) Name of the technical officer(customer)
e) Identification of the method used.
f) A description of the condition & unambiguous identification of item tested.
g) Date of receipt of sample and date of sampling whenever it is critical to validity and application of results
h) Date(s) of performance of testing
i) Date of issue of report
j) Reference to the sampling plan & procedure used by the laboratory(if any)
k) Statement that test results relate only to sample tested.
l) The test result with unit of measurement, where applicable.
m) Addition to, deviations, or exclusions from the method(if any)
n) The name, function & signature of the person authorizing the test report.

7.8.2.2 The lab is not responsible for sampling stage and Report states that results apply to the sample as received.

7.8.3 **Specific Requirement of Test Report**:

In addition to above, test report also includes, where necessary, the following:

a. Deviations from the test methods and test conditions including environmental condition.

b) Where relevant a statement of compliance/non-compliance with specified requirement / specification.

c) A statement on estimated uncertainty of measurement wherever applicable.

d) The laboratory does not give opinion or interpretation in the test report.

e) Additional information which may be required and specified by customer.

7.8.4 Specific Requirement for Calibration certificate Not Applicable

7.8.5 Reporting Sampling-specific requirements-Not Applicable

7.8.6 Reporting Statement of Conformity- Lab is not giving any statement of conformity.

7.8.7 **Reporting Opinions and Interpretations**- Not Applicable

7.8.8 Amendments to Report:

7.8.8.1 When an issued report needs to be amended and re-issued, any change in information is clearly identified and where appropriate reason for amendment included in the report.

7.8.8.2 Any amendment to a test report after issue is made in the form of a further document, or data transfer, which includes the statement: “Amendment to Test Report No .... , Dated…............”

7.8.8.3 In cases, where it is necessary to issue the complete new test report, it is uniquely identified and contains reference to the original it replaces. **Record**:

1. Test report (Form & Format)

7.9 COMPLAINTS

7.9.1. It is the policy of the laboratory to give top priority to complaint received from technical Officers and other parties. A documented procedure is in place to receive, evaluate and resolve the complaints to the satisfaction of officer.

7.9.2 A description of handling process for complaint is made available to any interested party on a written request. Upon receipt of complaint, it is ascertained whether complaint relates to lab activities that it is responsible for and if so deal with it. The lab or any personnel assigned by RD/HOO is responsible for all decisions at all levels of handling process of complaint.

7.9.3 It is the policy of the laboratory to give top priority to complaint received. The process includes

a) Process for receiving, validating, of all complaints, there root cause analysis and corrective and preventive action taken

b) recording/tracking including action taken to resolve complaints

c) Ensuring appropriate action is taken

7.9.4 Lab or any personnel assigned by RD/HOO is responsible for gathering and verifying necessary information to validate the complaint.

7.9.5 Whenever possible lab acknowledges receipt of complaint and progress report of outcome to complainant.

7.9.6 The outcomes communicated to complainant are made /reviewed/approved by individual not originally involved in original lab activity in question.

7.9.7 Whenever possible, the lab gives formal notice of end of complaint to the complainant.

Reference:

Procedure for Resolution of Complaints, - Lab procedure manual 2019

7.10 NON-CONFORMING TEST WORK

7.10.1 The laboratory has a policy to take immediate action(s) when any aspect of its testing, or the result of that test, do not conform to its own procedures or the agreed requirement of the officer. A procedure is established and maintained to initiate suitable action(s) whenever any nonconforming work is identified.

The policy and procedure ensures that-

a) The responsibilities and authorities for the management of nonconforming work are designated and actions are defined and taken as & when desired
b) Corrective action(s) are taken immediately, based on risk level established by lab.
c) An evaluation of the significance of the nonconforming work is made;
d) any decision about the acceptability of the nonconforming work;
e) Where ever necessary, the officer is notified and amended testing report is provided.
f) The responsibility for authorizing the resumption of work has been defined.

7.10.2 The lab retains records of NC work and actions taken.

7.10.3 When the evaluation reveals that such non-conformance could reoccur, due to the problem in procedure itself, the corrective action is initiated to modify the procedure (Lab procedure manual 2019).

Reference:

Procedure for Nonconforming Test Work, - Lab procedure manual 2019

7.11 CONTROL OF DATA INFORMATION MANAGEMENT

7.11.1 The lab has access to data and information needed to perform lab activities.

7.11.2 Laboratory maintains quality and technical records as objective evidence of implementation of the quality management system. A procedure is in place for identification, collection, indexing, access, filling, storage, maintenance, and disposal of these records. All records are legible and are stored and retained in such a way that they are readily retrievable. Laboratory also maintains some of the records in computers. Suitable measures are taken to preserve the records. Back up is taken as and when deem fit. Whenever there are any changes they are authorized, documented, validated before implementation.

7.11.3 The lab information system are:

a) All records are legible and are stored and retained in such a way that they are readily retrievable. It is ensured that a suitable environment is provided to prevent damage or deterioration and to prevent loss. A list of records (Master Control Register) is maintained by the OIC Chem, which defines the retention period and responsibility of person maintaining record.

b) Laboratory also maintains some of the records in computers. Suitable measures are taken to preserve the records. Back up is taken as and when deem fit.

c) Technical records of original observations, derived data, and sufficient information to establish an audit trail, calibration record of all relevant equipments, staff records, a copy of each test are retained for a defined period. The records also include the identification of personnel responsible for performance of each test, and approval of test results.

d) Test report is prepared by Hand or Computers. It is ensured that Procedures are established and implemented for protecting data and includes integrity and confidentiality of data entry, data storage, transmission and data processing.

e) Whenever required, system failures recorded and corrective action taken.

7.11.4 Lab information is not maintained off site. Not applicable.

7.11.5 Instruction manuals and reference data relevant to lab management system is readily available to lab personnel.

7.11.6 Calculations and data transfers checked in appropriate manner.

Reference:

8.0 MANAGEMENT SYSTEM REQUIREMENTS

8.1 OPTIONS

8.1.1 General

The laboratory functions under the supervision and guidance of Regional Director who is Head of Department. The laboratory has established, implemented and maintained a management system appropriate to the scope of its activities in a formal documented Management System in compliance to the requirements of ISO/IEC 17025-2017 meeting the requirements of clause 4 to 7 and in accordance with option A.

8.1.2 Option A

The management system complies with clause 8.2 - 8.9

8.2 MANAGEMENT SYSTEM DOCUMENTATION

8.2.1 The laboratory functions under the supervision and guidance of Regional Director who is Head of Department. The laboratory has established, implemented and maintained a management system appropriate to the scope of its activities in a formal documented Management System (as given in Section 8.2.4. The laboratory has documented its policies, system, procedures and instructions to the extent necessary to assure the quality of the test results in above stated documents. The OIC Chem ensures that documentation system is communicated to, understood by, available to, and implemented by the appropriate personnel. Laboratory quality policy and objectives are as given in Section 1.2 of this manual and objectives are reviewed during management review meetings.

8.2.2 The lab policies and objectives address the competence, impartiality and consistent operation of Lab. Trained personnel perform all laboratory tests under the direct supervision of the OIC Chem. The test results are carefully reviewed and approved by OIC Chem. If any test appears to be wrong or doubtful the technical people are instructed to repeat such test. The test results is then carefully evaluated and submitted to the concerned officer for further necessary action like data processing and report writing etc. The lab has procedures for protecting the hard copy and electronic storage and transmission of results.

8.2.3 Laboratory continuously make efforts for the improvement of the management system through quality policy and quality objectives, Proficiency Testing, Inter- laboratory/Analytical

Quality Comparison, effective Internal Audits, Replicate Testing and other Quality control activities.

8.2.4 Documentation of the system is arranged in four levels as given below-.

a. Quality Manual (CGWB/NR/QM/01)

This is the apex document, which describes the Laboratory Division policies, objectives with reference to ISO/IEC 17025:2005 requirements, along with outline of laboratory management structure and overall responsibilities of key personnel.

b. **Quality Procedure Manual (CGWB/NR/QP/01)**:

This is the second level document, which consists of Quality Procedures.

c. Standard Operating Procedure (CGWB/NR/SOP/01)/ Work Instruction Manual/ (CGWB/NR/WI/01)

This is the Third level document, which consists of Standard Procedures and Work Instruction Manual.

d. **Formats/ Forms/Registers (CGWB/ 01)**:

This is the fourth level document, which consists of Formats/Forms/Registers.

8.2.5 Roles and responsibilities of Chemist and the OIC Chem are defined in Section 5.0 of this manual for assuring the compliance with ISO / IEC 17025:2017. RD/HOO ensures that the integrity of the management system is maintained when changes to the management system are planned and implemented. This is done by communicating all important decisions to all relevant personnel.

8.3 CONTROL OF MANAGEMENT SYSTEM DOCUMENTS

8.3.1 The Laboratory is committed to provide the current/latest version of its documents to its Scientists and to ensure that they work as per latest scientific norms. OIC Chem is responsible to ensure that the documentation about the laboratory quality system and its management system are complete and the officials working in the laboratory have been provided with the relevant and current version of the procedures, instructions, forms and formats. Its system of the distribution of documents ensures the working needs of its scientific staff, and to maintain the records of the holders.

8.3.2 Lab ensures that

a) All documents issued to the personnel in the laboratory as part of the laboratory system are reviewed and approved for use by authorized personnel prior to issue as under:

S. No.	Document Name	Preparation	Approval & Review	Issue
1.	Quality Manual	OIC Chem	RD	OIC Chem
2.	Quality Procedure Manual	OIC Chem	RD	OIC Chem
3.	Standard Operating procedure	Chemist	OIC Chem	OIC Chem
4.	Work Instructions	Chemist	OIC Chem	OIC Chem
5.	Formats	Chemist	OIC Chem	OIC Chem

b) Documents are periodically reviewed and where necessary, updated to ensure continuing suitability and compliance with applicable requirements.

c) OIC Chem maintains a master list of documents (for external & internal documents). It includes current revision and issue status also.

d) Authorized additions of all appropriate documents are available at points of use and wherever necessary, distribution is controlled.

e) Documents are uniquely identified.

f) Invalid or obsolete documents are promptly removed from all points of issue or use. If any obsolete documents retained for either legal or knowledge preservation, reasons are suitably marked.

Reference: 1. Procedure for Control of Management System Documents, - Lab procedure manual 2019

8.4 CONTROL OF RECORDS

8.4.1 All records are legible. It is ensured that a suitable environment is provided to prevent damage or deterioration and to prevent loss. A list of records (Master Control register) is maintained by the OIC chem., which defines the retention period and responsibility of person maintaining record.

8.4.2 Laboratory maintains quality and technical records as objective evidence of implementation of the quality management system. A procedure is in place for identification, collection, indexing, access, filling, storage, maintenance, and disposal of these records. They are stored and retained in such a way that they are readily retrievable. It is ensured that all records are secure and safe.

Reference:

Procedure for Control of Records - Lab procedure manual 2019

8.5 ACTIONS TO ADDRESS RISKS AND OPPORTUNITIES

8.5.1 Lab considers the risks and opportunities associated with lab activity.

Potential source(s) of non-conformity and improvements needed in technical operation or management system can be identified by any staff and reported to OIC Chem. The sources for identification of areas for implementing preventive actions include feedback from staff, internal quality control checks, management review meetings, proficiency testing, inter- laboratory comparison analysis of data etc. Based on these, if required an action plan is developed, implemented and monitored not only to reduce the likelihood of the occurrence of the non-conformity but also to improve the system.

8.5.2 OIC Chem ensures that action(s) taken to address risks and opportunities, to integrate and implement are effective.

8.5.3 Actions taken to address risk and opportunities are proportional to potential impact on validity of lab results.

Records

Risk and Opportunity Assessment record. - Lab procedure manual 2019

8.6 IMPROVEMENT

8.6.1 The laboratory continually improves the effectiveness of its management system through the use of quality policy, quality objectives, audit results, analysis of data, corrective and preventive actions and management review. Areas of improvements are identified in the management review meeting. OIC Chem monitors the effectiveness of improvement identified. Records for the improvements identified are maintained.

8.6.2 Lab shall seek feedback both positive & negative from concerned officers / customers. The feedback shall be used for improving the management system. The feedback of the technical officer, if any, is analysed quarterly. This is done to identify areas of improvement in management system, testing and services.

Records:

1. Officer Feedback Record,
2. Evaluation of Officers Feedback
3. Internal Audit Non-Co formance Status Report
4. Management Review Meeting Status Report

8.7. CORRECTIVE ACTION

8.7.1 When non-conforming work or departures from the policies and procedures in the management system or technical operations have been identified.

a) The laboratory has a policy to take immediate action(s) when any aspect of its testing, or the result of that test, do not conform to its own procedures or the agreed requirement of the officer

b) The corrective action procedure includes the investigation carried out in order to determine the cause(s) of the problem. This includes careful analysis of potential causes of the problem such as field officer requirements, sample specifications or equipment.

c) Where action is required, the laboratory identifies the potential corrective action(s), select and implement actions to eliminate the problem and to prevent reoccurrence.

d) Results of corrective actions taken are monitored and it is ensured that they have been effective.

e) Update risks and opportunities if required and if necessary action plan is developed, implemented and monitored not only to reduce the likelihood of the occurrence of the non- conformity but also to improve the system.

f) Any change resulting from corrective action investigations is documented and implemented and changes made in management system if required.

8.7.2 Corrective actions are to be appropriate to the effects of the nonconformities encountered.

8.7.3 Records are to be retained as evidence of:

a) The nature of the nonconformities, cause(s) and any actions taken;

b) The results of corrective action.

Reference:

1. Procedure for Corrective Action - Lab procedure manual 2019

Annexure V

8.8 INTERNAL AUDIT

8.8.1 Internal Quality Audits are carried out for all parts of Laboratory management system including testing activities at least once a year with a predetermined schedule. When audit findings cast doubt on the effectiveness of the operations or on the correctness or validity of laboratory’s test results, the concerned personnel take timely corrective actions. If necessary officers are notified in writing.

a) to verify that its operations continue to comply with requirement of the management system and ISO / IEC 17025: 2017.

b) Lab in charge is responsible for organizing the internal quality audit. Trained and qualified personnel, who are independent of the activity to be audited, carry such audits. Records of activity audited, the audit findings and corrective actions arising from them are implemented and maintained.

8.8.2 The internal audit of the laboratory is

a) Conducted with a predetermined schedule for all the activities that have been completed in the preceding year. The internal audit of the laboratory is carried out in a systematic manner to cover responsibilities, planning requirements and reporting taking into consideration all lab activities, changes affecting lab and results of previous audits.

b) Criteria and scope of audit is defined.

c) The result of the audits are recorded & brought to the attention of RD/HOO.

d) When audit findings require corrections in the system timely corrective actions are initiated without delay.

e) Records of activity audited, the audit findings and corrective actions arising from them are maintained.

Reference:

Procedure for Internal Audit, - Lab procedure manual 2019

8.9 MANAGEMENT REVIEW MEETING

8.9.1 The Regional Director carries out a comprehensive review of the management system and testing activities at least once in one year to ensure their continuing suitability and effectiveness including policies and objectives related to fulfillment of ISO / IEC 17025: 2017.

8.9.2 The review considers and records the following points as minimum-

a) Changes in any internal and external issues relevant to lab.
b) Fulfillment of objectives.
c) Suitability of policies and procedures.
d) Status of actions from previous management review.
e) Outcome of recent audits.
f) Corrective actions
g) Assessment by external bodies.
h) Customer feedback
i) Changes in volume and type of work.
j) Complaints
k) Effectiveness of improvements implemented.
l) Adequacy of Resources
m) Results of risk identification
m) Outcomes of Result of the inter-laboratory comparisons and proficiency tests.
o) Any other relevant factors/point or training requirements.

8.9.3 The Minutes of Management Review Meeting are recorded. OIC Chem ensures effective implementation of the decisions taken. The Minutes of Management Review Meeting are recorded related to

a) Effectiveness of management system
b) Improvement in lab activities related to fulfillment of ISO / IEC 17025: 2017
c) Provision for required resources
d) Any need for change.

Reference:

1. **Procedure of Management Review,** - Lab procedure manual 2019

----END OF DOCUMENT----

Annexure VI

क्षेत्रीय रासायनिक प्रयोगशाला
केन्द्रीय भूमि जल बोर्ड, उत्तरपूर्वी क्षेत्र,
गुवाहाटी

CGWB/NER/6.4F-04

FUNCTIONAL CHECK RECORD

Equipment under Test:	**Parameter:**
Chemist Name:	**Date:**

Sl. No.	**Sample Name**	**Standard**	**Spiked sample**	**Recovery (%)**	**Acceptance criteria**
					80-110%
Mean					
Standard Deviation					
Relative Standard Deviation					

Chemist Signature:

Observation made by Quality Manager/Technical Manager

Signature:

Date:

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क्षेत्रीय रासायनिक प्रयोगशाला
केन्द्रीय भूमि जल बोर्ड, उत्तरपूर्वी क्षेत्र,
गुवाहाटी

CGWB/NER/6.4F-03

INTERMEDIATE CHECK RECORD

Equipment under Test:	**Parameter:**
Chemist Name:	**Date:**

Sl. No.	**Sample Name**	**Standard**	**Spiked sample**	**Recovery (%)**	**Acceptance criteria**
					80-110%
Mean					
Standard Deviation					
Relative Standard Deviation					

Chemist Signature:

Observation made by Quality Manager/Technical Manager

Signature: Date:

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क्षेत्रीय रासायनिक प्रयोगशाला
केन्द्रीय भूमि जल बोर्ड, उत्तरपूर्वी क्षेत्र,
गुवाहाटी

CGWB/NER/7.7F-02

ACCURACY CHECK RECORD

Equipment under Test:	**Parameter:**
Chemist Name:	**Date:**

Sl. No.	Sample Name	Spiked analyte concentration	Observed analyte concentration	Recovery (%)	Mean Recovery (%)	Acceptance criteria
						80-110%

Chemist Signature:

Observation made by Quality Manager/Technical Manager

Signature: Date:

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केन्द्रीय भूमि जल बोर्ड, उत्तरपूर्वी क्षेत्र,
गुवाहाटी

CGWB/NER/6.4F-02

INTERMEDIATE CHECK FOR BALANCE

Model name/Serial Number:	
Chemist Name:	**Date:**

For Accuracy:

Sl. No.	**Actual weight from certificate (X_t)**	**Observed value**	**Mean (X_{av})**	**Absolute Error ($X_{av} - X_t$)**	**% Relative Error (($X_{av} - X_t)/X_t) \times 100$)**	**Acceptance criteria**

For Repeatability-Precision:

Sl. No.	**Observed value (X_i)**	**Mean (X_{av})**	**$(X_i - X_{av})^2$**	**Standard Deviation**	**% Relative Standard Deviation**

Chemist Signature:

Observation made by Quality Manager/Technical Manager Signature: Date:

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केन्द्रीय भूमि जल बोर्ड, उत्तरपूर्वी क्षेत्र,
गुवाहाटी

CGWB/NER/7.7F-03

REPEATABILITY RECORD

Equipment under Test:	**Parameter:**
Chemist Name:	**Date:**

Day	Spiked Concentration	Measured Concentration	Mean Concentration	SD	RSD (%)	Mean RSD (%)
1						
2						
3						

Chemist Signature:

Observation made by Quality Manager/Technical Manager

Signature: Date:

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गुवाहाटी

CGWB/NER/7.7F-04

REPRODUCBILITY RECORD

Equipment under Test:	**Parameter:**
Date:	

Day	Chemist Name/Signature	Spiked Concentration	Measured Concentration	Mean Concentration	SD	RSD (%)	Mean RSD (%)
1							
2							
3							

Observation made by Quality Manager/Technical Manager

Signature: Date:

Annexure VI

क्षेत्रीय रासायनिक प्रयोगशाला
केंद्रीय भूमि जल बोर्ड, उत्तरपूर्वी क्षेत्र,
गुवाहाटी

CGWB/NER/7.7F-01

INTRA-LABORATORY RECORD

Equipment under Test:

Parameter:

Date:

Day	Chemist Name/Signature	Spiked Concentration	Measured Concentration	Mean Concentration	SD	Z-score
1						
2						
3						

Observation made by Quality Manager/Technical Manager

Signature: Date:

Annexure VI

क्षेत्रीय रासायनिक प्रयोगशाला
केन्द्रीय भूमि जल बोर्ड, उत्तरपूर्वी क्षेत्र,
गुवाहाटी

Format No.: Form1	**Format Name: Digital Balance Maintenance Data Sheet**	**Clause No.: 6.4.3**

Name of the equipment: Digital balance
Frequency: Daily
(If checked √)

Date	**Checking Points**	
	Cleaning	**Signature**

Observation made by Quality Manager/Technical Manager

Signature: Date:

Annexure VI

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केन्द्रीय भूमि जल बोर्ड, उत्तरपूर्वी क्षेत्र,
गुवाहाटी

Format No.: Form2	**Format Name: Sample Receiving Check List**	**Clause No.: 7.3**

Sl. No.	**Description**	**Yes**	**No**
1.	Container-Polypropylene White		
2.	Quantity of Sample (sufficient)		
3.	Quality of sample (Filtered/clear)		
4.	Labeling/Tagging (Proper)		
5.	Sealing/leak proof		
6.	Details of samples matching with the list		
7.	Location/District/Block/Date of collection given		
8.	Samples submitted within 24 hours of returning from the field		
9.	Refrigerated samples submitted		
10.	Icebox temperature recording checklist submitted		
11.	Hard copy submission of sample information as per protocol		

Received by:

Observation made by Quality Manager/Technical Manager

Signature:

Date:

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गुवाहाटी

CGWB/NER/8.6F–01

Officer Feedback Record

Name of the Technical Officer:
Designation :

I thank you very much for trusting our laboratory and using our services.

May I request if you could give a feedback on the quality of our services. Your extremely valuable input would be of great benefit to us in improving our quality. Thanking you and assuring you of our closest co-operation.

Technical Manager /Quality Manager

PLEASE TICK ANY ONE BOX IN EACH SECTION

(Higher Number indicate the higher Grade and lower number indicate lower grade)

☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐ ☐

Satisfaction with Test Results
1 2 3 4 5 6 7 8 9 10

Timely delivery of test report

1	2	3	4	5	6	7	8	9	10

Any other comments/Suggestions

Name:………………. Signature……………………..

Date………………………

Evaluation criteria:

More than 8 → Excellent
6-8 → Very Good
<6 → Average

If feedback found<6 then Root Cause Analysis to be carried out and Corrective & Preventive action to be taken.

Observation made by Quality Manager/Technical Manager

Signature: Date:

क्षेत्रीय रासायनिक प्रयोगशाला
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गुवाहाटी

Format No.: Form4	**Format Name: House Keeping Data Sheet**	**Clause No.: 6.3.4**

Name: House Keeping Records
Frequency: Daily
(IF DONE √)

Date	**House Keeping**		
	Cleaning (Dusting & Moping)		**Signature**
	Morning	Evening	

Observation made by Quality Manager/Technical Manager

Signature: Date:

Annexure VI

क्षेत्रीय रासायनिक प्रयोगशाला
केन्द्रीय भूमि जल बोर्ड, उत्तरपूर्वी क्षेत्र,
गुवाहाटी

Format No.: Form5	**Format Name: List Of Approved Vendors**	**Clause No.: 6.6.2**

Period: ....

Sl. No.	Name of the Vendor	Items approved for Vendor	Contact Person	Contact No.	Remarks
1.					
2.					
3.					
4.					
5.					
6.					
7.					
8.					

Observation made by Quality Manager/Technical Manager

Signature: Date:

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गुवाहाटी

Format No.: Form6	**Format Name: Vendor Evaluation**	**Clause No.: 6.6.2**

Period: ....

Sl. No.	Name of the Vendor	Supply Description	Quality Performance	Delivery Performance	Price consistency as per market	Remarks
1.						
2.						
3.						

Supplier Acceptable Criteria:
AAA: Acceptable
AAB: Acceptable, Deficiency to be improved
ABB: Acceptable, Subject to approved by Proprietor
BBB: Not Acceptable

Observation made by Quality Manager/Technical Manager

Signature: Date:

Annexure VI

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गुवाहाटी

Format No.: Form	**Format Name: Attendance Sheet**	**Clause No.: 8.8**

Laboratory:

Date & Time :

Type of Visit: ***Internal audit***

Sl.	**Assessors / Lab Personnel Present**	**Capacity/ Designation**	**Signature**

Observation made by Quality Manager/Technical Manager

Signature: Date:

Annexure VI

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गुवाहाटी

Format No.: Form10	**Format Name: Format For Handling Non-Conforming Work**	**Clause No.: 7.10.1**

1. **Work Instruction/Assigned No.:**
2. **Date**:
3. **Significance:** Major/Minor
4. **Root cause analysis:**
5. **Preventive/corrective action taken**:
6. **Signature:**
7. **Follow up:**

Observation made by Quality Manager/Technical Manager Signature: Date:

Annexure VI

क्षेत्रीय रासायनिक प्रयोगशाला
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गुवाहाटी

Format No.: Form12	**Format Name: Feedback on Training**	**Clause No.: 6.2.5**

1. **Name of Training:**
2. **Period:**
3. **Trainer:**

4. Instructions: Please give your feedback

Sl. No.		**Excellent**	**Very Good**	**Good**	**Poor**
1.	The objectives of the training were clearly defined.				
2.	Participation and interaction were encouraged				
3.	The topics covered were relevant to me.				
4.	The content was organized and easy to follow.				
5.	The materials distributed were helpful				
6.	This training experience will be useful in my work.				
7.	The trainer was knowledgeable about the training topics.				
8.	The trainer was well prepared.				
9.	The training objectives were met.				
10.	The time allotted for the training was sufficient.				

4. **What did you like most about this training?**
5. **What aspects of the training could be improved?**
6. **How do you hope to change your practice as a result of this training?**

Thank you for your feedback!

Observation made by Quality Manager/Technical Manager

Signature:

Date:

Annexure VI

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गुवाहाटी

Format No.: Form14	**Format Name: Trainee Evaluation Form**	**Clause No.: 6.2.5**

1. Name of Training :
2. Period :
3. Name of Trainee:
4. Trainer :

Please evaluate the trainee's competencies according to the following evaluation scale:

1. Poor 2. Satisfactory 3. Quite Good 4. Good 5. Very Good 6. Excellent						
	1	**2**	**3**	**4**	**5**	**6**
1. Adaptation To Working Environment						
2. Knowledge of the Subject						
3. Attitude						
4. Ability To Analyse Situation						
5. Readiness To Take Initiative						
6. Sense Of Responsibility						
7. Managerial Skills						
8. Organisational Skills						
9. Professionalism						
10. General Competences						

Comments on the trainee`s development of other professional competences, specific for the professional profile:

Observation made by Quality Manager/Technical Manager

Signature: Date:

Annexure VI

क्षेत्रीय रासायनिक प्रयोगशाला
केंद्रीय भूमिजल बोर्ड, उत्तरपूर्वी क्षेत्र,
गुवाहाटी

Format No.: Form15	**Format Name: Training Authorization**	**Clause No.: 6.2.5**

AUTHORIZATION

Employee Information	
Name:	
(First)	(Last)
Designation:	
Email:	
Ph No.:	
Department:	

Training	
Course Title:	
Course Date:	

It is certified that, Mr./Ms/Dr ....is hereby authorized to carry out the following parameters …………………………………………………………………………………

Using the following Instruments/Equipments……………………………………

independently w.e.f. …………………..

Observation made by Quality Manager/Technical Manager

Signature: Date:

Annexure VI

क्षेत्रीय रासायनिक प्रयोगशाला
केन्द्रीय भूमि जल बोर्ड, उत्तरपूर्वी क्षेत्र,
गुवाहाटी

Format No.: Form18	**Format Name: Sample Refrigerating Check List**	**Clause No.: 7.3**

Ice box Code..

Sl.No.	Date	Location	Morning		Evening		Signature of Field Officer/Official
			Ice filling	Temp (°C)	Ice filling	Temp (°C)	

Observation made by Quality Manager/Technical Manager

Signature: Date:

Annexure VI

क्षेत्रीय रासायनिक प्रयोगशाला
केंद्रीय भूमि जल बोर्ड, उत्तरपूर्वी क्षेत्र,
गुवाहाटी

Format No.: Form17	**Format Name: RISK ASSESSMENT**	**Clause No.: 4.1 to 7.6 (as per 8.5)**

RISK IDENTIFIED AND ADDRESSED

SL. NO.	**RISK IDENTIFIED**						**RISK ADDRESSED**		
	ISO/IEC 17025:2017 CLAUSE NO.	**LAB SITUATIONS**	**RISK**	**IMPACT**	**PROBABILITY**	**RISK RATING**	**LAB ACTION**	**REMARK**	**RISK RATING**

Observation made by Quality Manager/Technical Manager

Signature: Date:

Annexure VII

MEASUREMENT UNCERTAINITY

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Measurement Uncertainty Calculation for Bench Top Type Instruments

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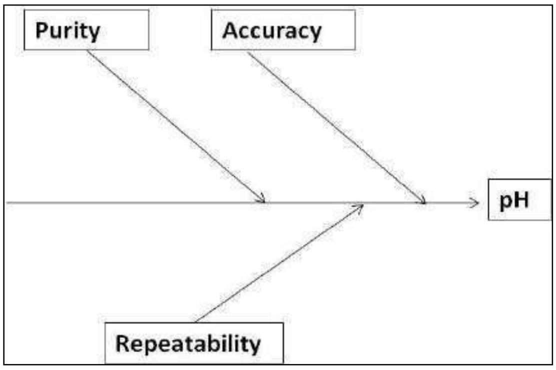
Evaluation of Measurement Uncertainty in Determination of pH in Ground Water Sample.

1. **Title:** Evaluation of Measurement Uncertainty in Determination of pH in Ground Water Sample.
2. **Reference Method**: 4500-H$^+$-B, Page 45-95 to 45-99, APHA 23rd Edition 2017.
3. **Environmental condition:** Temperature: 25±3 °C
4. **Fish Bone Diagram**



5. **Information**

Sl. No.	Equipment/ Apparatus/Material	Lot No./ Sl. No.	Temp.	Certified Value	U	K	CL
1.	Buffer solution pH 4.00	HC60772035	27°C	4.01	±0.02	2	95%
2.	Buffer solution pH 7.00	HC60941339	27°C	7.00	±0.02	2	95%
3.	Buffer solution pH 9.00	HC67802961	27°C	9.01	±0.03	2	95%
4.	pH meter	Systronics 1200	25°C		±0.01	2	95%

6. **Steps**

Calibration of the instrument using CRM Buffer solutions of pH 4.00, 7.00 and 9.00. Then note the reading of the sample as shown in the pH-meter.

7. **Evaluation of Standard Uncertainties**
   i. **Uncertainty associated with CRM Buffer solutions:**

a) Uncertainty associated with CRM Buffer solution of pH 4.00

The certified value of CRM buffer 4.00 is 4.01 as given in the supplier certificate with quoted uncertainty of ±0.02 at 95 % confidence level and coverage factor of 2, so the uncertainty is;

$$\frac{\pm 0.02}{2} = \pm 0.01$$

$$u_{P_{4.00}} = \frac{\pm 0.01}{\sqrt{3}} = \pm 0.00577 \ldots\ldots\ldots\ldots\ldots Type\ B)$$

a) Uncertainty associated with CRM Buffer solution of pH 7.00

The certified value of CRM buffer 7.00 is 7.00 as given in the supplier certificate with quoted uncertainty of ±0.02 at 95 % confidence level and coverage factor of 2, so the uncertainty is;

$$\frac{\pm 0.02}{2} = \pm 0.01 \ldots\ldots\ldots\ldots\ldots Type\ B)$$

$$u_{P_{7.00}} = \frac{\pm 0.01}{\sqrt{3}} = \pm 0.00577 \ldots\ldots\ldots\ldots\ldots Type\ B)$$

b) Uncertainty associated with CRM Buffer solution of pH 9.00

The certified value of CRM buffer 9.00 is 9.01 as given in the supplier certificate with quoted uncertainty of ±0.03 at 95 % confidence level and coverage factor of 2, so the uncertainty is;

$$\frac{\pm 0.03}{2} = \pm 0.015$$

$$u_{P_{9.00}} = \frac{\pm 0.015}{\sqrt{3}} = \pm 0.00866 \ldots\ldots\ldots\ldots\ldots Type\ B)$$

ii. Uncertainty associated with the pH meter

Uncertainty associated with the pH meter is known from the calibration certificate of the instrument, which shows the expanded uncertainty of ± 0.01 at 95% confidence level and coverage factor of 2, so the uncertainty is

$$\frac{\pm 0.01}{2} = \pm 0.005$$

$$u_{pH-meter} = \frac{\pm 0.005}{\sqrt{3}} = \pm 0.00288 \ldots\ldots\ldots\ldots\ldots Type\ B)$$

8. Combined Uncertainty Associated with determination of pH in ground water sample

Conduct an independent experiment as per the procedural steps and note the reading as shown in the pH-meter

S. No.	Observed Value (x)	(x-M)	$(x-M)^2$	$\sum (x-M)^2$	(n-1)	Standard Deviation (SD)
1	7.92	0.0034	0.00001	0.00760	9	**0.03082**
2	7.89	-0.0266	0.00070			
3	7.9	-0.0166	0.00027			
4	7.94	0.0234	0.00054			
5	7.96	0.0434	0.00188			
6	7.89	-0.0266	0.00070			
7	7.93	0.0134	0.00017			
8	7.95	0.0334	0.00111			
9	7.87	-0.0466	0.00217			
10	7.92	0.0034	0.00001			
Mean	**7.91666**					

$$u^{repeatability} = \frac{0.03082}{\sqrt{10}}$$

$$u_{repeatability} = \pm 0.00974 \ldots\ldots\ldots\ldots\ldots .Type\ A)$$

The Combined uncertainty associated with experiment of determination of pH in the sample can be calculated by combining all above standard uncertainties by product form mathematical model i.e.

$$u_c(y) = (y)\ \ X\ \ \sqrt{\sum_{i=1}^{n} \left(\frac{c_i(u\, x_i)}{x_i} \right)^2}$$

Where	
$u_c(y)$	Combined uncertainty associated with the function (y)
(y)	function of various independent variables
(c_i)	Sensitivity factor
ux_i	Uncertainty associated with different independent variables

Values and uncertainties associated with Determination of pH

Sl. No.	Description	Values (x)	Standard uncertainty u(x)	Relative Std. Uncertainty u(x)/x
1	Repeatability	7.916	±0.00974	±0.001231
2	CRM Buffer 4.00	4.01	±0.00577	±0.001439
3	CRM Buffer 7.00	7.00	±0.00577	±0.000824
4	CRM Buffer 9.00	9.01	±0.00866	±0.000961
5	pH-meter		±0.00288	

$$u_{pH,sample} = pH_{sample}\sqrt{\left(\frac{u_{pH_{repetability}}}{pH}\right)^2 + \left(\frac{u_{4.00}}{Buffer\ 4.00}\right)^2 + \left(\frac{u_{7.00}}{Buffer\ 7.00}\right)^2 + \left(\frac{u_{9.00}}{Buffer\ 9.00}\right)^2 + \left(\frac{u_{V_{pH-meter}}}{V_{pH-meter}}\right)^2}$$

$$u_{pH,sample} = 7.916 \times \sqrt{(\pm 0.001231)^2 + (\pm 0.00143)^2 + (\pm 0.00082)^2 + (\pm 0.00096)^2 + (\pm 0.00288)^2}$$

$$u_{pH,sample} = 7.916 \times \pm 0.00367$$

$$\boldsymbol{u_{pH,sample} = \pm 0.02910}$$

9. Effective Degree of Freedom

Effective degree of freedom (v_{eff}) can be obtained by **Welch-Satterthwaite formula** given as:

$$v_{eff} = \frac{\{u_c^4(y)\}}{\sum_{i=1} \{u_i^4(y)\}/v_i}$$

Where	
V	

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Approved & Issued by: Radha Pyari **Quality Manager/OIC**	**Prepared by:** **Technical Manager**

5.	pH-meter	±0.00288	1		∞
6.	$u_{Combined}$	± 0.02910	1		?

$$v_{eff} = \frac{(u_{combined})^4}{\frac{(u_{repeatability})^4}{v_{repeatability}} + \frac{(u_{4.00})^4}{v_{4.00}} + \frac{(u_{7.00})^4}{v_{7.00}} + \frac{(u_{9.00})^4}{v_{9.00}} + \frac{(u_{pHmeter})^4}{v_{pHmeter}}}$$

$$v_{eff} = \frac{(0.029108)^4}{\left\{\frac{(0.009746794)^4}{9}\right\} + \left\{\frac{(0.005773)^4}{\infty}\right\} + \left\{\frac{(0.005773)^4}{\infty}\right\} + \left\{\frac{(0.00866)^4}{\infty}\right\} + \left\{\frac{0.002886^{\ 4}}{\infty}\right\}}$$

$$\boldsymbol{v_{eff} = \infty\ (\text{infinity})}$$

The effective degree of freedom for the experiment (Evaluation of measurement uncertainty in Determination of total alkalinity concentration in mg/liter is found infinity (∞) which gives a value coverage factor (k) 1.96 ≈ 2 (from student ‘t’ table) at 95 % confidence level.

10. Expanded Uncertainty

Expanded uncertainty can be obtained by multiplying the combined standard uncertainty with the coverage factor (k), so the expanded uncertainty is equal to:

$$Expanded\ Uncertainty\ (U) = 2 \text{ x } u_{combined}$$

$$Expanded\ Uncertainty\ (U) = 2 \text{ x } \pm 0.02910$$

$$\boldsymbol{Expanded\ Uncertainty\ (U) = \pm 0.0582}$$

11. Expression of Result

$$\boldsymbol{pH = (7.92\ \pm 0.0582\ )}$$

12. Uncertainty Budget

Sl. No.	Quantity	Estimated Value (X_i)	Uncertainty (u_i)	Probability Distribution/ Type A or B	Degree of Freedom (v)
1	Repeatability	7.916	±0.00974	Normal, Type A	9
2	$u_{4.00}$	4.01	±0.00577	Normal, Type B	∞
3	$u_{7.00}$	7.00	±0.00577	Normal, Type B	∞
4	$u_{9.00}$	9.01	±0.00866	Normal, Type B	∞
5	pH-meter		±0.00288	Normal, Type B	∞
6	pH of sample	7.916	± 0.0582	Normal	∞

13. References

Eurachem/ CITAC Guide CG4, Quantifying Uncertainty in Analytical Measurement, Third Edition

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Measurement Uncertainty Calculation For Flame photometer

Annexure VII

Evaluation of Measurement Uncertainty in Determination of Sodium Concentration in Ground Water Sample.

1. **Title:** Evaluation of Measurement Uncertainty in Determination of Sodium Concentration in Ground Water Sample.
2. **Reference Method**: 3500 Na B, Page 3-99 to 3-100, Flame Photometric Method, APHA 23rd Ed. 2017, 3500 Na B
3. **Environmental condition:** Temperature: 25±3 °C
4. **Mathematical Model:**

A) For Preparation of Intermediate Standards from Sodium standard (CRM).

$$C_{Na} = \frac{\mathrm{C}_{\mathrm{CRM}}\ \mathrm{X}\ \ V_{CRM}}{V_{Total}}$$

Where:	
C_{Na}	Concentration of Intermediate standard Solution (mg/litre)
V_{Total}	Final Volume of Intermediate solution (mL)
C_{CRM}	Actual concentration of Sodium Standard (CRM) solution (mg/litre) as in the certificate.
V_{CRM}	Volume of Sodium standard (CRM) solution (ml)

5. Cause and Effect Diagram

A) For Preparation of standard Sodium solution for calibration of Instrument

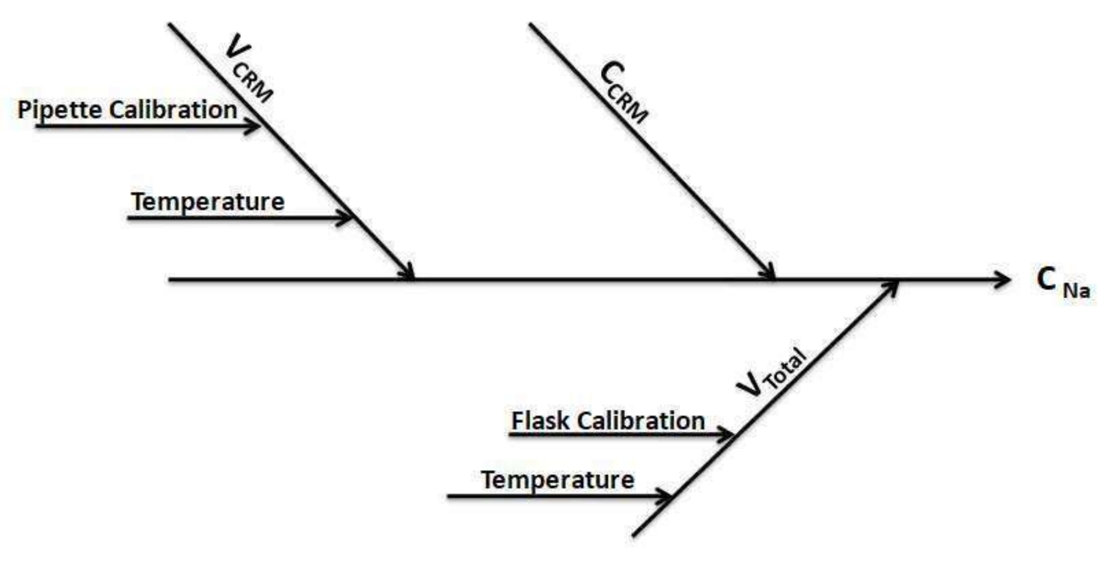


Fig.1- Cause and Effect diagram of Sodium standard for calibration

B) For Concentration of Sodium (mg/liter)

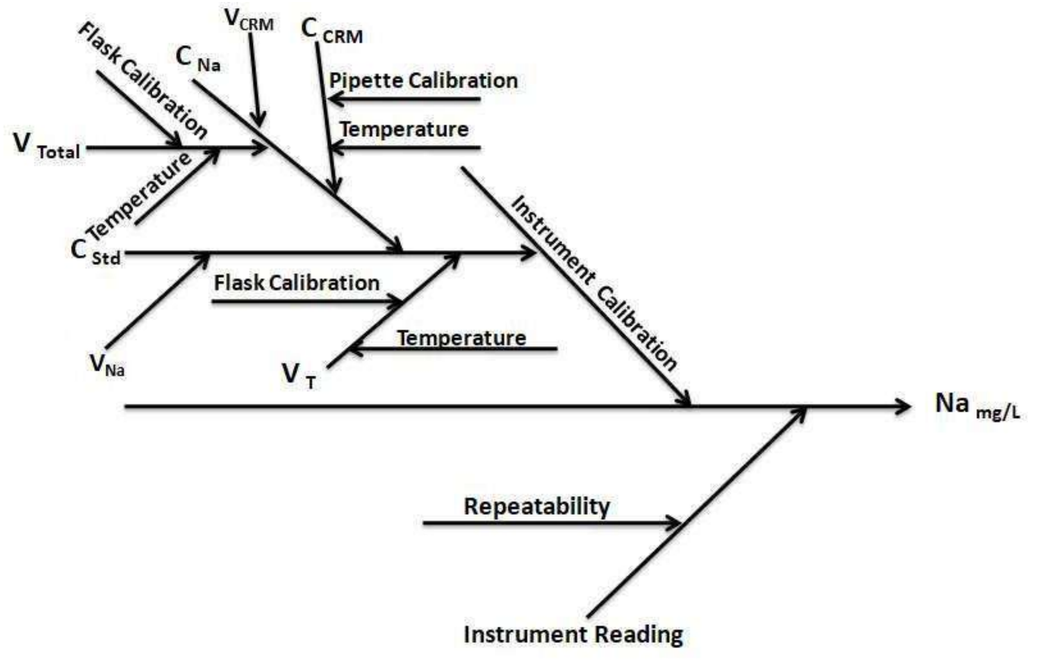


Fig.1- Cause and Effect diagram of Sodium standard for calibration

6. Information

Sl. No.	Equipment/ Apparatus/Material	Lot No./ Sl. No.	Temp.	Purity/ Capacity	U	K	CL
1.	Na standard (CRM)	HC42583338 (Merck)	-	998 mg/l Na	± 4 mg/kg Na	2	95%
2.	25 mL Pipette	BR020288U	27 °C	24.990 mL	±0.005 mL	2	95%
3.	250 mL Flask	MT140161U	27 °C	250.002 mL	±0.03 mL	2	95%
4.	100 ml Flask	MK 8189T	27 °C	100.031 mL	±0.002 mL	2	95%
5.	Flame Photometer	-	-	-	±0.05 mg/L		

7. Steps

i. **Preparation of 100 mg/L Na standard stock solutions:** Dilute 25ml, Na standard (CRM) solution to 250 ml in a volumetric flask.

ii. **Preparation of Intermediate Na standards:** Dilute 5ml, 12.5ml, 25ml and 50ml of stock solution to 100ml in volumetric flasks.

iii. **Analysis of unknown sample:**

I) Set the reading in the Flame Photometer to zero with distilled water and run the intermediate Sodium standards in the ascending order to get a linear calibration curve.

II) Determine the concentration of Sodium in the unknown samples from the curve by aspirating into the Flame Photometer.

8. Evaluation of Standard Uncertainties

A. Uncertainty associated with preparation of stock solution.

First of all prepare a stock solution of 100 mg/L Na as per procedure from 1000 mg/L Na CRM solution, and then calculate the exact concentration of prepared solutions by the given mathematical formula i.e

$$C_{Na} = \frac{C_{CRM} \text{ X } V_{CRM}}{V_{Total}}$$

Sl. No.	Symbol	Description	Value
1	C_{Na}	Concentration of Stock solution	100 mg/L
2	C_{CRM}	Actual concentration of Sodium Standard (CRM) solution (mg/litre) as in the certificate.	998 mg/L Na
4	V_{CRM}	Volume of CRM	24.990 mL
5	V_{Total}	Total Volume of Stock Solution	250.002 mL

$$C_{Na} = \frac{998 \text{ X } 24.990}{250.002}$$

$$\boldsymbol{C_{Na} = 99.7593\ mg/L}$$

The Combined uncertainty associated with preparation of 100 mg/L Sodium Stock solution is calculated by combining all the function used in the above equation in the following manner;

i. Uncertainty due to Purity of Sodium Standard (CRM)

Purity of Sodium standard (CRM) is given in the supplier certificate as 998 mg/L Na with quoted uncertainty of ± 4 mg/Kg Na (or 0.004) at 95 % confidence level and coverage factor of 2, so the uncertainty is;

$$= \frac{\pm 0.004}{2} = \pm 0.002\ mg/L$$

The standard uncertainty is calculated using the assumption of a rectangular distribution for the Purity of the CRM i.e.

$$u_{C_{CRM}} = \frac{\pm 0.002}{\sqrt{3}} = \pm 0.00116\ mg/L \ldots\ldots\ldots\ldots\ldots.Type\ B)$$

ii. Uncertainty due to Calibration of Pipette volume (V_{CRM})

a) Uncertainty due to calibration

This is calculated from calibration certificate of 25 mL pipette, the calibration certificated quote the volume of pipette is 24.990 mL @ 27°C and value of standard uncertainty of ±0.005 mL at 95% confidence level and coverage factor of 2, so uncertainty due to V, $_{calibration}$ is;

$$= \frac{\pm 0.005\, mL}{} = \pm 0.0025\, mL2$$

The standard uncertainty is calculated using the assumption of a triangular distribution i.e.,

$$u_{V_{calibration}} = \frac{\pm 0.0025\, mL}{\sqrt{6}} = \pm 0.0010206\, mL \; \ldots\ldots\ldots . (Type\ B)$$

b.) Uncertainty due to temperature (± 3°C)

Laboratory temperature varies between the limits ± 3°C. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficientof the volume expansion. The volume expansion of the water is considerable larger thanthat of flask, so only former need to be considered. The coefficient of volume expansionof water is 2.1 x 10^{-4} ˚C^{-1}. It leads to a volume variation of:

$$Volume\ variation = \pm(24.990\ X\ 3\ X\ 2.1\ X 10^{-4}\ )\ mL = \ \pm 0.01574\, mL$$

The standard uncertainty is calculated using rectangular distribution for the temperature variation i.e.

$$u_{V_{temperature}} = \frac{\pm 0.01574\ \text{mL}}{\sqrt{3}} \ = \ \pm 0.00908\ \text{mL} \ldots\ldots . (\text{Type B})$$

The two contributions are combined to give standard uncertainty for the total volume of Sodium (CRM).

$$u_{V\ CRM} = \sqrt{(\mu_{V\ \ calibration}\ )^2 + (\mu_{V\ \ temperature}\ )^2}$$

$$u_{V\,CRM} = \pm \mathbf{0.009137}\ \boldsymbol{mL} \ldots\ldots\ldots\ldots . (\textbf{Type B})$$

i. Uncertainty due to calibration of 250 mL Volumetric flask (V_{Total})

a). Uncertainty due to calibration

This is calculated from calibration certificate of 250 mL volumetric flask, the calibration certificated quote the volume of flask is 250.002 mL @ 27°C and value of standard uncertainty of ±0.03 mL at 95% confidence level and coverage factor of 2, ;

$$= \frac{\pm 0.030\, mL}{2} = \pm 0.015\, mL$$

The standard uncertainty is calculated using traingular distribution i.e.

$$u_{V_{calibration}} = \frac{\pm 0.015\ \ mL}{\sqrt{6}} = \pm 0.006124\, mL \ldots\ldots\ldots\ldots(Type\ B)$$

b). Uncertainty due to temperature (± 3°C)

Laboratory temperature varies between the limits ± 3°C. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. The volume expansion of the water is considerable larger than that of flask, so only former need to be considered. The coefficient of volume expansion of water is 2.1 x 10^{-4} $^{\circ}C^{-1}$. It leads to a volume variation of;

$$Volume\ variation = \pm(250.002\ X\ 3\ X\ 2.1\ X10^{-4}\ )\ mL = \ \pm 0.158\, mL$$

The standard uncertainty is calculated using rectangular distribution for the temperature variation i.e.

$$u_{V_{temperature}} = \frac{\pm 0.158\ \ mL}{\sqrt{3}} = \pm 0.091\, mL \ldots\ldots\ldots\ldots\ldots\ldots(Type\ B)$$

The two contribution are combined to give standard uncertainty for the total volume of Na stock solution (250 mL)

$$u_{V_{Total}} = \sqrt{(\mu_{V\ \ calibration}\ )^2 + (\mu_{V\ \ temperature}\ )^2}$$

$$u_{V_{Total}} = \sqrt{(0.006124)^2 + (0.091)^2}$$

$u_{V_{Total}} = \pm 0.0912\ mL$................(Type B)

The Combined uncertainty associated with preparation of 100 mg/L Sodium stock solution can be calculate by combining all above three standard uncertainties by product form mathematical modal i.e.

$$u_c(y) = (y) \;\; X \;\; \sqrt{\sum_{i=1}^{n} \left(\frac{c_i(u\, x_i)}{x_i} \right)^2}$$

Where	
$u_c(y)$	Combined uncertainty associated with the function (y)
(y)	function of various independent variables
(c_i)	Sensitivity factor (1)
ux_i	Uncertainty associated with different independent variables

Values and uncertainties associated with different variables in the preparation of 100 mg/L Na Stock solution

Sl. No.	Description/ independent factors	Values (x)	Standard uncertainty u(x)	Relative Std. Uncertainty u(x)/x
1	Purity (C_{CRM})	998 mg/L	±0.00116 mg/L	±0.0000012
2	Volume (V_{CRM})	24.990 mL	± 0.009137 mL	±0.0003656
3	Volume (V_{total})	250.002 mL	±0.0912 mL	±0.0003648

$$u_{C_{C_{Na}}} = C_{Na} \sqrt{\left(\frac{u_{C_{CRM}}}{C_{CRM}}\right)^2 + \left(\frac{u_{V_{CRM}}}{V_{CRM}}\right)^2 + \left(\frac{u_{V_{Total}}}{V_{Total}}\right)^2}$$

$$u_{C_{C_{Na}}} = 99.7593\, mg/L \times \left(\sqrt{(\pm 0.0000012)^2 + (\pm 0.0003656)^2 + (\pm 0.0003648)^2}\right)$$

$$u_{C_{C_{Na}}} = 99.7593\, mg/L \times (\pm 0.0005165)$$

$$\boldsymbol{u_{C_{C_{Na}}} = \pm 0.05153\ \mathbf{mg/L} \ldots\ldots\ldots\ldots (\mathbf{Type\ B})}$$

This is the combined standard uncertainty associated for the preparation of 100 mg/L Na standard stock solution, since it is measured from a single experiment so its degree of freedom will be linfinity (∞), which gives a coverage factor of 1.96 ≈2 at 95 % confidence level.

B. Uncertainty associated with preparation of 5 mg/L Intermediate Na standards solution.

The uncertainty associated with the preparation of Intermediate sodium standard solution can be calculated similarly as above and the actual concemtration of the solution can be calculated by using the formula i.e

$$N_{Std1} = \frac{\mathrm{C_{Na}} \text{ X } V_{Na}}{V_T}$$

Sl. No.	Symbol	Description	Value
1	N $_{\mathrm{Std1}}$	Concentration of Intermediate standard solution	5.0 mg/L
2.	C $_{\mathrm{Na}}$	Concentration of Stock solution as calculated above	99.7593 mg/L
3.	V $_{\mathrm{Na}}$	Volume of Na stock solution	4.990 mL
4.	V $_{\mathrm{T}}$	Total Volume of the standard solution	100.031 mL

$$N_{Std1} = \frac{99.7593 \text{ X } 4.990}{100.031}$$

$$N_{Std1} = 4.9765\, mg/L$$

The Combined uncertainty associated with preparation of 5mg/L Intermediate Sodium standard is calculated by combining all the variables used in the above equation in the following manner;

i) Uncertainty due to Volume, (V_{Na})

a) Uncertainty due to calibration

This is calculated from calibration certificate of 25 mL pipette, the calibration certificated quote the volume of pipette is 24.990 mL @ 27°C and value of standard uncertainty of ±0.005 mL at 95% confidence level and coverage factor of 2, so uncertainty due to V, $_{\mathrm{calibration}}$ is;

$$= \frac{\pm 0.005\, mL}{} = \pm 0.0025\, mL2$$

The standard uncertainty is calculated using the assumption of a triangular distribution i.e.,

$$u_{V_{calibration}} = \frac{\pm 0.0025\, mL}{\sqrt{6}} = \pm 0.0010206\, mL \;\ldots\ldots\ldots..(Type\ B)$$

c.) Uncertainty due to temperature (± 3°C)

Laboratory temperature varies between the limits ± 3°C. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. The volume expansion of the water is considerable larger thanthat of flask, so only former need to be considered. The coefficient of volume expansionof water is 2.1 x 10^{-4} °C^{-1}. It leads to a volume variation of:

$$Volume\ variation = \pm(4.990\ X\ 3\ X\ 2.1\ X10^{-4})\ mL = \pm 0.003143\ mL$$

The standard uncertainty is calculated using rectangular distribution for the temperature variation i.e.

$$u_{V_{temperature}} = \frac{\pm 0.003143\ \mathrm{mL}}{\sqrt{3}} = \pm 0.001815\ \mathrm{mL}\ \ldots\ldots.(\mathrm{Type\ B})$$

The two contributions are combined to give standard uncertainty for the total volume of Sodium (CRM).

$$u_{V\ Na} = \sqrt{(\mu_{V\ \ calibration})^2 + (\mu_{V\ temperature})^2}$$

$$u_{V_{Na}} = \sqrt{(0.0010206)^2 + (0.001815)^2}$$

$$u_{V_{Na}} = \boldsymbol{\pm 0.002082\ mL}\ \ldots\ldots\ldots\ldots.\mathbf{(Type\ B)}$$

ii) Uncertainty due to Volume of the 100 mL Flask , V_T

a.) Uncertainty due to calibration

This is calculated from calibration certificate of 100 mL volumetric flask, the calibration certificated quote the volume of flask is 100.031 mL @ 27°C and value of standard uncertainty of ±0.002 mL at 95% confidence level and coverage factor of 2, so uncertainty due to V$_{,\ calibration}$ is;

$$= \frac{\pm 0.002\,mL}{} = \pm 0.001\,mL2$$

The standard uncertainty is calculated by assuming triangular distribution as

$$u_{V_{calibration}} = \frac{\pm 0.001\ \ mL}{\sqrt{6}} = \pm 0.000408\,mL\ \ \ldots\ldots\ldots.(Type\ B)$$

Laboratory temperature varies between the limits ± 3°C. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. The volume expansion of the water is considerable larger than that of flask, so only former need to be considered. The coefficient of volume expansion of water is 2.1 x 10^{-4} °C^{-1},that leads to a volume variation of:

$$Volume\ variation = \pm(100\ X\ 3\ X\ 2.1\ X10^{-4}\ )\ mL = \ \pm 0.063\ mL$$

The standard uncertainty is calculated using rectangular distribution for the temperature variation i.e.

$$u_{V_{temperature}} = \frac{\pm 0.063\ \ mL}{\sqrt{3}} = \ \pm 0.0364\ mL \dots\dots\dots\dots\dots\dots..(Type\ B)$$

The two contributions are combined to give standard uncertainty for the total volume

$$u_{V_T} = \sqrt{(\mu_{V\ calibration}\ )^2 + (\mu_{V\ temperature}\ )^2}$$

$$u_{V_T} = \sqrt{(0.000408\ )^2 + (0.0364)^2}$$

$$u_{V_T} = \pm 0.0364\ mL\text{................(Type B)}$$

The Combined uncertainty associated with preparation of 5 mg/L Sodium Intermediate standard solution can be calculate by combining all above three standard uncertainties by product form mathematical modal i.e.

$$u_c(y) = (y)\ \ X\ \ \sqrt{\sum_{i=1}^{n}\left(\frac{c_i(u\ x_i)}{x_i}\right)^2}$$

Where	
$u_c(y)$	Combined uncertainty associated with the function (y)
(y)	function of various independent variables
(c_i)	Sensitivity factor (1)
ux_i	Uncertainty associated with different independent variables

Values and uncertainties associated with different variables in the preparation of 100 mg/L Na Stock solution

Sl.	Description/	Values (x)	Standard	Relative Std.

No.	independent factors		uncertainty u(x)	Uncertainty u(x)/x
1	Purity (C_{Na})	99.7593mg/L	±0.00116 mg/L	±0.00001163
2	Volume (V_{Na})	4.99 mL	± 0.002082 mL	±0.00041723
3	Volume (V_T)	100.031 mL	±0.0364 mL mL	±0.00036389

$$u_{C_{N_{Std1}}} = N_{Std1}\sqrt{\left(\frac{u_{C_{Na}}}{C_{Na}}\right)^2 + \left(\frac{u_{V_{Na}}}{V_{Na}}\right)^2 + \left(\frac{u_{V_T}}{V_T}\right)^2}$$

$$u_{C_{N_{Std1}}} = 4.9765\ mg/L \times \left(\sqrt{(\pm0.00001163)^2 + (\pm0.00041723)^2 + (\pm0.00036389)^2}\right)$$

$$u_{C_{N_{Std1}}} = 4.9765\ mg/L \times (\pm0.0005537)$$

$$\mathbf{u_{C_{N_{Std1}}} = \pm 0.002755\ mg/L \ldots\ldots\ldots\ldots (Type\ B)}$$

This is the combined standard uncertainty associated for the preparation of 5 mg/L Na standard stock solution, since it is measured from a single experiment so its degree of freedom will be Iinfinity (∞), which gives a coverage factor of 1.96 ≈2 at 95 % confidence level.

C. Uncertainty associated with preparation of 12.50 mg/L Intermediate Na standards solution.

The uncertainty associated with the preparation of Intermediate sodium standard solution can be calculated similarly as above and the actual concemtration of the solution can be calculated by using the formula i.e

$$N_{Std2} = \frac{C_{Na}\ X\ V_{Na}}{V_T}$$

Sl. No.	Symbol	Description	Value
1	N_{Std2}	Concentration of Intermediate standard solution	12.50 mg/L
2.	C_{Na}	Concentration of Stock solution as calculated above	99.7593 mg/L
3.	V_{Na}	Volume of Na stock solution	12.49 mL
4.	V_T	Total Volume of the standard solution	100.031 mL

$$N_{Std2} = \frac{99.7593\ X\ 12.49}{100.031}$$

$$N_{Std2} = 12.456\,mg/L$$

The Combined uncertainty associated with preparation of 12.50 mg/L Intermediate Sodium standard is calculated by combining all the variables used in the above equation in the following manner;

iii) Uncertainty due to Volume, (V_{Na})

b) Uncertainty due to calibration

This is calculated from calibration certificate of 25 mL pipette, the calibration certificated quote the volume of pipette is 24.990 mL @ 27°C and value of standard uncertainty of ±0.005 mL at 95% confidence level and coverage factor of 2, so uncertainty due to V$_{,\ \text{calibration}}$ is;

$$= \frac{\pm 0.005\,mL}{} = \pm 0.0025\,mL2$$

The standard uncertainty is calculated using the assumption of a triangular distribution i.e.,

$$u_{V_{calibration}} = \frac{\pm 0.0025\,mL}{\sqrt{6}} = \pm 0.0010206\,mL\ \ldots\ldots\ldots..(Type\ B)$$

d.) Uncertainty due to temperature (± 3°C)

Laboratory temperature varies between the limits ± 3°C. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. The volume expansion of the water is considerable larger than that of flask, so only former need to be considered. The coefficient of volume expansion of water is 2.1 x 10^{-4} °C^{-1}. It leads to a volume variation of:

$$Volume\ variation = \pm(12.49\ X\ 3\ X\ 2.1\ X 10^{-4}\ )\ mL = \pm 0.007869\ mL$$

The standard uncertainty is calculated using rectangular distribution for the temperature variation i.e.

$$u_{V_{temperature}} = \frac{\pm 0.007869\ \text{mL}}{\sqrt{3}} = \pm 0.004542\ \text{mL}\ \ldots\ldots.(\text{Type B})$$

The two contributions are combined to give standard uncertainty for the total volume

$$u_{V\,Na} = \sqrt{(\mu_{V\ calibration})^2 + (\mu_{V\ temperature})^2}$$

$$u_{V_{Na}} = \sqrt{(0.0010206)^2 + (0.004542)^2}$$

$$u_{V_{Na}} = \boldsymbol{\pm 0.004656\ mL} \ldots\ldots\ldots\ldots.(\textbf{Type B})$$

iv) Uncertainty due to Volume of the 100 mL Flask , V_T

c.) Uncertainty due to calibration

This is calculated from calibration certificate of 100 mL volumetric flask, the calibration certificated quote the volume of flask is 100.031 mL @ 27°C and value of standard uncertainty of ±0.002 mL at 95% confidence level and coverage factor of 2, so uncertainty due to $V_{,\ calibration}$ is;

$$= \frac{\pm 0.002\,mL}{2} = \pm 0.001\,mL$$

The standard uncertainty is calculated by assuming triangular distribution as

$$u_{V_{calibration}} = \frac{\pm 0.001\ \ mL}{\sqrt{6}} = \pm 0.000408\,mL\ \ldots\ldots\ldots.(Type\ B)$$

d.) Uncertainty due to temperature (± 3°C)

Laboratory temperature varies between the limits ± 3°C. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. The volume expansion of the water is considerable larger than that of flask, so only former need to be considered. The coefficient of volume expansion of water is 2.1 x 10^{-4} $^{\circ}C^{-1}$, that leads to a volume variation of:

$$Volume\ variation = \pm(100\ X\ 3\ X\ 2.1\ X 10^{-4})\ mL = \pm 0.063\,mL$$

The standard uncertainty is calculated using rectangular distribution for the temperature variation i.e.

$$u_{V_{temperature}} = \frac{\pm 0.063\ \ mL}{\sqrt{3}} = \pm 0.0364\,mL \ldots\ldots\ldots\ldots\ldots\ldots..(Type\ B)$$

The two contributions are combined to give standard uncertainty for the total volume

$$u_{V_T} = \sqrt{(\mu_{V\ calibration})^2 + (\mu_{V\ temperature})^2}$$

$$u_{V_T} = \sqrt{(0.000408)^2 + (0.0364)^2}$$

$$u_{V_T} = \pm 0.0364\ mL \ldots\ldots\ldots\ldots\ldots\ \text{(Type B)}$$

The Combined uncertainty associated with preparation of 12.5 mg/L Sodium Intermediate standard solution can be calculate by combining all above three standard uncertainties by product form mathematical modal i.e.

$$u_c(y) = (y)\ X\ \sqrt{\sum_{i=1}^{n}\left(\frac{c_i(u\,x_i)}{x_i}\right)^2}$$

Where	
$u_c(y)$	Combined uncertainty associated with the function (y)
(y)	function of various independent variables
(c_i)	Sensitivity factor (1)
ux_i	Uncertainty associated with different independent variables

Values and uncertainties associated with different variables in the preparation of 100 mg/L Na Stock solution

Sl. No.	Description/ independent factors	Values (x)	Standard uncertainty u(x)	Relative Std. Uncertainty u(x)/x
1	Purity (C_{Na})	99.7593mg/L	±0.00116 mg/L	±0.00001163
2	Volume (V_{Na})	12.49 mL	± 0.004656 mL	±0.00037278
3	Volume (V_T)	100.031 mL	$\pm 0.0364\ mL$ mL	±0.00036389

$$u_{C_{N\,Std2}} = N_{Std2}\sqrt{\left(\frac{u_{C_{Na}}}{C_{Na}}\right)^2 + \left(\frac{u_{V_{Na}}}{V_{Na}}\right)^2 + \left(\frac{u_{V_T}}{V_T}\right)^2}$$

$$u_{C_{N\,Std2}} = 12.456\ mg/L \times \left(\sqrt{(\pm 0.00001163)^2 + (\pm 0.00037278)^2 + (\pm 0.00036389)^2}\right)$$

$$u_{C_{N_{Std2}}} = 4.9765\ mg/L \times (\pm 0.0005211)$$

$$\mathbf{u_{C_{N_{Std2}}} = \pm 0.002593\ mg/L \ldots\ldots\ldots\ldots\ (Type\ B)}$$

This is the combined standard uncertainty associated for the preparation of 5 mg/L Na standard stock solution, since it is measured from a single experiment so its degree of freedom will be linfinity (∞), which gives a coverage factor of 1.96 ≈2 at 95 % confidence level.

D. Uncertainty associated with preparation of 25 mg/L Intermediate Na standards solution.

The uncertainty associated with the preparation of Intermediate sodium standard solution can be calculated similarly as above and the actual concemtration of the solution can be calculated by using the formula i.e

$$N_{Std3} = \frac{\mathrm{C_{Na}}\ \mathrm{X}\ \ V_{Na}}{V_T}$$

Sl. No.	Symbol	Description	Value
1	$\mathrm{N}_{\mathrm{Std3}}$	Concentration of Intermediate standard solution	25.0 mg/L
2.	C_{Na}	Concentration of Stock solution as calculated above	99.7593 mg/L
3.	V_{Na}	Volume of Na stock solution	24.990 mL
4.	V_{T}	Total Volume of the standard solution	100.031 mL

$$N_{Std3} = \frac{99.7593\ \mathrm{X}\ 24.990}{100.031}$$

$$N_{Std3} = 24.9221\, mg/L$$

The Combined uncertainty associated with preparation of 25mg/L Intermediate Sodium standard is calculated by combining all the variables used in the above equation in the following manner;

v) Uncertainty due to Volume, ($\mathrm{V_{Na}}$)

c) Uncertainty due to calibration

This is calculated from calibration certificate of 25 mL pipette, the calibration certificated quote the volume of pipette is 24.990 mL @ 27°C and value of standard uncertainty of ±0.005 mL at 95% confidence level and coverage factor of 2, so uncertainty due to V, $_{\text{calibration}}$ is;

$$= \frac{\pm 0.005\, mL}{} = \pm 0.0025\, mL2$$

The standard uncertainty is calculated using the assumption of a triangular distribution i.e.,

$$u_{V_{calibration}} = \frac{\pm 0.0025\, mL}{\sqrt{6}} = \pm 0.0010206\, mL \;\ldots\ldots\ldots..(Type\ B)$$

e.) Uncertainty due to temperature (± 3°C)

Laboratory temperature varies between the limits ± 3°C. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficientof the volume expansion. The volume expansion of the water is considerable larger thanthat of flask, so only former need to be considered. The coefficient of volume expansionof water is 2.1 x 10^{-4} $^{\circ}C^{-1}$. It leads to a volume variation of:

$$Volume\ variation = \pm(24.990\ X\ 3\ X\ 2.1\ X 10^{-4}\ )\ mL = \pm 0.01574\, mL$$

The standard uncertainty is calculated using rectangular distribution for the temperature variation i.e.

$$u_{V_{temperature}} = \frac{\pm 0.01574\ \mathrm{mL}}{\sqrt{3}} = \pm 0.009087\ \mathrm{mL} \ldots\ldots.(\mathrm{Type\ B})$$

The two contributions are combined to give standard uncertainty for the total volume of Sodium (CRM).

$$u_{V_{Na}} = \sqrt{(\mu_{V\ calibration}\ )^2 + (\mu_{V\ temperature}\ )^2}$$

$$u_{V_{Na}} = \sqrt{(0.0010206)^2 + (0.009087)^2}$$

$$u_{V_{Na}} = \mathbf{\pm 0.009145\, mL} \ldots\ldots\ldots\ldots.(\mathbf{Type\ B})$$

vi) Uncertainty due to Volume of the 100 mL Flask , V_T

e.) Uncertainty due to calibration

This is calculated from calibration certificate of 100 mL volumetric flask, the calibration certificated quote the volume of flask is 100.031 mL @ 27°C and value of standard uncertainty of ±0.002 mL at 95% confidence level and coverage factor of 2, so uncertainty due to $V_{,\ calibration}$ is;

$$= \frac{\pm 0.002\, mL}{2} = \pm 0.001\, mL$$

The standard uncertainty is calculated by assuming triangular distribution as

$$u_{V_{calibration}} = \frac{\pm 0.001\ \ mL}{\sqrt{6}} = \pm 0.000408\, mL\ \ldots\ldots\ldots.(Type\ B)$$

f.) Uncertainty due to temperature (± 3°C)

Laboratory temperature varies between the limits ± 3°C. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. The volume expansion of the water is considerable larger than that of flask, so only former need to be considered. The coefficient of volume expansion of water is 2.1 x 10^{-4} $^{\circ}C^{-1}$,that leads to a volume variation of:

$$Volume\ variation = \pm(100\ X\ 3\ X\ 2.1\ X 10^{-4}\ )\ mL = \ \pm 0.063\, mL$$

The standard uncertainty is calculated using rectangular distribution for the temperature variation i.e.

$$u_{V_{temperature}} = \frac{\pm 0.063\ mL}{\sqrt{3}} = \pm 0.0364\, mL \ldots\ldots\ldots\ldots\ldots\ldots..(Type\ B)$$

The two contributions are combined to give standard uncertainty for the total volume

$$u_{V_T} = \sqrt{(\mu_{V\ calibration}\ )^2 + (\mu_{V\ temperature}\ )^2}$$

$$u_{V_T} = \sqrt{(0.000408\ )^2 + (0.0364)^2}$$

u_{V_T} = $\pm 0.0364\, mL$................(Type B)

The Combined uncertainty associated with preparation of 25 mg/L Sodium Intermediate standard solution can be calculate by combining all above three standard uncertainties by product form mathematical modal i.e.

$$u_c(y) = (y)\ \ X\ \ \sqrt{\sum_{i=1}^{n}\left(\frac{c_i(u\,x_i)}{x_i}\right)^2}$$

Where	
u_c(y)	Combined uncertainty associated with the function (y)
(y)	function of various independent variables
(c_i)	Sensitivity factor (1)

Calculation of Measurement Uncertainty

ux_i	Uncertainty associated with different independent variables

Values and uncertainties associated with different variables in the preparation of 100 mg/L Na Stock solution

Sl. No.	Description/ independent factors	Values (x)	Standard uncertainty u(x)	Relative Std. Uncertainty u(x)/x
1	Purity (C_{Na})	99.7593mg/L	±0.00116 mg/L	±0.00001163
2	Volume (V_{Na})	24.99 mL	± 0.009145 mL	±0.00036594
3	Volume (V_T)	100.031 mL	$\pm 0.0364\, mL$ mL	±0.00036389

$$u_{C_{N_{Std3}}} = N_{Std1}\sqrt{\left(\frac{u_{C_{Na}}}{C_{Na}}\right)^2 + \left(\frac{u_{V_{Na}}}{V_{Na}}\right)^2 + \left(\frac{u_{V_T}}{V_T}\right)^2}$$

$$u_{C_{N_{Std3}}} = 24.9221\, mg/L \times \left(\sqrt{(\pm 0.00001163)^2 + (\pm 0.00036594)^2 + (\pm 0.00036389)^2}\right)$$

$$u_{C_{N_{Std3}}} = 24.9221\, mg/L \times (\pm 0.0005162)$$

$$\mathbf{u_{C_{N_{Std3}}} = \pm 0.01286\ mg/L \ldots\ldots\ldots\ldots (Type\ B)}$$

This is the combined standard uncertainty associated for the preparation of 25 mg/L Na standard stock solution, since it is measured from a single experiment so its degree of freedom will be linfinity (∞), which gives a coverage factor of 1.96 ≈2 at 95 % confidence level.

E. Uncertainty associated with preparation of 50 mg/L Intermediate Na standards solution.

The uncertainty associated with the preparation of Intermediate sodium standard solution can be calculated similarly as above and the actual concemtration of the solution can be calculated by using the formula i.e

$$N_{Std4} = \frac{C_{Na}\ X\ V_{Na}}{V_T}$$

Sl. No.	Symbol	Description	Value
1	N_{Std2}	Concentration of Intermediate standard solution	50 mg/L
2.	C_{Na}	Concentration of Stock solution as calculated above	99.7593 mg/L

Approved & Issued by: Radha Pyari **Quality Manager/OIC**	**Prepared by:** **Technical Manager**

Calculation of Measurement Uncertainty

3.	V_{Na}	Volume of Na stock solution	49.98 mL
4.	V_T	Total Volume of the standard solution	100.031 mL

$$N_{Std4} = \frac{99.7593\ X\ 49.98}{100.031}$$

$$N_{Std4} = 49.844\ mg/L$$

The Combined uncertainty associated with preparation of 50 mg/L Intermediate Sodium standard is calculated by combining all the variables used in the above equation in the following manner;

vii) Uncertainty due to Volume, (V_{Na})

a) Uncertainty due to calibration

This is calculated from calibration certificate of 25 mL pipette, the calibration certificated quote the volume of pipette is 24.990 mL @ 27°C and value of standard uncertainty of ±0.005 mL at 95% confidence level and coverage factor of 2, so uncertainty due to $V_{, calibration}$ is;

$$= \frac{\pm 0.005\ mL}{} = \pm 0.0025\ mL2$$

The standard uncertainty is calculated using the assumption of a triangular distribution i.e.,

$$u_{V_{calibration}} = \frac{\pm 0.0025\ mL}{\sqrt{6}} = \pm 0.0010206\ mL\ \ldots\ldots\ldots..(Type\ B)$$

b.) Uncertainty due to temperature (± 3°C)

Laboratory temperature varies between the limits ± 3°C. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. The volume expansion of the water is considerable larger than that of flask, so only former need to be considered. The coefficient of volume expansion of water is 2.1 x $10^{-4}\,^{\circ}C^{-1}$. It leads to a volume variation of:

$$Volume\ variation = \pm(49.98\ X\ 3\ X\ 2.1\ X10^{-4}\ )\ mL = \pm 0.0314874\ mL$$

The standard uncertainty is calculated using rectangular distribution for the temperature variation i.e.

$$u_{V_{temperature}} = \frac{\pm 0.0314874\ \mathrm{mL}}{\sqrt{3}} = \pm 0.018179\ \mathrm{mL} \ldots\ldots(\text{Type B})$$

The two contributions are combined to give standard uncertainty for the total volume of Sodium (CRM).

$$u_{V_{Na}} = \sqrt{(\mu_{V\ calibration})^2 + (\mu_{V\ temperature})^2}$$

$$u_{V_{Na}} = \sqrt{(0.0010206)^2 + (0.018179)^2}$$

$$u_{V_{Na}} = \pm \mathbf{0.018208}\ \boldsymbol{mL} \ldots\ldots\ldots\ldots(\textbf{Type B})$$

viii) Uncertainty due to Volume of the 100 mL Flask , V_T

a.) Uncertainty due to calibration

This is calculated from calibration certificate of 100 mL volumetric flask, the calibration certificated quote the volume of flask is 100.031 mL @ 27°C and value of standard uncertainty of ±0.002 mL at 95% confidence level and coverage factor of 2, so uncertainty due to V$_{,\ calibration}$ is;

$$= \frac{\pm 0.002\ mL}{2} = \pm 0.001\ mL$$

The standard uncertainty is calculated by assuming triangular distribution as

$$u_{V_{calibration}} = \frac{\pm 0.001\ \ mL}{\sqrt{6}} = \pm 0.000408\ mL\ \ldots\ldots\ldots(Type\ B)$$

b.) Uncertainty due to temperature (± 3°C)

Laboratory temperature varies between the limits ± 3°C. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. The volume expansion of the water is considerable larger than that of flask, so only former need to be considered. The coefficient of volume expansion of water is $2.1 \times 10^{-4}\ ^{\circ}C^{-1}$, that leads to a volume variation of:

$$Volume\ variation = \pm(100\ X\ 3\ X\ 2.1\ X10^{-4}\ )\ mL = \ \pm 0.063\ mL$$

The standard uncertainty is calculated using rectangular distribution for the temperature variation i.e.

$$u_{V_{temperature}} = \frac{\pm 0.063\ \ mL}{\sqrt{3}} = \pm 0.0364\ mL \ldots\ldots\ldots\ldots\ldots\ldots..(Type\ B)$$

The two contributions are combined to give standard uncertainty for the total volume of $AgNO_3$ (20 mL)

$$u_{V_T} = \sqrt{(\mu_{V\ calibration}\ )^2 + (\mu_{V\ temperature}\ )^2}$$

$$u_{V_T} = \sqrt{(0.000408\ )^2 + (0.0364)^2}$$

$$u_{V_T} \ = \pm 0.0364\ mL\text{................(Type B)}$$

The Combined uncertainty associated with preparation of 50 mg/L Sodium Intermediate standard solution can be calculate by combining all above three standard uncertainties by product form mathematical modal i.e.

$$u_c(y) = (y)\ \ X\ \ \sqrt{\sum_{i=1}^{n}\left(\frac{c_i(u\ x_i)}{x_i}\right)^2}$$

Where	
$u_c(y)$	Combined uncertainty associated with the function (y)
(y)	function of various independent variables
(c_i)	Sensitivity factor (1)
ux_i	Uncertainty associated with different independent variables

Values and uncertainties associated with different variables in the preparation of 50 mg/L Na Stock solution

Sl. No.	Description/ independent factors	Values (x)	Standard uncertainty u(x)	Relative Std. Uncertainty u(x)/x
1	Purity (C_{Na})	99.7593mg/L	±0.00116 mg/L	±0.00001163
2	Volume (V_{Na})	49.98 mL	± 0.018208 mL	±0.00036431
3	Volume (V_T)	100.031 mL	$\pm 0.0364\ mL$ mL	±0.00036389

$$u_{C_{N\ Std4}} \quad u_{C_{Na}}^{\ 2} \quad u_{V_{Na}}^{\ 2} \quad u_V^{\ 2}$$

V_{Na} $+\left(\frac{\ \ _T}{V_T}\right)$

$$u_{C_{N_{Std4}}} = 49.844\, mg/L \times \left(\sqrt{(\pm 0.00001163)^2 + (\pm 0.00036431)^2 + (\pm 0.00036389)^2}\right)$$

$$u_{C_{N_{Std4}}} = 49.844\, mg/L \times (\pm 0.0005151)$$

$$\mathbf{u_{C_{N_{Std4}}} = \pm 0.025675\ mg/L \ldots\ldots\ldots\ldots (Type\ B)}$$

This is the combined standard uncertainty associated for the preparation of 50mg/L Na standard stock solution, since it is measured from a single experiment so its degree of freedom will be Iinfinity (∞), which gives a coverage factor of 1.96 ≈2 at 95 % confidence level.

F. Combined Uncertainty Associated with Sodium concentration in ground water sample

The Combined uncertainty associated with measurement of Sodium concentration (mg/liter) is calculated by combining all the variables used in the above equation in the following manner;

i) Uncertainty due to repeatability

Uncertainty due to repeatability is calculated from the data obtained by the calculation of Sodium concentration (mg/liter) based on the following 10 repeated measurements;

$$u_{repeatibility} = \frac{SD}{\sqrt{n}}$$

Sl. No	$Na_{mg/liter}$ (X_i)	$(X_i-\bar{x})$	$(X_i-\bar{x})^2$
1	8.15	-0.462	0.213444
2	8.65	0.038	0.001444
3	8.64	0.028	0.000784
4	8.72	0.108	0.011664
5	8.57	-0.042	0.001764

6	8.63	0.018	0.000324

7	8.8	0.188	0.035344
8	8.68	0.068	0.004624
9	8.72	0.108	0.011664
10	8.56	-0.052	0.002704
Mean ($\bar{x}$)		8.612	
Sum		86.12	0.28376

$$Standard\ deviation\ (SD) = \sqrt{\sum_{i=1}^{n} \frac{(X_i - \bar{x})^2}{n-1}}$$

$$u_{repeatability} = \frac{0.28376}{\sqrt{10}}$$

$u_{repeatability} = \pm 0.08973$............(Type A)

The Combined uncertainty associated with experiment of determination of Sodium concentration (mg/liter) can be calculate by combining all above standard uncertainties by product form mathematical modal i.e.

$$u_c(y) = (y)\ X\ \sqrt{\sum_{i=1}^{n} \left(\frac{c_i(u\,x_i)}{x_i} \right)^2}$$

Where	
$u_c(y)$	Combined uncertainty associated with the function (y)
(y)	function of various independent variables
(c_i)	Sensitivity factor
ux_i	Uncertainty associated with different independent variables

Values and uncertainties associated with determination of Sodium concentration (mg/liter)

Sl. No.	Description	Values (x)	Standard uncertainty u(x)	Relative Std. Uncertainty u(x)/x
1	Repeatability	8.612 mg/liter	± 0.08973 mg/litre	±0.010419
2	C_{Na}	99.7593 mg/litre	± 0.05153 mg/litre	±0.000517
3	N_{Std1}	4.9765 mg/litre	± 0.002755 mg/litre	±0.000554

Calculation of Measurement Uncertainty

4	N_{Std2}	12.456 mg/litre	±0.002593 mg/litre	±0.000208
4	N_{Std3}	24.9221 mg/litre	± 0.01286 mg/litre	±0.000516
6	N_{Std4}	49.844 mg/litre	±0.025675 mg/litre	±0.000515

$$u_{C_{Na\,mg/liter}} = Na_{mg/liter}\sqrt{\left(\frac{u_{Na_{repetibility}}}{Na_{mg/liter}}\right)^2 + \left(\frac{u_{C_{Na}}}{C_{Na}}\right)^2 + \left(\frac{u_{N_{Std1}}}{N_{Std1}}\right)^2 + \left(\frac{u_{N_{Std2}}}{N_{Std2}}\right)^2 + \left(\frac{u_{N_{Std3}}}{N_{Std3}}\right)^2 + \left(\frac{u_{N_{Std4}}}{N_{Std4}}\right)^2}$$

$$u_{C_{Na_{mg/liter}}} = 8.612\,mg/litre\sqrt{(\pm 0.010419)^2 + (\pm 0.000517)^2 + (\pm 0.000554)^2 + (\pm 0.000208)^2 + (\pm 0.000516)^2 + (\pm 0.000515)^2}$$

$$u_{C_{Na_{mg/liter}}} = 8.612\,\frac{mg}{litre} \times (\pm 0.010474)$$

$$u_{C_{Na_{mg/liter}}} = 0.090202\,mg/litre$$

1. Effective Degree of Freedom

Effective degree of freedom (v_{eff}) can be obtained by **Welch-Satterthwaite formula** given as:

$$v_{eff} = \frac{\{u_c^4(y)\}}{\sum_{i=1} \{u_i^4(y)\}/v_i}$$

Where	
V_{eff}	Effective degree of freedom
u_i (y)	Is the contribution to the standard uncertainty associated with the output estimate y resulting from the standard uncertainty associated with the input estimate X_i
V_i	Effective degree of freedom for each standard uncertainty component

u_c (y)	Combined standard uncertainty for the function Y

Observations

Calculation of Measurement Uncertainty

Sl. No.	Description of uncertainty component	Value {ui (y)}	No of Observations (n)	Degree of Freedom (v_i) = n-1
1	$u_{repeatability}$	±0.08973 mg/L	10	9
2	$u_{C_{C_{Na}}}$	± 0.05153 mg/L	1	∞
3	$u_{C_{N_{Std1}}}$	± 0.002755 mg/L	1	∞
4	$u_{C_{N_{Std2}}}$	± 0.002593 mg/L	1	∞
5	$u_{C_{N_{Std3}}}$	± 0.01286 mg/L	1	∞
6	$u_{C_{N_{Std4}}}$	±0.025675 mg/liter	1	∞

$$v_{eff} = \frac{(u_{combined})^4}{\frac{(u_{repeatability})^4}{v_{repeatability}} + \frac{(u_{C_{Na}})^4}{v_{Na}} + \frac{(u_{C_{N_{Std1}}})^4}{v_{Std1}} + \frac{(u_{C_{N_{Std2}}})^4}{v_{Std2}} + \frac{(u_{C_{N_{Std3}}})^4}{v_{Std3}} + \frac{(u_{C_{N_{Std4}}})^4}{v_{Std4}}}$$

$$v_{eff} = \frac{(0.090202)^4}{\frac{(0.08973)^4}{9} + \frac{(0.05153)^4}{\infty} + \frac{(0.002755)^4}{\infty} + \frac{(0.002593)^4}{\infty} + \frac{(0.01286)^4}{\infty} + \frac{(0.025675)^4}{\infty}}$$

$$v_{eff} = \infty\ (\textbf{infinity})$$

The effective degree of freedom for the experiment (Evaluation of measurement uncertainty in determination of Sodium concentration (mg/liter) is found to be infinity (∞) which gives a value coverage factor (k) 1.96 ≈ 2 (from student 't' table) at 95 % confidence level.

9. Expanded Uncertainty

Expanded uncertainty can be obtained by multiplying the combined standard uncertainty with the coverage factor (k), so the expanded uncertainty, at coverage factor (k) = 2 and 95 % confidence level, is equal to:

$$Expanded\ Uncertainty\ (U) = 2 \text{ x } u_{C_{Na_{mg/liter}}}$$

$$Expanded\ Uncertainty\ (U) = 2 \times (\pm 0.090202\ \frac{mg}{liter})$$

$$Expanded\ Uncertainty\ (U) = \pm 0.1804\ \frac{mg}{liter}$$

Approved & Issued by:	Prepared by:
Radha Pyari Quality Manager/OIC	Technical Manager

$$Concentration\ of\ Sodium = (\,8.63\ \pm 0.1804)\ mg/liter$$

11. Uncertainty Budget

Sl. No.	Quantity	Estimated Value (X_i)	Standard Uncertainties (u_i)	Probability Distribution/ Type A or B	Degree of Freedom (v)
1	Repeatability	8.612 mg/liter	± 0.08973 mg/litre	Normal, Type A	9
2	C_{Na}	99.7593 mg/litre	± 0.05153 mg/litre	Normal, Type B	∞
3	N_{Std1}	4.9765 mg/litre	± 0.002755 mg/litre	Normal, Type B	∞
4	N_{Std2}	12.456 mg/litre	±0.002593 mg/litre	Normal, Type B	∞
5	N_{Std3}	24.9221 mg/litre	± 0.01286 mg/litre	Normal, Type B	∞
6	N_{Std4}	49.844 mg/litre	±0.025675 mg/litre	Normal, Type B	∞
7	Na (mg/litre)	8.63 mg/litre	±0.090202 mg/litre	Normal	∞

12. References

1. EURACHEM/ CITAC Guide CG4, Quantifying Uncertainty in Analytical Measurement, Third Edition

Annexure VII

Measurement Uncertainty Calculation For Titration

Evaluation of Measurement Uncertainty in Determination of Calcium concentration (mg/liter) in Ground Water Sample.

1. **Title:** Evaluation of Measurement Uncertainty in Determination of Calcium concentration (mg/liter) in Ground Water Sample.
2. **Reference Method**: 3500 Ca B, Page 3-69 to 3-70 APHA 23rd Edition 2017.
3. **Environmental condition:** Temperature: 25±3 °C
4. **Mathematical Model:**

A) For Preparation of 0.02 *N* $CaCO_3$ (CRM) Solution

$$N_{CaCO3} = \frac{M_{CaCO3} \text{ X } 1000 \text{ X } P_{CaCO3}}{Eq.Wt._{CaCO3} \text{ X } V_{Total}}$$

Where:	
N_{CaCO3}	Normality of $CaCO_3$ Solution (N)
P_{CaCO3}	Purity of $CaCO_3$ Salt (CRM) in mass fraction
$Eq.Wt._{CaCO3}$	Equivalent weight of $CaCO_3$
V_{total}	Final Volume of $CaCO_3$ solution (mL)
M_{CaCO3}	Mass of $CaCO_3$ (g)

B) For Standardization of 0.02 *N* EDTA with 0.02 *N* $CaCO_3$ Solution

$$N_{EDTA} = \frac{N_{CaCO3} \text{ X } V_{CaCO3}}{V_{EDTA}}$$

Where:	
N_{EDTA}	Normality of EDTA Solution (N)
V_{EDTA}	Volume of EDTA solution (mL)
V_{CaCO3}	Volume of 0.02 N $CaCO_3$ Solution (CRM) taken for standardization of 0.02 N EDTA Solution (mL)
N_{CaCO3}	Normality of $CaCO_3$ (CRM) Solution (N)

C) For Calcium, mg/liter

$$Calcium_{\ mg/liter} = \frac{(V_A - V_B)\ X\ N_{EDTA} X\ \ Eq.\ Wt_{Ca}.\ X\ 1000}{V_{Sample}}$$

$$Calcium_{\ mg/liter} = \frac{(V_A - V_B)\ X\ N_{EDTA} X\ \ 20.04\ X\ 1000}{V_{Sample}}$$

Where:	
N_{EDTA}	Normality of EDTA Solution (N)
V_{sample}	Volume of unknown sample (mL)
V_A	Volume of standard EDTA Solution (0.02 N approx.) required for titration of known volume of sample (mL)
V_B	Volume of standard EDTA Solution (0.02 N approx.) required for titration of blank (mL)
$Eq.\ Wt._{ca}$	Equivalent Weight of Calcium (20.04)

5. Fish Bone Diagram

A) For Preparation of 0.02 $CaCO_3$ (CRM) Solution

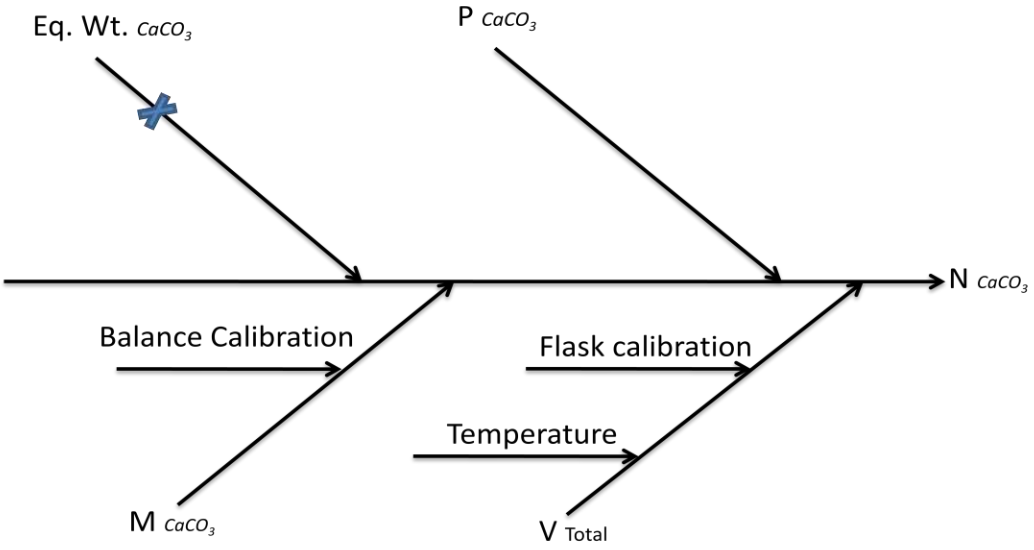


Fig. 1- Fish Bone Diagram for Preparation of 0.02 *N* $CaCO_3$Solution

B) For Standardization of 0.02 *N* EDTA with 0.02 *N* $CaCO_3$ Solution

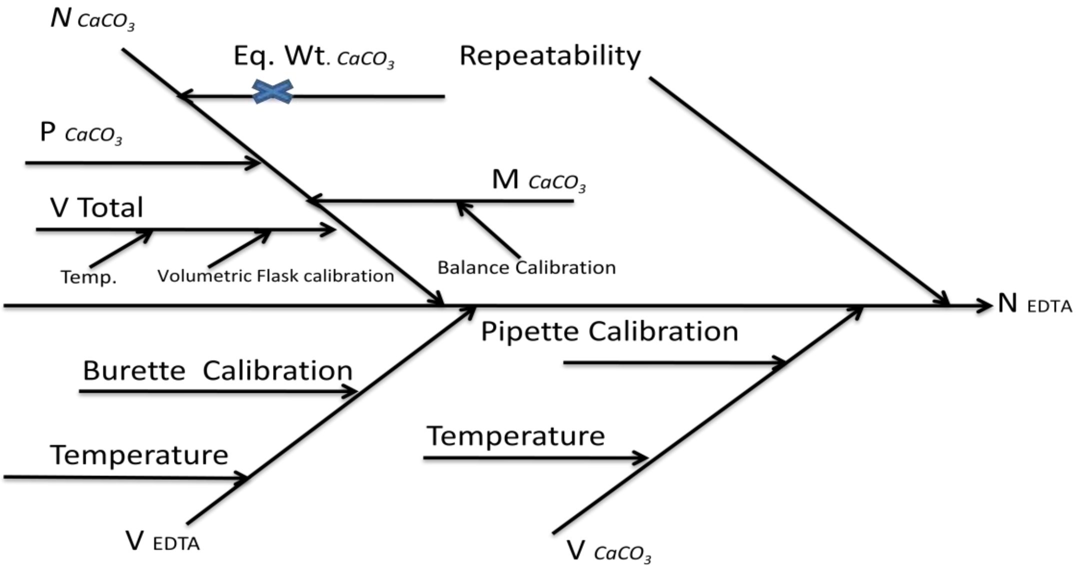


Fig. 2- Fish Bone Diagram for Standardization of EDTA Solution

C) For Concentration of Calcium (mg/liter)

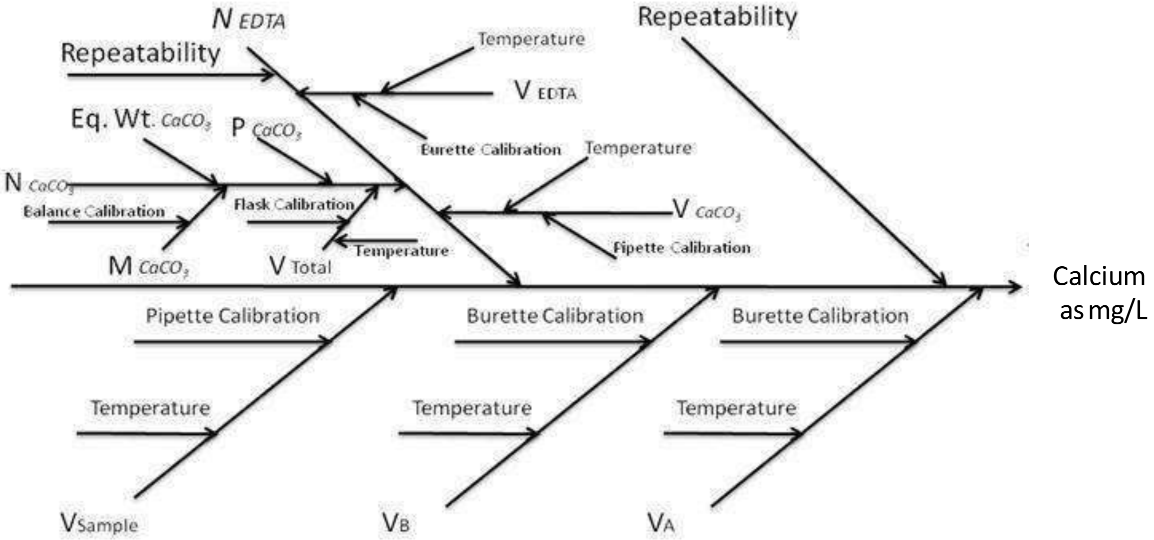


Fig. 3- Fish bone diagram for calcium (mg/L)

6. Information

Sl. No.	Equipment/ Apparatus/Material	Lot No./ Sl. No.	Temp.	Purity/ Capacity	U	K	CL
1.	$CaCO_3$ (CRM)	152410K(Merck)	-	99.98%	± 0.05%	2	95%
2.	50 mL Burette	BD014271U	27 °C	50.033 mL	±0.005 mL	2	95%
3.	25 mL Pipette	BR020288U	27 °C	24.990 mL	±0.005 mL	2	95%
4.	1000 mL Flask	BX051263U	27 °C	999.98 mL	±0.30 mL	2	95%
5.	Weighing Balance	BSA2245-CW	27±4°C	200 g	±0.3 mg	2	95%

7. Steps

i. **Preparation of 0.02 N $CaCO_3$ (CRM) Solution:** Weight 1.000 g anhydrous $CaCO_3$ (Primary standard) into a 500 mL Erlenmeyer flask. Place a funnel in the flask neck and add, a little at time, 1+1 HCl until all $CaCO_3$ has dissolved. Add 200 mL distill or deionised water and boil for few minutes to expel CO_2. Cool, add a few drops of methyl red indicator, and adjust to the intermediate orange color by adding 3N ammonium hydroxide or 1+1 HCl, as required. Dilute to 1000 mL with distill or deionised water;

ii. **Preparation of Standard EDTA titrant, 0.02 *N*:** Weigh 3.723 g analytical reagent grade disodium ethylenediaminetetraacetate di hydrate, dissolve in distill or deionised water, and dilute to 1000 mL. Standardize against standard calcium solution and keep the solution, in polyethylene or borosilicate glass bottles.

iii. 1 N sodium hydroxide: Dissolve 4 g of NaOH in 100 ml distilled water.

iv. Murexide indicator: Mix 0.2 g of ammonium purpurate with 100 g NaCl and grind.

v. **Titration of unknown sample:**

- **a.** Take 20 mL sample or a suitable portion and add 1 to 2 mL 1 N sodium hydroxide solution.
- **b.** Add 1 or 2 drops indicator solution or an appropriate amount of dry powder indicator formulation.
- **c.** Titrate against EDTA solution until the colour changes from pink to purple.
- **d.** Run a blank in parallel taking 20 ml distilled/deionised water in place of sample and note down the reading(B).
- **e.** Standardize EDTA titrant with primary standard, $CaCO_3$ solution.
- **f.** Take 20 ml $CaCO_3$ standard solution, add buffer, indicator and inhibitor in sequence and titrate with EDTA (0.02 N) solution, and note down the reading (V_{EDTA}).

8. Evaluation of Standard Uncertainties

A. Uncertainty associated with preparation of 0.02 *N* $CaCO_3$ (CRM) Solution.

First of all we prepare a solution of 0.02 N $CaCO_3$ as per procedure by using CRM, and calculate the exact normality of prepared solution by the given mathematical formula i.e.

$$N_{CaCO3} = \frac{M_{CaCO3}\ X\ 1000\ X\ P_{CaCO3}}{Eq.Wt._{CaCO3}\quad X\ V_{Total}}$$

Sl. No.	Symbol	Description	Value
1	N_{CaCO3}	Normality of $CaCO_3$ (N)	0.02 N
2	M_{CaCO3}	Weight of $CaCO_3$ for preparation of 0.02N $CaCO_3$ Solution	1.0010g (99.98 %)
3	P_{CaCO3}	Purity of $CaCO_3$ (Mass Fraction)	0.9998
4	$Eq.Wt._{CaCO3}$	Equivalent Weight of $CaCO_3$	50.0434
5	V_{Total}	Total Volume of $CaCO_3$ Solution	999.98 mL

$$N_{CaCO_3} = \frac{1.0010X\ 1000\ X\ 0.9998}{50.0434X\ 999.98}$$

$$\boldsymbol{N_{CaCO_3} = 0.01999\ N}$$

The Combined uncertainty associated with preparation of 0.02 N of $CaCO_3$ is calculated by combining all the function used in the above equation in the following manner;

i. Uncertainty due to weighing balance

Uncertainty in weighing of $CaCO_3$ (CRM) is calculated from the calibration certificate of balance, which shows the expanded uncertainty of ± 0.3 mg at 95 % confidence level and coverage factor of 2, so the uncertainty associated with weighing of $CaCO_3$ is calculated using rectangular distribution i.e.

$$u_{M_{CaCO3}} = \frac{\pm 0.3\,mg}{2} = \pm 0.15mg = \frac{\pm 0.15\ mg}{\sqrt{3}} = \pm\mathbf{0.0866025}\ \ldots\ldots\ldots\ (Type\ B)$$

ii. Uncertainty due to Purity of $CaCO_3$

Purity of $CaCO_3$ is given in the supplier certificate as 99.98 % with quoted uncertainty of ± 0.05 % (or 0.0005) at 95 % confidence level and coverage factor of 2, so the uncertainty is calculated using rectangular distribution;

$$u_{P_{CaCO3}} = \frac{\pm 0.0005}{2} = \frac{\pm 0.00025}{\sqrt{3}} = \pm \mathbf{0.000144} \ldots\ldots\ldots\ldots\ldots Type\ B)$$

iii. **Uncertainty due to Volume V_{Total}**

a.) **Uncertainty due to calibration of Volumetric flask (1000 mL)**

This is calculated from calibration certificate of 1000 mL volumetric flask, the calibration certificated quote the volume of flask is 999.98 mL @ 27°C and value of standard uncertainty of ±0.30 mL at 95% confidence level and coverage factor of 2, so uncertainty due to $V_{,\ calibration}$ is calculated using triangular distribution;

$$u_{V_{calibration}} = \frac{\pm 0.30\ mL}{2} = \frac{\pm 0.15\ mL}{\sqrt{6}} = \pm \mathbf{0.06123\ mL} \ldots\ldots\ldots\ldots\ldots\ldots (Type\ B)$$

b.) **Uncertainty due to temperature (± 3°C)**

Laboratory temperature varies between the limits ± 3°C. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. The volume expansion of the water is considerable larger than that of flask, so only former need to be considered. The coefficient of volume expansion of water is $2.1 \times 10^{-4}\ ^{\circ}C^{-1}$. It leads to a volume variation of;

$$Volume\ variation = \pm(999.98\ X\ 3\ X\ 2.1\ X10^{-4}\ )\ mL = \pm 0.629\ mL$$

The standard uncertainty is calculated using rectangular distribution for the temperature variation i.e.

$$u_{\ temperature} = \frac{\pm 0.629\ mL}{\sqrt{3}} = \pm 0.363\ mL \ldots\ldots\ldots\ldots\ldots\ldots\ldots (Type\ B)$$

The two contribution are combined to give standard uncertainty for the total volume of $CaCo_3$ (1000mL)

$$u_{V_{Total}} = \sqrt{(\mu_{V_{calibration}})^2 + (\mu_{V_{\ temperature}})^2}$$

$$u_{V_{Total}} = \sqrt{(0.06123)^2 + (0.363)^2}$$

$$u_{V_{Total}} = \pm 0.36812\ mL \ldots\ldots\ldots\ldots\ldots (\text{Type B})$$

The Combined uncertainty associated with preparation of 0.02 N $CaCO_3$ can be calculate by combining all above three standard uncertainties by product form mathematical modal i.e.

$$u_c(y) = (y)\ \ X\ \ \sqrt{\sum_{i=1}^{n} \left(\frac{c_i(u\, x_i)}{x_i}\right)^2}$$

Where	
u_c (y)	Combined uncertainty associated with the function (y)
(y)	function of various independent variables
(c_i)	Sensitivity factor (1)
ux_i	Uncertainty associated with different independent variables

Values and uncertainties associated with different variables in the preparation of 0.02 N $CaCO_3$

Sl. No.	Description/ independent factors	Values (x)	Standard uncertainty u(x)	Relative Std. Uncertainty u(x)/x
1	**Purity (P)**	**0.9998**	**± 0.000144**	**±0.000144**
2	**Mass(M)**	**1001.0 mg**	**± 0.0866025 mg**	**±0.0000865**
3	**Volume (V_{total})**	**999.98 mL**	**±0.36812 mL**	**±0.0003681**

$$u_{C_{N_{CaCO3}}} = N_{Caco3} \sqrt{\left(\frac{u_{M_{CaCO3}}}{M_{CaCO3}}\right)^2 + \left(\frac{u_{P_{CaCO3}}}{P_{CaCO3}}\right)^2 + \left(\frac{u_{V_{CaCO3}}}{V_{Total}}\right)^2}$$

$$u_{C_{N_{CaCO3}}} = 0.01999\ N\ \boldsymbol{X} \pm \sqrt{(0.0000865)^2 + (0.000144)^2 + (0.0003681)^2}$$

$$u_{C_{N_{CaCO3}}} = 0.01999 N\ \text{X} \pm 0.000404618$$

$$\boldsymbol{u_{C_{N_{CaCO3}}} = \pm 0.00000808\ \text{N} \ldots\ldots\ldots\ldots (\text{Type B})}$$

This is the combined standard uncertainty associated with preparation of 0.02 N $CaCO_3$, since it is measured from a single experiment so its degree of freedom will be infinity (∞), which gives a coverage factor of 1.96 ≈2 at 95 % confidence level.

B. Uncertainty associated with Standardization of 0.02 *N* EDTA Solution.

Conduct an independent experiment as per the procedural steps and calculate the normality of secondary standard, EDTA Solution, as per the given formula i.e

$$N_{EDTA} = \frac{N_{CaCO3} \text{ X } V_{CaCO3}}{V_{EDTA}}$$

Observations and previously calculated relevant data		
N_{EDTA}	Normality of EDTA Solution (N)	?
V_{EDTA}	Volume of EDTA solution used for standardization(mL)	19.9 mL
V_{CaCO3}	Volume of 0.02 N $CaCO_3$ Solution (CRM) taken for standardization of 0.02N EDTA Solution (mL)	19.99 mL
N_{CaCO3}	Normality of $CaCO_3$ (CRM) Solution (N)	0.01999 N

$$N_{EDTA} = \frac{0.01999 \text{ X } 19.99}{20.1}$$

$$N_{EDTA} = 0.01988\ N$$

The Combined uncertainty associated with standardization of EDTA solution (secondary solution) is calculated by combining all the variables used in the above equation in the following manner;

i) Uncertainty due to Volume, V_{CaCO3}

a) Uncertainty due to calibration

This is calculated from calibration certificate of 25 mL pipette, the calibration certificated quote the volume of pipette is 24.990 mL @ 27°C and value of standard uncertainty of ±0.005 mL at 95% confidence level and coverage factor of 2, so uncertainty due to $V_{, calibration}$ is;

$$u_{V_{calibration}} = \frac{\pm 0.005\, mL}{2} = \frac{\pm 0.0025\, mL}{\sqrt{6}} = \pm \mathbf{0.00102\ ml} \ldots..(Type\ B)$$

b.) Uncertainty due to temperature (± 3°C)

Laboratory temperature varies between the limits ± 3°C. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. The volume expansion of the water is considerable larger than that of flask, so only former need to be considered. The coefficient of volume expansion of water is 2.1 x 10^{-4} $^{\circ}C^{-1}$. It leads to a volume variation of:

$$Volume\ variation = \pm(24.990\ X\ 3\ X\ 2.1\ X 10^{-4}\ )\ mL = \pm 0.01574\ mL$$

The standard uncertainty is calculated using rectangular distribution for the temperature variation i.e.

$$u_{V_{temperature}} = \frac{\pm 0.01574\ mL}{\sqrt{3}} = \pm 0.00908\ \text{mL} \ldots \ldots .(\text{Type B})$$

The two contribution are combined to give standard uncertainty for the total volume of $CaCO_3$

$$u_{V_{CaCO3}} = \sqrt{(\mu_{V_{calibration}})^2 + (\mu_{V\ temperature})^2}$$

$$u_{V_{CaCO3}} = \sqrt{(0.00102)^2 + (0.00908)^2}$$

$$u_{V_{CaCO3}} = \pm \mathbf{0.009114\ mL} \ldots \ldots \ldots \ldots .(\textbf{Type B})$$

ii) Uncertainty due to Volume of EDTA , V_{EDTA}

a.) Uncertainty due to calibration

This is calculated from calibration certificate of 50 mL burette, the calibration certificated quote the volume of burette is 50.033mL @ 27°C and value of standard uncertainty of ±0.005 mL at 95% confidence level and coverage factor of 2, so uncertainty due to V, $_{calibration}$ is;

$$u_{V_{calibration}} = \frac{\pm 0.005\ mL}{2} = \frac{\pm 0.0025\ ml}{\sqrt{6}} = \pm\mathbf{0.00102\ ml} \ldots\ldots\ldots.(Type\ B)$$

b.) Uncertainty due to temperature (± 2°C)

Laboratory temperature varies between the limits ± 3°C. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. The volume expansion of the water is considerable larger than that of flask, so only former need to be considered. The coefficient of volume expansion of water is 2.1 x 10^{-4} $^{\circ}C^{-1}$, since 20.1 ml of EDTA is used in experiment, that leads to a volume variation of:

$$Volume\ variation = \pm(20.1\ X\ 3\ X\ 2.1\ X 10^{-4})\ mL = \pm 0.01266 mL$$

The standard uncertainty is calculated using rectangular distribution for the temperature variation i.e.

$$u_{V_{temperature}} = \frac{\pm 0.01266\ ml}{\sqrt{3}} = \pm 0.00730\ mL \ldots\ldots\ldots\ldots\ldots\ldots..(Type\ B)$$

The two contribution are combined to give standard uncertainty for the total volume of EDTA

$$u_{V_{EDTA}} = \sqrt{(\mu_{V_{calibration}})^2 + (\mu_{V\ temperature})^2}$$

$$u_{V_{EDTA}} = \sqrt{(0.00102)^2 + (0.0073)^2}$$

$$u_{V_{EDTA}} = \pm 0.007370916\ mL \ldots\ldots\ldots\ldots\ldots (Type\ B)$$

The 0.01999 N $CaCO_3$ solution has been prepared in laboratory with a standard uncertainty of ± 0.0000167 N at coverage factor of 2 and 95% confidence level.

$$u_{C_{N_{CaCO3}}} = \pm 0.00000808N \ldots\ldots\ldots\ldots (Type\ B)$$

iv) Uncertainty due to repeatability in standardization, u $_{repeatability}$

Uncertainty due to repeatability is calculated from the data obtained by the calculation of normality of EDTA based on the following 7 repeated measurements;

Sl. No	V_{CaCO3}	V_{EDTA}	N_{CaCO3}	N_{EDTA} (X_i)	(X_i-$\bar{X}$)	$(X_i-\bar{X})^2$
1	19.99	20.1mL	0.01999	0.020080407	8.57735E-05	7.35708E-09
2	19.99	19.9mL	0.01999	0.019980005	-1.46286E-05	2.13995E-10
3	19.99	20.0 mL	0.01999	0.019880602	-0.000114032	1.30032E-08
4	19.99	20.1 mL	0.01999	0.019980005	-1.46286E-05	2.13995E-10
5	19.99	20.0 mL	0.01999	0.020080407	8.57735E-05	7.35708E-09
6	19.99	19.9 mL	0.01999	0.020080407	8.57735E-05	7.35708E-09
7	19.99	19.9 mL	0.01999	0.019880602	-0.000114032	1.30032E-08
			Sum	**0.139962435**		4.85057E-08
			Mean ($\bar{x}$)	**0.019994634**		
			SD			**0.0000899126**

$$Mean = \sum_{i=1}^{n} \frac{X_i}{n}$$

$$Standard\ deviation\ (SD) = \sqrt{\sum_{i=1}^{n} \frac{(X_i - \bar{x})^2}{n-1}}$$

$$u_{repeatibility} = \frac{SD}{\sqrt{n}}$$

u $\underline{0.0000899126}$

$repeatability \;=$ $\sqrt{7}$

$$u_{repeatibility} \quad = \quad \pm 0.000033983 \text{..........(Type A)}$$

The Combined uncertainty associated with standardization of 0.02 N EDTA can be calculate by combining all above four standard uncertainties by product form mathematical model i.e.

$$u_c(y) = (y) \;\; X \;\; \sqrt{\sum_{i=1}^{n} \left(\frac{c_i(u\,x_i)}{x_i}\right)^2}$$

Where	
u_c (y)	Combined uncertainty associated with the function (y)
(y)	function of various independent variables
(c_i)	Sensitivity factor
ux_i	Uncertainty associated with different independent variables

Values and uncertainties associated with Standardization of 0.02 N EDTA

Sl. No.	Description	Values (x)	Standard uncertainty u(x)	Relative Std. Uncertainty u(x)/x
1	Repeatability	0.019994N	± 0.000033983N	±0.00108988
2	N_{CaCO3}	0.01999 N	± 0.00000808 N	±0.0004042
3	V_{CaCO3}	19.99 mL	± 0.009114 mL	±0.0004559
4	V_{EDTA}	20.1mL	± 0.0037091 mL	±0.0003666

$$u_{C_{N_{EDTA}}} = N_{EDTA} \sqrt{\left(\frac{u_{N_{CaCO3}}}{N_{CaCO3}}\right)^2 + \left(\frac{u_{V_{CaCO3}}}{V_{CaCO3}}\right)^2 + \left(\frac{u_{V_{EDTA}}}{V_{EDTA}}\right)^2 + \left(\frac{u_{N_{CaCO3}\,repeatibility}}{N_{CaCO3_{Repeatibility}}}\right)^2}$$

$$u_{C_{N_{EDTA}}} = 0.01988\sqrt{(\pm 0.0004042)^2 + (\pm 0.0004559)^2 + (\pm 0.0003666)^2 + (\pm 0.00108988)^2}$$

$$u_{C_{N_{EDTA}}} = 0.01994\, X 0.0013013$$

$$= \pm\;\; 0.000025948 \text{ N}$$

$EDTA$

C. Combined Uncertainty Associated with determination of Calcium concentration

Conduct an independent experiment as per the procedural steps and calculate the Calcium concentration in mg/liter by the given formula i.e

$$Calcium_{\ mg/liter} = \frac{(\mathrm{V_A} - \mathrm{V_B})\ \mathrm{X}\ \ N_{EDTA}\mathrm{X}\ \ 20.04\ \mathrm{X}\ 1000}{V_{Sample}}$$

Observations and previously calculated relevant data		
N EDTA	Normality of EDTA Solution (N)	0.01988 N
Vsample	Volume of unknown sample (mL)	19.99 mL
VA	Volume of standard EDTA Solution (0.02N approx.) required for titration of known volume of sample (mL)	1.3 mL
VB	Volume of standard EDTA Solution (0.02 N approx.) required for titration of blank (mL)	0 mL

$$Calcium_{\ mg/liter} = \frac{(1.3)\mathrm{X}\ \ 0.01988\ \mathrm{X}\ \ 20.04\ \mathrm{X}\ 1000}{19.99}$$

$$Calcium_{\ mg/liter} = 25.908\ \ mg/liter$$

The Combined uncertainty associated with Determination of calcium concentration, mg/liter, is calculated by combining all the variables used in the above equation in the following manner;

i) Uncertainty due to repeatability

Uncertainty due to repeatability is calculated from the data obtained by the calculation of Calcium concentration based on the following 10 repeated measurements;

Sl. No	V sample	VA	VB	N EDTA	Ca mg/liter (Xi)	(Xi-x̅)	(Xi-x̅)2
1	19.99	1.3	0	0.01988	25.909	0.797	0.635510293
2	19.99	1.2	0	0.01988	23.916	-1.196	1.429898159

3	19.99	1.3	0	0.01988	25.909	0.797	0.635510293
4	19.99	1.2	0	0.01988	23.916	-1.196	1.429898159
5	19.99	1.2	0	0.01988	23.916	-1.196	1.429898159
6	19.99	1.3	0	0.01988	25.909	0.797	0.635510293
7	19.99	1.3	0	0.01988	25.909	0.797	0.635510293
8	19.99	1.3	0	0.01988	25.909	0.797	0.635510293
9	19.99	1.3	0	0.01988	25.909	0.797	0.635510293
10	19.99	1.2	0	0.01988	23.916	-1.196	1.429898159
				Mean($\bar{x}$)	24.314		
				SD	1.572078		

$$Standard\ deviation\ (SD) = \sqrt{\sum_{i=1}^{n} \frac{(X_i - \bar{x})^2}{n-1}}$$

$$u_{repeatability} = \frac{1.572078}{\sqrt{10}}$$

$u_{repeatability} = \pm 0.49714$............(Type A)

ii) Uncertainty due to Volume of EDTA consumed for Sample (V_A)

a) Uncertainty due to calibration

This is calculated from calibration certificate of 50 mL burette, the calibration certificated quote the volume of pipette is 50.033 mL @ 27°C and value of standard uncertainty of ±0.005 mL at 95% confidence level and coverage factor of 2, so uncertainty due to $V_{,\text{calibration}}$ is calculated using triangular distribution;

$$u_{V_{calibration}} = \frac{\pm 0.005\, mL}{2} \qquad \frac{\pm 0.0025\, ml}{\sqrt{6}} \quad \dots.(Type\ B)$$

b) Uncertainty due to temperature (± 2°C)

Laboratory temperature varies between the limits ± 3°C. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. The volume expansion of the water is considerable larger than that of flask, so only former need to be considered. The coefficient of volume expansion of water is 2.1 x 10^{-4} $^{\circ}C^{-1}$. It leads to a volume variation of:

$$Volume\ variation = \pm(1.3\ X\ 3\ X\ 2.1\ X 10^{-4}\ )\ mL = \ \pm 0.000819\ mL$$

The standard uncertainty is calculated using rectangular distribution for the temperature variation i.e.

$$u_{V_{temperature}} = \frac{\pm 0.000819\ \ mL}{\sqrt{3}} = \ \pm 0.0004728\ mL \dots\dots\dots\dots\dots\dots..(Type\ B)$$

The two contributions are combined to give standard uncertainty for the total volume of EDTA

$$u_{V_A} = \sqrt{(\mu_{V_{calibration}}\ \ )^2 + (\mu_{V\ temperature}\ )^{\ 2}}$$

$$u_{V_A} = \sqrt{(0.00102\ \ )^2\ + (0.0004728)^{\ 2}}$$

$$u_{V_A} = \pm 0.00128978\ mL \dots\dots\dots\dots\dots (\text{Type B})$$

iii) Uncertainty due to Volume of EDTA consumed for Blank (V_B)

Uncertainty due to Volume of EDTA consumed for blank is no effect since Blank (V_B) is zero.

iv) Uncertainty due to Volume of sample (V_{sample})

a) Uncertainty due to calibration

This is calculated from calibration certificate of 25 mL pipette, the calibration certificated quote the volume of pipette is 24.99 mL@ 27°C and value of standard uncertainty of ±0.005 mL at 95% confidence level and coverage factor of 2, so uncertainty due to $V_{, calibration}$ is;

$$u_{V_{calibration}} = \frac{\pm 0.005\ mL}{2} \qquad \frac{\pm 0.0025\ mL}{\sqrt{6}}$$

b) Uncertainty due to temperature (± 3°C)

Laboratory temperature varies between the limits ± 3°C. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. The volume expansion of the water is considerable larger than that of flask, so only former need to be considered. The coefficient of volume expansion of water is $2.1 \times 10^{-4}\ ^{\circ}C^{-1}$. It leads to a volume variation of:

$$Volume\ variation = \pm(24.99\ X\ 3\ X\ 2.1\ X10^{-4}\ )\ mL = \ \pm 0.01574\ mL$$

The standard uncertainty is calculated using rectangular distribution for the temperature variation i.e.

$$u_{V_{temperature}} = \frac{\pm 0.01574\ mL}{\sqrt{3}} = \ \pm 0.00908\ mL \ldots\ldots\ldots\ldots\ldots\ldots..(Type\ B)$$

The two contribution are combined to give standard uncertainty for the total volume of sample

$$u_{V_{sample}} = \sqrt{(\mu_{V_{calibration}})^2 + (\mu_{V_{temperature}})^2}$$

$$u_{V_{sample}} = \sqrt{(0.00102\ )^2 + (0.00908)^2}$$

$$u_{V_{sample}} = \pm 0.00987\ mL \ldots\ldots\ldots\ldots\ldots\ (\text{Type B})$$

i) Uncertainty due to Normality of EDTA

Uncertainty associated with Normality of EDTA has been calculated previously i.e

$$u_{EDTA} = \pm\ 0.00002594\ \text{N}$$

The Combined uncertainty associated with experiment of determination of total hardness as mg $CaCO_3$/L can be calculated by combining all above four standard uncertainties by product form mathematical model i.e.

$$u_c(y) = (y)\ X\ \sqrt{\sum_{i=1}^{n} \left(\frac{c_i(u\,x_i)}{x_i}\right)^2}$$

Where	
u_c (y)	Combined uncertainty associated with the function (y)
(y)	function of various independent variables
(c_i)	Sensitivity factor
ux_i	Uncertainty associated with different independent variables

Values and uncertainties associated with Determination of Calcium, mg/liter

Sl. No.	Description	Values (x)	Standard uncertainty u(x)	Relative Std. Uncertainty u(x)/x
1	Repeatability	24.314 mg/liter	± 0.49714	±0.020446
2	V_A	1.3 mL	± 0.00128978	±0.000992
3	V_B	0 mL	0	0
4	V_{Sample}	19.99 mL	±0.0098732 ml	±0.0004939
5	N_{EDTA}	0.01988 N	±0.0000259 N	±0.0013028

$$u_{C_{Calcium\ mg/liter}} = Ca_{mg/liter}\sqrt{\left(\frac{u_{Ca_{repetability}}}{Ca_{mg/liter}}\right)^2 + \left(\frac{u_{N_{EDTA}}}{N_{EDTA}}\right)^2 + \left(\frac{u_{V_A}}{V_A}\right)^2 + \left(\frac{u_{V_B}}{V_B}\right)^2 + \left(\frac{u_{V_{sample}}}{V_{sample}}\right)^2}$$

$$u_{C_{Calcium\ mg/liter}} = Ca_{mg/liter}\sqrt{(0.020446)^2 + (0.0013028)^2 + (0.000992)^2 + (0.0004939)^2}$$

$$u_{C_{Calcium\ mg/liter}} = 24.314\ mg/liter\ X\ 0.02051734$$

$$u_{C_{Calcium\ mg/liter}} = \pm 0.49885\ mg/liter$$

9. Effective Degree of Freedom

Effective degree of freedom (v_{eff}) can be obtained by **Welch-Satterthwaite formula** given as:

$$v_{eff} = \frac{\{u_c^4(y)\}}{\sum_{i=1}^{n}\{u_i^4(y)\}/v_i}$$

Where	
v_{eff}	Effective degree of freedom
u_i (y)	Is the contribution to the standard uncertainty associated with the output estimate y resulting from the standard uncertainty associated with the input estimate X_i
v_i	Effective degree of freedom for each standard uncertainty component
u_c (y)	Combined standard uncertainty for the function Y

Observations

Annexure VII

Sl. No.	Description of uncertainty component	Value {ui (y)}	No of Observations (n)	Degree of Freedom $(v_i) = n-1$
1	$u_{\text{repeatability}}$	±0.49714mg/liter	10	9

Approved & Issued by: Radha Pyari Quality Manager/OIC	Prepared by: Technical Manager

2	$u_{N\ EDTA}$	±0.00003707 N	1	∞
3	u_{VA}	±0.00128978mL	1	∞

4	**u_{VB}**	**-**	**-**	**-**
5	**u_{VS}**	**±0.0098732 ml**	**1**	**∞**
6	**$u_{combined}$**	**±0.49885 mg/liter**	**1**	**?**

$$v_{eff} = \frac{(u_{combined})^4}{\frac{(u_{NEDTA})^4}{v_{NEDTA}} + \frac{(u_{VA})^4}{v_{VA}} + \frac{(u_{VB})^4}{v_{VB}} + \frac{(_{repeatibility})^4}{v_{repeatibilty}} + \frac{(u_{Vsample})^4}{v_{Vsample}}}$$

$$v_{eff} = \frac{(0.49885)^4}{\left\{\frac{(0.00003707)^4}{\infty}\right\} + \left\{\frac{(0.00128978)^4}{\infty}\right\} + \left\{\frac{(0.49714)^4}{9}\right\} + \left\{\frac{(0.0098732)^4}{\infty}\right\}}$$

$$v_{eff} = \infty \; (\textbf{infinity})$$

The effective degree of freedom for the experiment (Evaluation of measurement uncertainty in Determination of calcium concentration in mg/liter is found infinity (∞) which gives a value coverage factor (k) 1.96 ≈ 2 (from student 't' table) at 95 % confidence level.

10. Expanded Uncertainty

Expanded uncertainty can be obtained by multiplying the combined standard uncertainty with the coverage factor (k), so the expanded uncertainty is equal to:

$$Expanded\ Uncertainty\ (U) = 2 \text{ x } u_{combined}$$

$$Expanded\ Uncertainty\ (U) = 2 \text{ x } \pm 0.49885 \ as\, mg\ CaCO3/L$$

$$Expanded\ Uncertainty\ (U) = \pm 0.9977\ \frac{mg}{liter}$$

11. Expression of Result

$$\boldsymbol{Concentration\, of\ calcium} = (\mathbf{24.314} \pm \mathbf{0.9977})\ \boldsymbol{mg/liter}$$

12. Uncertainty Budget

Calculation of Measurement Uncertainty

Sl. No.	Quantity	Estimated Value (X_i)	Uncertainty (u_i)	Probability Distribution/ Type A or B	Degree of Freedom (ν)
1	Repeatability	25.11 mg/liter	±0.49714	Normal, Type A	9

2	V_A	1.3 mL	± 0.00128978	Normal, Type B	∞
3	V_B	0 mL	Nil	-	**-**
4	V_{sample}	19.99 mL	±0.0098732 ml	Normal, Type B	∞
5	N_{EDTA}	0.01988 N	±0.00003707 N	Normal, Type B	∞
6	Ca (mg/liter)	24.314 mg/liter	± 0.4988 mg/liter	Normal	∞

13. References

1. Eurachem/ CITAC Guide CG4, Quantifying Uncertainty in Analytical Measurement, Third Edition

Annexure VII

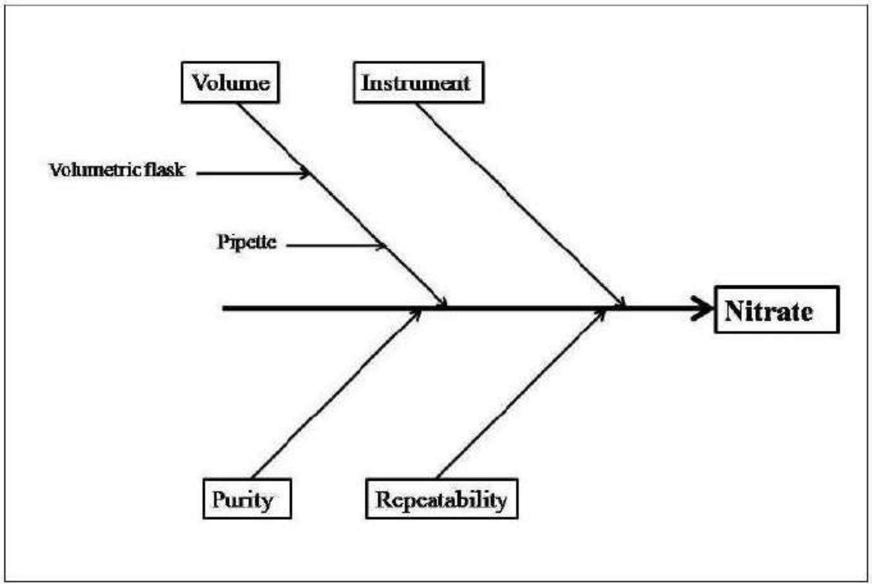
Measurement Uncertainty Calculation For UV-Visible Spectrophotometer

Annexure VII

Evaluation of Measurement Uncertainty in Determination of Nitrate concentration (mg/litre) in Ground Water Sample.

PREPARED BY:	ISSUED BY:
TECHNICAL MANAGER	Radha Pyari QUALITY MANAGER

1. **Title:** Evaluation of Measurement Uncertainty in Determination of Nitrate concentration (mg/litre) in Ground Water Sample
2. **Reference Method:** Ultraviolet Spectrophotometric Screening Method, APHA 23rd Ed. 2017, 4500-NO_3^- B
3. **Environmental Condition:** Temperature 25±5°C
4. **Requirements:**
    a. Nitrate standard solution,
    b. pipette (0.1 ml & 1 ml),
    c. volumetric flask (25 ml) and
    d. HCl (1M).
5. **Fish Bone diagram**



6. Observations & Calculations

S. No.	Observed Value (x)	Mean (M)	(x-M)	$(x-M)^2$	$\sum (x-M)^2$	(n-1)	Standard Deviation (SD)
1	2.9094	2.8936	0.016	0.0002	0.4702039	10	0.2168
2	2.8136	2.8936	-0.080	0.0064			
3	3.0000	2.8936	0.106	0.0113			
4	3.1815	2.8936	0.288	0.0829			
5	2.4310	2.8936	-0.463	0.2140			
6	3.1059	2.8936	0.212	0.0451			
7	2.9033	2.8936	0.010	0.0001			
8	3.1372	2.8936	0.244	0.0593			
9	2.8015	2.8936	-0.092	0.0085			
10	2.8552	2.8936	-0.038	0.0015			
11	2.6914	2.8936	-0.202	0.0409			
No. of Observation Taken (n) = 11							

7. Evaluation Of Standard Uncertainty

TYPE A Uncertainty: U_1

$$Std.\,U_1 = \frac{\underline{Std.deviation}}{SQRT\ of\ n} \qquad U_1 = \mathbf{0.06538}$$

TYPE B Uncertainty:

i. Uncertainty due to CRM (Std. NO_3^- Solution), U_2

$$U_E = \pm\ 0.01,\ \text{k} = 2$$

$$\text{Uncertainty, } U_2 = U_E/\text{k} = 0.005$$

ii. Uncertainty due to UV-Visible Spectrophotometer, U_3

$$\text{Uncertainty} = \pm 0.002$$

iii. Uncertainty due to volumetric flask 25 ml, U_4

$$U_E = \pm 0.002,\ \text{k} = 2$$

$$\text{Uncertainty, } U_4 = U_E/\text{k} = 0.001$$

v. Uncertainty due to pipette 1 ml, U_5

$$U_E = \pm 0.0015,\ \text{k} = 2$$

$$\text{Uncertainty, } U_5 = U_E/\text{k} = 0.00075$$

vi. Uncertainty due to pipette 0.1 ml, U_6

$$U_E = \pm\ 0.002,\ \text{k} = 2$$

$$\text{Uncertainty, } U_6 = U_E/\text{k} = 0.001$$

Uncertainty Parameter	Value	**Deviation**	**Unit**	**Distribution**	**Distribution Factor**	**Standard Uncertainty**
Type A						
Repeatability (U_1)	2.8936					0.06538
Type B						
CRM, Std. NO_3^- Solution (U_2)	1002	0.002		Rectangular	√3	0.00289
UV-Visible Spectrophotometer (U_3)		0.002		Rectangular	√3	0.00115
Volumetric flask 25 ml, U_4	25	0.001	ml	Triangular	√6	0.00041
Pipette 1 ml, U_5	1	0.00075	ml	Triangular	√6	0.00031
Pipette 0.1 ml, U_6	0.1	0.001	ml	Triangular	√6	0.00041

8. Results:

Combined Uncertainty (U_C)

$$(U_C) = \sqrt{(U_1)^2 + (U_2)^2 + (U_3)^2 + (U_4)^2 + (U_5)^2 + (U_6)^2}$$

$$(U_C) = 0.0655$$

Expanded Uncertainty (U_E)

(U_E) = Combined uncertainty * 2 (95% Confidence Level) = 0.1309

Hence, test results would be expressed as

Nitrate (mg/l) = Mean value ± Expanded uncertainty @95% Confidence Level

Nitrate (mg/l) = 2.8936 ± 0.1309 @95% CL

PREPARED BY:	ISSUED BY:
TECHNICAL MANAGER	Radha Pyari QUALITY MANAGER

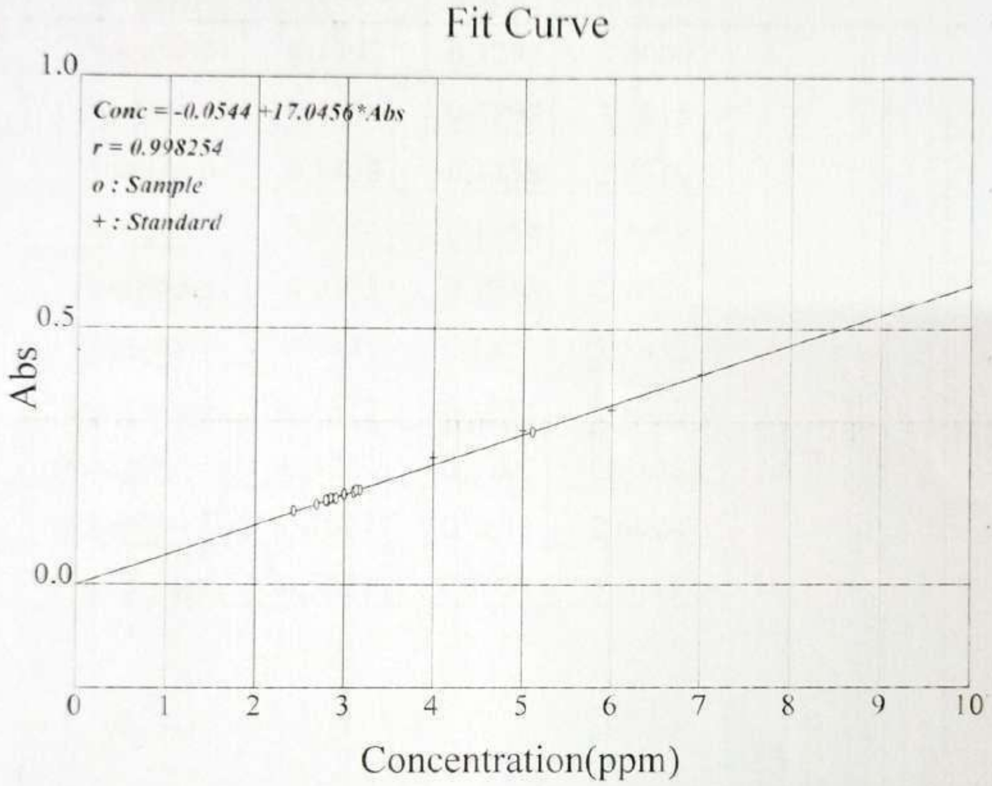
Annexure VII

Nitrate

Operator:Smith

Date & Time:February 03 14:28:01 2022

Memo:


Fit Curve

Sample name	220.0nm	Abs(eff)	ppm
Standard-1	-0.0001	-0.0001	0.0000
Standard-2	0.1755	0.1755	3.0000
Standard-3	0.2508	0.2508	4.0000
Standard-4	0.3043	0.3043	5.0000
Standard-5	0.3449	0.3449	6.0000
Standard-6	0.4104	0.4104	7.0000

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Technical Manager
Regional Chemical Laboratory,
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Annexure VII

Sample name	220.0nm	Abs(eff)	ppm
Blank	0.0001	0.0001	-0.0527
Sample-2	0.1739	0.1739	2.9094
Sample-3	0.1683	0.1683	2.8136
Sample-4	0.1792	0.1792	3.0000
Sample-5	0.1898	0.1898	3.1815
Sample-6	0.1458	0.1458	2.4310
Sample-7	0.1854	0.1854	3.1059
Sample-8	0.1735	0.1735	2.9033
Sample-9	0.1872	0.1872	3.1372
Sample-10	0.1675	0.1675	2.8015
Sample-11	0.1707	0.1707	2.8552
Sample-12	0.1611	0.1611	2.6914
QC 5 ppm	0.3031	0.3031	5.1119

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Technical Manager
Regional Chemical Laboratory,
CGWB, NER

Annexure VII

Measurement Uncertainty for Atomic Absorption Spectrophotometer

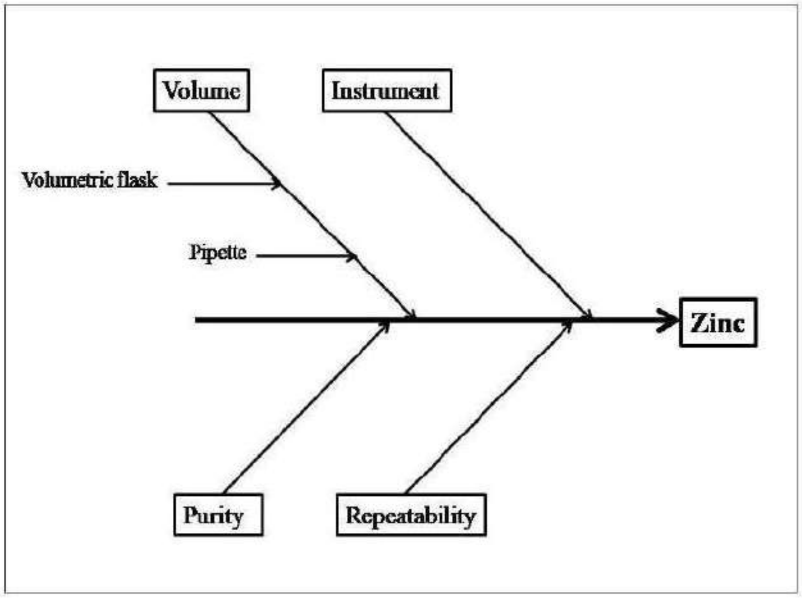
Annexure VII

	Regional Chemical Laboratory **Central Ground Water Board, North Eastern Region** **Betkuchi, Guwahati**	**Doc No.: CGWB/NER/RCL/CMU-Zn** **Issue date: 13.01.2022** **Issue No.:01** **Revision No.:00**
	Calculation of Measurement Uncertainty	**Page No. | 1 of 5**

Evaluation of Measurement Uncertainty in Determination of Zinc concentration (mg/litre) in Ground Water Sample.

PREPARED BY:	ISSUED BY:
TECHNICAL MANAGER	Radha Pyari QUALITY MANAGER

1. **Title:** Evaluation of Measurement Uncertainty in Determination of Zinc concentration (mg/litre) in Ground Water Sample
2. **Reference Method:** Direct Air-Acetlyene Flame method, APHA 23rd Ed. 2017, 3111 B
3. **Environmental Condition:** Temperature 25±5ºC
4. **Requirements:**
   a. Zinc standard solution,
   b. pipette (0.1 ml & 1 ml) and
   c. volumetric flask (25 ml).
   d. conc. HNO_3,
   e. conc. HCl
5. **Fish Bone diagram**



6. Observations & Calculations

S. No.	Observed Value (x)	Mean (M)	(x-M)	$(x\text{-}M)^2$	$\sum (x\text{-}M)^2$	(n-1)	Standard Deviation (SD)
1	3.877	3.913	-0.0362	0.0013	0.0288511	10	0.0537
2	3.913	3.913	0.0000	0.0000			
3	3.949	3.913	0.0360	0.0013			
4	3.895	3.913	-0.0180	0.0003			
5	3.842	3.913	-0.0710	0.0050			
6	3.949	3.913	0.0360	0.0013			
7	4.003	3.913	0.0900	0.0081			
8	3.967	3.913	0.0540	0.0029			
9	3.895	3.913	-0.0180	0.0003			
10	3.824	3.913	-0.0890	0.0079			
11	3.931	3.913	0.0180	0.0003			
No. of Observation Taken (n) = 11							

7. Evaluation Of Standard Uncertainty

TYPE A Uncertainty: U_1

$$Std.U_1 = \frac{\underline{Std.deviation}}{SQRT\ of\ n} \qquad U_1 = \mathbf{0.01619}$$

TYPE B Uncertainty:

i. Uncertainty due to CRM (Std. Zn Solution), U_2

$$U_E = \pm\, 0.005,\ k = 2$$

Uncertainty, $U_c = U_E/k = 0.0025$

ii. Uncertainty due to Atomic Absorption Spectrophotometer, U_3

$$\text{Uncertainty} = \pm 0.005$$

iii. Uncertainty due to volumetric flask 25 ml, U_4

$$U_E = \pm 0.002,\ \text{k} = 2$$

$$\text{Uncertainty, } U_4 = U_E/\text{k} = 0.001$$

v. Uncertainty due to pipette 1 ml, U_5

$$U_E = \pm 0.0015,\ \text{k} = 2$$

$$\text{Uncertainty, } U_5 = U_E/\text{k} = 0.00075$$

vi. Uncertainty due to pipette 0.1 ml, U_6

$$U_E = \pm\ 0.002,\ \text{k} = 2$$

$$\text{Uncertainty, } U_6 = U_E/\text{k} = 0.001$$

Uncertainty Parameter	Value	Deviation	Unit	Distribution	Distribution Factor	Standard Uncertainty
Type A						
Repeatability (U_1)	3.913					**0.01619**
Type B						
CRM, Std. Zn Solution (U_2)	990	0.0025		Rectangular	√3	0.00144
AAS (U_3)		0.005		Rectangular	√3	0.00289
Volumetric flask 25 ml (U_4)	25	0.001	ml	Triangular	√6	0.00041
Pipette 1 ml (U_5)	1	0.00075	ml	Triangular	√6	0.00031

Uncertainty Parameter	Value	Deviation	Unit	Distribution	Distribution Factor	Standard Uncertainty
Pipette 0.1 ml (U_6)	0.1	0.001	ml	Triangular	$\sqrt{6}$	0.00041

8. Results:

Combined Uncertainty (U_C)

$$(U_C) = \sqrt{(U_1)^2 + (U_2)^2 + (U_3)^2 + (U_4)^2 + (U_5)^2 + (U_6)^2}$$

$$(U_C) = 0.0165$$

Expanded Uncertainty (U_E)

(U_E) = Combined uncertainty * 2 (95% Confidence Level)= 0.033

Hence, test results would be expressed as

Zinc (mg/l) = Mean value ± Expanded uncertainty @95% Confidence Level

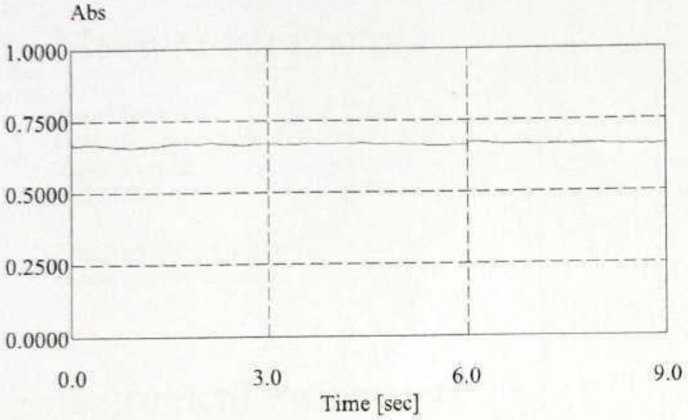
Zinc (mg/l) = 3.913 ± 0.033 @95% CL

PREPARED BY:	ISSUED BY:
TECHNICAL MANAGER	Radha Pyari QUALITY MANAGER

Annexure VII

AA500 [Zn] Signal Curve 2022/01/11 11:59:54

File Name: Zn 714-753 cal.amdx
Element Name: Zn
Sample Name:
Company:
Analyser:
Experimental Records:



Std 4 ppm Repeat 11

Conc: 3.931 ppm
SD: 0.0004
RSD: 0.0573
Sensitivity correction:
Blank:
Measurement time: 2022/01/11 11:56:57

Average: 0.667
Number of measurement: 3

No.	Abs
1.	0.667
2.	0.667
3.	0.667

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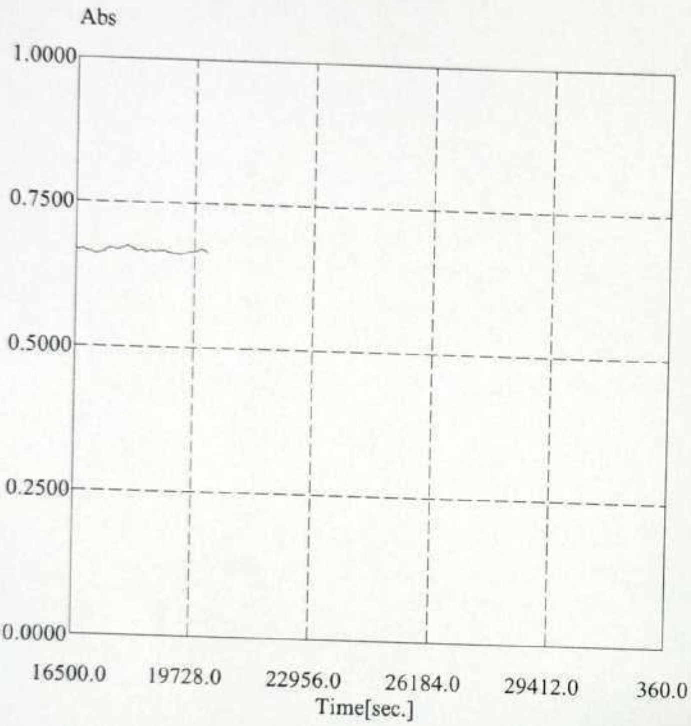
Annexure VII

AA500 [Zn] Measure Curve 2022/01/11 11:59:24

File Name: Zn 714-753 cal.amdx
Element Name: Zn
Sample Name:
Company:
Analyser:
Experimental Records:



Technical Manager/ तकनीकी प्रबंधक
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Quality Manager/ गुणवत्ता प्रबंधक
Regional Chemical Laboratory

Annexure VII

File Name:	Zn 714-753 cal.amdx
Element Name:	Zn
Sample Name:	
Company:	
Analyser:	
Experimental Records:	

Measure Parameters

Signal Process	Serial
Integration time (Sec):	3.0
Range Expand:	1.0
Filter Factor:	0.30
Repeat number of standard:	3
Repeat number of sample:	3

Instrument Parameters

Measure Method:	Flame absorption
Wavelength(nm):	213.86
Slit(nm):	0.4
High Voltage(V):	309.75
Lamp Current(mA):	3.0
Lamp Element:	Zn
Background Correction:	No

Flame mode parameters

Fuel flow rate (mL/min):	1200
Burner height (mm):	10
Burner Location (mm):	-3.0

Technical Manager/ तकनीकी प्रबंधक
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क्षेत्रीय रासायनिक प्रयोगशाला
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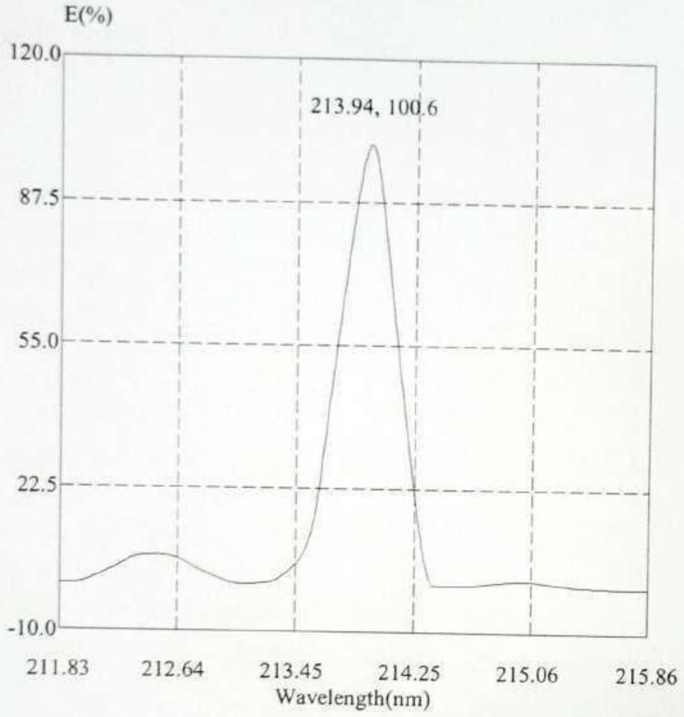
Quality Manager/ गुणवत्ता प्रबंधक
Regional Chemical Laboratory

Annexure VII

AA500 [Zn] Result of peak searching 2022/01/11 11:59:41

File Name:	Zn 714-753 cal.amdx
Element Name:	Zn
Sample Name:	
Company:	
Analyser:	
Experimental Records:	



Zn

Slit(nm):	0.4nm
Peak(nm):	213.94
Energy(%):	100.6
Lamp Current(mA):	3.0
High Voltage(V):	309.75

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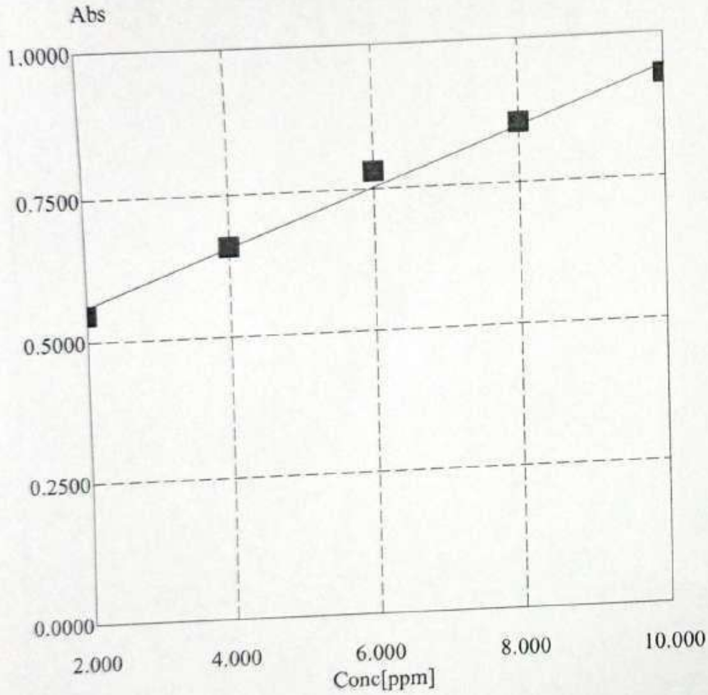
Annexure VII

AA50 [Zn]

Calibration Curve

2022/01/11 12:00:09

File Name: Zn 714-753 cal.amdx
Element Name: Zn
Sample Name:
Company:
Analyser:
Experimental Records:



Curve Equatioi1st [A]=K1[C]+K0
Equation FactcK1=0.0477, K0=0.4674,
Dependency: 0.99346

No.	Abs	Conc[ppm]
1.	0.548	2.000
2.	0.659	4.000
3.	0.780	6.000
4.	0.853	8.000
5.	0.928	10.000

Technical Manager/ तकनीकी प्रबंधक
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Quality Manager/ गुणवत्ता प्रबंधक
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Annexure VII

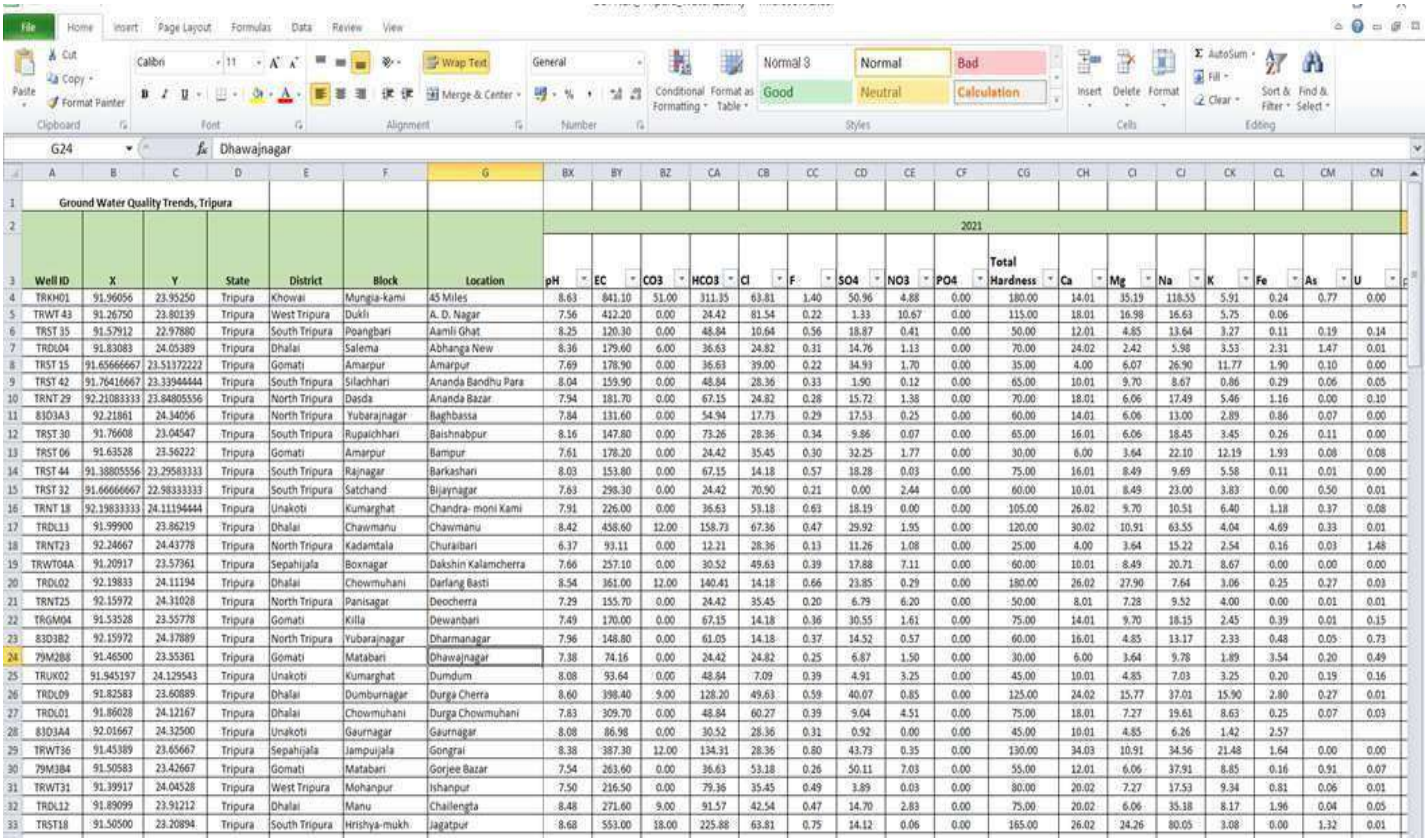
File Name: Zn 714-753 cal.amdx
Element Name: Zn
Sample Name:
Company:
Analyser:
Experimental Records:

No.	Measure	Sample	Abs	Conc [ppm]	Actual Conc [ppm]	SD	RSD [%]	Date	Time
1.	Standard	Zn Std1	0.548	2.000		0.0021	0.3818	2022/01/11	11:17:1
2.	Standard	Zn Std2	0.659	4.000		0.0043	0.6586	2022/01/11	11:17:
3.	Standard	Zn Std3	0.780	6.000		0.0026	0.3387	2022/01/11	11:18:1
4.	Standard	Zn Std4	0.853	8.000		0.0034	0.3972	2022/01/11	11:18:
5.	Standard	Zn Std5	0.928	10.000		0.0013	0.1366	2022/01/11	11:22:1
6.	Sample	Std 4 ppm Repeat 1	0.664	3.877	3.877	0.0017	0.2519	2022/01/11	11:51:
7.	Sample	Std 4 ppm Repeat 2	0.666	3.913	3.913	0.0050	0.7501	2022/01/11	11:51:
8.	Sample	Std 4 ppm Repeat 3	0.668	3.949	3.949	0.0061	0.9074	2022/01/11	11:52:
9.	Sample	Std 4 ppm Repeat 4	0.665	3.895	3.895	0.0023	0.3475	2022/01/11	11:52:
10.	Sample	Std 4 ppm Repeat 5	0.662	3.842	3.842	0.0038	0.5793	2022/01/11	11:53:
11.	Sample	Std 4 ppm Repeat 6	0.668	3.949	3.949	0.0024	0.3629	2022/01/11	11:54:1
12.	Sample	Std 4 ppm Repeat 7	0.671	4.003	4.003	0.0066	0.9793	2022/01/11	11:54:
13.	Sample	Std 4 ppm Repeat 8	0.669	3.967	3.967	0.0043	0.6357	2022/01/11	11:55:
14.	Sample	Std 4 ppm Repeat 9	0.665	3.895	3.895	0.0026	0.3869	2022/01/11	11:55:
15.	Sample	Std 4 ppm Repeat 10	0.661	3.824	3.824	0.0042	0.6336	2022/01/11	11:55:
16.	Sample	Std 4 ppm Repeat 11	0.667	3.931	3.931	0.0004	0.0573	2022/01/11	11:56:

Technical Manager/ तकनीकी प्रबंधक
Regional Chemical Laboratory
क्षेत्रीय रासायनिक प्रयोगशाला
CGWB NER, Guwahati
कें.भू.ज. ... क्षेत्र, गुवाहाटी

Quality Manager/ गुणवत्ता प्रबंधक
Regional Chemical Laboratory
क्षेत्रीय रासायनिक प्रयोगशाला
CGWB, NER, Guwahati
कें.भू.ज.बो उत्तर पूर्वी क्षेत्र, गुवाहाटी

Annexure VIII



Ground Water Quality Trends, Tripura

							2021															
Well ID	**X**	**Y**	**State**	**District**	**Block**	**Location**	**pH**	**EC**	**CO3**	**HCO3**	**Cl**	**F**	**SO4**	**NO3**	**PO4**	**Total Hardness**	**Ca**	**Mg**	**Na**	**K**	**Fe**	**As**	**U**
TRKH01	91.96056	23.95250	Tripura	Khowai	Mungia-kami	45 Miles	8.63	841.10	51.00	311.35	63.81	1.40	50.96	4.88	0.00	180.00	14.01	35.19	118.55	5.91	0.24	0.77	0.00
TRWT 43	91.26750	23.80139	Tripura	West Tripura	Dukli	A. D. Nagar	7.56	412.20	0.00	24.42	81.54	0.22	1.33	10.67	0.00	115.00	18.01	16.98	16.63	5.75	0.06		
TRST 35	91.57912	22.97880	Tripura	South Tripura	Poangbari	Aamli Ghat	8.25	120.30	0.00	48.84	10.64	0.56	18.87	0.41	0.00	50.00	12.01	4.85	13.64	3.27	0.11	0.19	0.14
TRDL04	91.83083	24.05389	Tripura	Dhalai	Salema	Abhanga New	8.36	179.60	6.00	36.63	24.82	0.31	14.76	1.13	0.00	70.00	24.02	2.42	5.98	3.53	2.31	1.47	0.01
TRST 15	91.65666667	23.51372222	Tripura	Gomati	Amarpur	Amarpur	7.69	178.90	0.00	36.63	39.00	0.22	34.93	1.70	0.00	35.00	4.00	6.07	26.90	11.77	1.90	0.10	0.00
TRST 42	91.76416667	23.33944444	Tripura	South Tripura	Silachhari	Ananda Bandhu Para	8.04	159.90	0.00	48.84	28.36	0.33	1.90	0.12	0.00	65.00	10.01	9.70	8.67	0.86	0.29	0.06	0.05
TRNT 29	92.21083333	23.84805556	Tripura	North Tripura	Dasda	Ananda Bazar	7.94	181.70	0.00	67.15	24.82	0.28	15.72	1.38	0.00	70.00	18.01	6.06	17.49	5.46	1.16	0.00	0.10
83D3A3	92.21861	24.34056	Tripura	North Tripura	Yubarajnagar	Baghbassa	7.84	131.60	0.00	54.94	17.73	0.29	17.53	0.25	0.00	60.00	14.01	6.06	13.00	2.89	0.86	0.07	0.00
TRST 30	91.76608	23.04547	Tripura	South Tripura	Rupaichhari	Baishnabpur	8.16	147.80	0.00	73.26	28.36	0.34	9.86	0.07	0.00	65.00	16.01	6.06	18.45	3.45	0.26	0.11	0.00
TRST 06	91.63528	23.56222	Tripura	Gomati	Amarpur	Bampur	7.61	178.20	0.00	24.42	35.45	0.30	32.25	1.77	0.00	30.00	6.00	3.64	22.10	12.19	1.93	0.08	0.08
TRST 44	91.38805556	23.29583333	Tripura	South Tripura	Rajnagar	Barkashari	8.03	153.80	0.00	67.15	14.18	0.57	18.28	0.03	0.00	75.00	16.01	8.49	9.69	5.58	0.11	0.01	0.00
TRST 32	91.66666667	22.98333333	Tripura	South Tripura	Satchand	Bijaynagar	7.63	298.30	0.00	24.42	70.90	0.21	0.00	2.44	0.00	60.00	10.01	8.49	23.00	3.83	0.00	0.50	0.01
TRNT 18	92.19833333	24.11194444	Tripura	Unakoti	Kumarghat	Chandra- moni Kami	7.91	226.00	0.00	36.63	53.18	0.63	18.19	0.00	0.00	105.00	26.02	9.70	10.51	6.40	1.18	0.37	0.08
TRDL13	91.99900	23.86219	Tripura	Dhalai	Chawmanu	Chawmanu	8.42	458.60	12.00	158.73	67.36	0.47	29.92	1.95	0.00	120.00	30.02	10.91	63.55	4.04	4.69	0.33	0.01
TRNT23	92.24667	24.43778	Tripura	North Tripura	Kadamtala	Churaibari	6.37	93.11	0.00	12.21	28.36	0.13	11.26	1.08	0.00	25.00	4.00	3.64	15.22	2.54	0.16	0.03	1.48
TRWT04A	91.20917	23.57361	Tripura	Sepahijala	Boxnagar	Dakshin Kalamcherra	7.66	257.10	0.00	30.52	49.63	0.39	17.88	7.11	0.00	60.00	10.01	8.49	20.71	8.67	0.00	0.00	0.00
TRDL02	92.19833	24.11194	Tripura	Dhalai	Chowmuhani	Darlang Basti	8.54	361.00	12.00	140.41	14.18	0.66	23.85	0.29	0.00	180.00	26.02	27.90	7.64	3.06	0.25	0.27	0.03
TRNT25	92.15972	24.31028	Tripura	North Tripura	Panisagar	Deocherra	7.29	155.70	0.00	24.42	35.45	0.20	6.79	6.20	0.00	50.00	8.01	7.28	9.52	4.00	0.00	0.01	0.01
TRGM04	91.53528	23.55778	Tripura	Gomati	Killa	Dewanbari	7.49	170.00	0.00	67.15	14.18	0.36	30.55	1.61	0.00	75.00	14.01	9.70	18.15	2.45	0.39	0.01	0.15
83D3B2	92.15972	24.37889	Tripura	North Tripura	Yubarajnagar	Dharmanagar	7.96	148.80	0.00	61.05	14.18	0.37	14.52	0.57	0.00	60.00	16.01	4.85	13.17	2.33	0.48	0.05	0.73
79M2B8	91.46500	23.55361	Tripura	Gomati	Matabari	Dhawajnagar	7.38	74.16	0.00	24.42	24.82	0.25	6.87	1.50	0.00	30.00	6.00	3.64	9.78	1.89	3.54	0.20	0.49
TRUK02	91.945197	24.129543	Tripura	Unakoti	Kumarghat	Dumdum	8.08	93.64	0.00	48.84	7.09	0.39	4.91	3.25	0.00	45.00	10.01	4.85	7.03	3.25	0.20	0.19	0.16
TRDL09	91.82583	23.60889	Tripura	Dhalai	Dumburnagar	Durga Cherra	8.60	398.40	9.00	128.20	49.63	0.59	40.07	0.85	0.00	125.00	24.02	15.77	37.01	15.90	2.80	0.27	0.01
TRDL01	91.86028	24.12167	Tripura	Dhalai	Chowmuhani	Durga Chowmuhani	7.83	309.70	0.00	48.84	60.27	0.39	9.04	4.51	0.00	75.00	18.01	7.27	19.61	8.63	0.25	0.07	0.03
83D3A4	92.01667	24.32500	Tripura	Unakoti	Gaurnagar	Gaurnagar	8.08	86.98	0.00	30.52	28.36	0.31	0.92	0.00	0.00	45.00	10.01	4.85	6.26	1.42	2.57		
TRWT36	91.45389	23.65667	Tripura	Sepahijala	Jampuijala	Gongrai	8.38	387.30	12.00	134.31	28.36	0.80	43.73	0.35	0.00	130.00	34.03	10.91	34.56	21.48	1.64	0.00	0.00
79M3B4	91.50583	23.42667	Tripura	Gomati	Matabari	Gorjee Bazar	7.54	263.60	0.00	36.63	53.18	0.26	50.11	7.03	0.00	55.00	12.01	6.06	37.91	8.85	0.16	0.91	0.07
TRWT31	91.39917	24.04528	Tripura	West Tripura	Mohanpur	Ishanpur	7.50	216.50	0.00	79.36	35.45	0.49	3.89	0.03	0.00	80.00	20.02	7.27	17.53	9.34	0.81	0.06	0.01
TRDL12	91.89099	23.91212	Tripura	Dhalai	Manu	Challengta	8.48	271.60	9.00	91.57	42.54	0.47	14.70	2.83	0.00	75.00	20.02	6.06	35.18	8.17	1.96	0.04	0.05
TRST18	91.50500	23.20894	Tripura	South Tripura	Hrishya-mukh	Jagatpur	8.68	553.00	18.00	225.88	63.81	0.75	14.12	0.06	0.00	165.00	26.02	24.26	80.05	3.08	0.00	1.32	0.01

Annexure-IX

Format for Water quality data sharing (Common excel format for CGWB-CPCB)

Details of Ground Water Quality Monitoring Station																	
S. No.	Agency Name	Well No	State/UT	District	Block/ Taluk	GP	Village	Station Name/ Location	Details of Location	Longitude (DD)	Latitude (DD)	Basin	Sub-Basin	Sample Source	Use	Depth of Sample	Sampling Date
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18

Physical Parameters		Chemical Parameters																
		Basic Parameters																
Temp (° C)	Turbidity (NTU	pH	EC (µS/cm at 25° C)	TDS (mg/L)	CO_3 (mg/L)	HCO_3 (mg/L)	Total Alkalinity (mg/L)	Cl (mg/L)	NO_3 (mg/L)	SO_4 (mg/L)	PO_4 (mg/L)	SiO_2 (mg/L)	F (mg/L)	TH (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37

Chemical Parameters										Biological Parameters				
Heavy Metals														
Fe (mg/L)	As (mg/L)	U (mg/L)	Mn (mg/L)	Cu (mg/L)	Pb (mg/L)	Zn (mg/L)	Ni (mg/L)	Cd (mg/L)	Cr (mg/L)	BOD (mg/L)	COD (mg/L)	TOC (mg/L)	Faecal Coliform (MPN/100ml)	Total Coliform (MPN/100ml)
38	39	40	41	42	43	44	45	46	47	48	49	50	51	52