PAKISTAN STANDARD SPECIFICATION FOR BOTTLED DRINKING WATER (3RD REV.)

FOREWORD:

1 This Pakistan Standard was adopted by the Pakistan Standards & Quality Control Authority, Standards Development Centre, on 11-09-2004, after the draft finalized by the Food Hygiene Sectional Committee had been approved by the Agriculture & Food Products Divisional Council.

2 This Pakistan Standard specification was established in 2001, first revised in 2002, and 2nd revised in 2003 keeping in view the latest developments made in the industries, the committee felt it necessary to revise.

3 All the parameters prescribed in the standard such as physical , chemical , bacteriological, organic/ inorganic constituents, pesticides / insecticide residues , are mandatory for compliance. However the testing of physical, chemical and microbiological parameters are routine tests. The testing of pesticide , insecticide residues and heavy metals / contaminants as type tests, shall be conducted / performed once a year.

4 For the purpose of deciding whether a particular requirement of this specification is complied with the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with PS:103-1991 (R) Method of Rounding Off Numerical Values. The number of significant places retained in the rounded off value, should be the same as that of the specified value in this specification.

SCOPE:

1 This specification prescribes the requirements, methods of sampling and test for bottled drinking water.

DEFINITION:

1 For the purpose of this specification the following definition shall apply :

1.1 Bottled Drinking Water : Bottled drinking water is water other than natural mineral water which is filled into hermetically sealed containers/bottles of various compositions forms, and capacities that is safe and suitable for direct consumption. Bottled drinking water is included in the category of food.

2 Supplementary Definitions:

2.1 Underground water : Water such as spring water, stream water, well water originating from subsurface aquifers.

2.2 Protected underground water is water coming from a unique environmental resource, not directly influenced by surface water (water such as streams, rivers, lakes, ponds and reservoirs) or the surface environment.

2.3 Prepared Water : Water such as demineralised water, distilled water which are not characterized by their origin (for example, tap water) and remineralized water. Other definitions for various kinds of water are prescribed in Pakistan Standard for Glossary of Terms Relating to water Quality Standard (to be prepared).

REQUIREMENTS:

1 General

1.1 SUITABILITY : The assessment of the suitability of water for human consumption shall be based on consideration of its physical, chemical and microbiological requirements and limits for toxic substances.

2 REQUIREMENTS : The bottled drinking water shall be free from all chemicals and bacteriological contaminations which are hazardous to health.

2.1 The product shall conform to the permissible levels given under the following Tables:

1. Table –I Physical characteristic for bottled drinking water.
2. Table –II chemical characteristic for bottled drinking water.
3. Table –III Chemical characteristics/microorganisms for bottled drinking water.
4. Table – IV Microbiological Limits.

Table –I Physical characteristic for bottled drinking water.

.No.	Characteristics	Max. Permissible level	Technique of the method	Methods of Test Ref. to
(1)	(2)	(3)	(4)	
1)	Colour,Hazen units	5	Colormetry – tristimulus filter method (Reference Method)	PS: ISO:7887-1994
2)	Odour	Unobjectionable	Sensory evaluation	-
3)	Taste	Unobjectionable	Sensory evaluation	-
4)	Turbidity NTU	0.5	visual method - candle turbidmeter (Reference method)	PS: ISO:7027-1999

TABLE-II CHEMICAL CHARACTERISTICS FOR BOTTLED DRINKING WATER

S.No.	Elements or compounds	Maximum admissible concentration (ppm)	Methods of test Ref.. to App.
(1)	(2)	(3)	(4)
1.	pH range	6.5 – 8.5	A.
2.	Total Dissolved Solids (TDS)	500	B.
3.	Nitrite (NO_2) as Nitrogen	1.0	C
4.	Chloride	250	D
5.	Sulphate (SO_4)	250	E
6.	Potassium (K)	10	F & G
7.	Sodium (Na)	50	F & G
8.	Magnesium (Mg)	50	H & I
9.	Calcium (Ca)	100	H & 1
10.	Chlorine (Cl)	0.1	J

TABLE – III FOR CHEMICAL CHARACTERISTICS / MICROORGANISMS FOR BOTTLED DRINKING WATER.

S.No.	Elements or compounds	Maximum admissible concentration (ppm)	Methods of Test Ref. to
(1)	(2)	(3)	(4)
1)	Antimony (Sb)	0.005	PS:ISO 11885-98
2)	Arsenic (As)	0.01	PS:ISO 11969 – 1996
3)	Barium (Ba)	0.7	ASTM VOL. 11.01 D 4382-95
4)	Borate (BO_3)	0.3	PS:ISO: 9390 – 1990
5)	Cadmium (Cd)	0.003	PS:ISO 8288 – 1986
6)	Iron as (Fe)	0.3	ASTM VOL.11.01, D 1068 –98
7)	Zinc as (Zn)	3.0	PS:ISO: 8288 –1986
8)	Chromium (Cr)	0.05	PS:ISO: 9174-1998

9)	Copper (Cu)	1.0	PS:ISO 8288 – 1986
10)	Cyanide (CN)	0.07	PS:ISO 6703 –1 – 1984
11)	Fluoride (F)	0.7	PS:ISO 10359 –1-1992
12)	Lead (Pb)	0.01	PS:ISO:8288 - 1986
13)	Manganese (Mn)	0.05	ASTM VOL. 11.01, D 858-95
14)	Mercury (Hg)	0.001	PS:ISO : 16590 – 2000
15)	Nickle (Ni)	0.02	PS:ISO 8288 – 1986
16)	Nitrate (NO_3) as Nitrogen	10.0	PS:ISO: 7890 – 1 – 1986
17)	Selemium (Se)	0.01	PS:ISO : 9965 – 1993
18)	Silver (Ag)	0.1	PS:ISO 11885 – 98
19)	Benzene	0.001	(Methods to be prepared)
20)	Benzo (a) Pyrene	0.0002	=
21)	Bromate	0.01	ASTM VOL. 11.01 D 6581
22)	Carbon tetrachloride	0.002	(Methods under preperation)
23)	Dichloromethane	0.003	=
24)	P-dichlorobenzene	0.02	=
25)	1,2 dichloroethene	0.02	=
26)	Cis-1,2 dichloroethene	0.07	=
27)	Trans-1,2 dichloroeathylene	0.1	=
28)	1,2-dichloropropane	0.005	=
29)	Ethylbenze	0.3	=
30)	Monochlorobenze	0.05	=
31)	Styrene	0.1	=

32)	Tetrachloroethylene	0.001	=
33)	Trichloroethylene	0.001	=
34)	Toluene	1.0	=
35)	1.1-1 Trichloroethane	0.03	=
36)	1.1-2.2 Tetrachloroethane	0.04	=
37)	Vinyl chloride	0.002	=
38)	Xylenes	1.0	=
39)	Alachlor	0.002	=
40)	Aldicarb	0.003	=
41)	Atrazin	0.003	=
42)	Carbofuran	0.04	=
43)	Chlordane	0.002	=
44)	1,2 dibromo-3 chloropropane	0.001	=
45)	2,4- Dichlorophenoxy acetic acid	0.07	=
46)	Heptachlor	0.0004	=
47)	Heptachlor & epoxide	0.0002	=
48)	Lindane	0.0002	=
49)	Methoxychlor	0.04	=
50)	Pentachlorophenol	0.001	=
51)	Simazine	0.004	=
52)	Aldrin/Dieldrin	0.002	=
53)	2,4, 5-TP	0.01	=
54)	Di (2-ethryloxy) adipate	0.08	=
55)	Di (2-ethylexy) Phthalate	0.006	=

56)	Total trichlorobenzenes	0.009	=
57)	Hexachlorobenzene	0.001	=
58)	Diquat	0.02	=

3 MICROBIOLOGICAL REQUIREMENTS :

The product shall conform to the limits given in Table-IV.

TABLE – IV: MICROBIOLOGICAL LIMITS

.No	Organisms	Recommended value	Methods of Test Ref. to
)	Total coliform	0/250 ml	PS:ISO-9308-2-1990* APP. K of this standard
[)	E-Coli	0/250 ml	ASTM Vol.11.02 D 5392
[I)	Feceal enterococci/ streptococci	0/250 ml	PS:ISO 7899-2-2000**/ASTM Vol.11.02, D 5916
V)	Pseudomonas aeruginosa	0/250 ml	ASTM Vol. 11.02 D 5246
')	Total viable count at 20 – 22 ^{0}C	< 100 / 1ml	Total viable count should be within 12 hrs of bottling
'I)	Total viable count at 37 ^{0}C	< 20 / 1ml	

Water quality – Detection and enumeration of Escherichia coli and coliforms bacteria part 2.

* Water Quality Detection & enumeration of intestinal enterococci part 2

HYGIENE

1 Drinking Water for the purpose of bottling shall be prepared in accordance with PS:3944-1997 for Code of Practice – General Principles of food Hygiene.

PACKAGING

1 The containers/bottles shall be hygienic suitable completely clean and shall not cause any undesirable change in taste, odour or colour or quality of the water. It can be inspected at random just prior to being filled and sealed.

2 It shall be packed in hermetically sealed containers of food grade material to prevent contamination of bottled water.

3 Filling and sealing operations of containers/bottles shall be done in an aseptic atmosphere so as to prevent any contamination.

4 Transportation. Bottled water shall be transported by any suitable means of transport to protect it from contamination.

5 Marking

In addition to the PS:1485-1994 (R) for Pakistan Standard for the Labelling of Pre-Packaged Foods, the following provisions shall apply :

(a) Name of the product – e.g. " Bottled Drinking Water
(b) Brand name or trade name if any,
(c) Net volumes in System International/Metric System,
(d) Name and address of the manufacturer,
(e) Batch number or code number
(f) Date of Expiry,
(g) Chemical composition for e.g. Sulphate, Sodium, Magnesium, Potassium, Chloride,
(h) This Pakistan Standard Number, PS Mark & Licence Number.
(i) Date of Bottling
(j) Location and name of the source.

SAMPLING

1 LOT: In any consignment all the bottles of the same size and belonging to one batch of manufacture or supply shall constitute a lot.

2 General Requirements of Sampling

2.1 Each bottle of the sample shall be marked with necessary details of sampling and the bottles for bacteriological testing shall be marked separately.

2.2 The bottles of the sample shall be stored in such a manner that there shall be no deterioration of quality of water.

2.3 The bottles for bacteriological testing shall be brought to the testing laboratory within one hour, of sampling. If this is not possible the bottles shall be stored at 10 ^{0}C or below and transported to the testing laboratory within 24 hours. In case of small units, the original packing shall be treated as sample.

3 Scale of Sample:

3.1 Samples shall be tested from each lot for ascertaining its conformity to the requirements of this specification.

3.2 The number of bottles to be selected from a lot shall be in accordance with the Table – V.

TABLE - V - SCALE OF SAMPLING

Number of Bottles in the Lot	Number of bottles to be selected
Up To 1000	15
1001 to 3000	17
3001 to 10,000	18
10001 and above	24

3.3 If the bottles are packed in cases, 10 percent of the cases subject to a minimum of five cases shall be selected from the lot and as far as possible an equal number of bottles shall be selected from each case so selected to form a sample of size given in 6.3.2.

4 Number of tests:

4.1 Each bottle selected as in 6.3.2 or 6.3.3 shall be inspected for packaging and marking requirements.

4.2 Ten bottles shall be selected from the bottles, selected as in 6.3.2 or 6.3.3 and tested individually for the microbiological limits.

4.3 A sufficient quantity of water shall be drawn from each of the remaining bottles and mixed to form a composite sample and the composite sample thus obtained shall be tested for the requirements given in 3.2 and 3.3.

CRITERIA FOR CONFORMITY:

A lot shall be declared as conforming to the requirements of this specification, if the following conditions are satisfied.

1 Each bottle inspected as in 6.4.1 satisfies the relevant requirements.

2 Each bottle when tested as in 6.4.3 satisfies the relevant requirements.

3 Composite sample when tested as in 6.4.3 satisfies the relevant requirements.

APPENDIX – A.
DETERMINATION OF pH

Measurement of pH is one of the most important and frequently basic used tests in bottled water analysis. This parameter define a logarithmic activity of hydrogen ions is an indicator of acidic or basic character of a water and is used for monitoring of bottling process, water treatment carbon dioxide measurements, and many other acid-basic equilibria.

This determination is temperature dependent (0 ^{0}C to 60 ^{0}C) and can not be applied for water samples with values of pH lower than 1 or higher than 11.

PRINCIPLE

The basic principle of pH measurement is the determination of the activity of the hydrogen ions by potentiometry using a standard hydrogen electrode (generally a glass electrode) and a reference electrode. The potential difference between these two electrodes both immersed in a same solution is a linear function of this solution pH value.

This linear relationship is described by plotting the measured potential produced in the glass electrode against the known pH of different buffers.

REAGENTS

Potassium Chloride (KCl)
Buffer solution 500 ml – pH 4.00*
Buffer solution 500 ml – pH 7.00*
Buffer solution 500 ml – pH 10.00*
Thymol, crystals
Potassium hydrogen phtalate ($KHC_8H_4O_4$)
Potassium dihydrogen phosphate (KH_2PO_4)
Sodium borate decahydrate (borax) ($Na_2B_4O_7.10H_2O$

*If these buffer solutions are not commercially available, you can prepare these standard solutions as follows at 25 ^{0}C.

- Buffer solution pH 4.00 : Dry 10.12 g of potassium hydrogen phtalate ($KHC_8H_4O_4$) at 103 ^{0}C and dissolve in 1 L distilled and degassed water.
- Buffer solution pH 7.41 : Dry 1.179 g of potassium dihydrogen phosphate (KH_2PO_4) and 4.303 g of Na_2HPO_4 between 110 and 130 ^{0}C and dissolve in 1 l distilled and degassed water.
- Buffer solution pH 9.18 : Dissolve 3.81 g of sodium borate decahydrate (borax) $Na_2B_4O_7.10H_2O$ in 1 litre distilled and degassed water.

Where preparing these buffer solutions make sure that the salts are completely dissolved and store in polyethylene bottles at room temperature after adding one thymol crystal (8 mm diameter) per 200 ml solution. In routine use, replace buffer solutions every four weeks.

APPARATUS

1 - pH meter VTW Profiline pH 197 / pH 597 reference electrode Ag/AgCl with standard combined glass electrode and integrated temperature or equivalent.
Technical data :

pH Range : 2.00 …. 16.00

Resolution : 0.01

Accuracy : 0.01 ± 1 digit at operating temperature (-10 ^{0}C ... + 55 ^{0}C)

Measuring rate : 1.2 sec

Adjust ranges : Temperature: -20 ^{0}C … 130 ^{0}C

pH calibration : Assymetry of ± 30 mV

Slope of – 50 mV/pH … - 62 mV/pH

One or two points calibration

2 A glass electrode
at 25 ^{0}C

Slope pH 4.00 … pH 7.00 :> 98 %
Zero point pH : pH 7.00 ± 0.25
Response time : < 20 sec.

3 - Electrode Stand RADIOMETER E 190

4 - Magnetic stirrer

5 - Polyethylene or Teflon beakers

PROCEDURE

1 - Instrument calibration

Follow manufacturer's instructions for putting into operation pH meter and for storage and preparation of electrodes.
Generally saturated KCl solution is used for storage of reference electrode.
Follow manufacturer's instructions for maintaining level of saturated KCl solution.

Demineralized water or buffer solution pH 4.00 or pH 7.00 are recommended for short-term storage of glass electrode. Anyway, keep electrodes wet by returning them to storage solution whenever pH meter is not in used.

Select calibration mode on your apparatus (one or two points calibration) and the two buffer solutions for pH range (4.00 to 7.41 or 7.41 to 9.18 or 4.00 to 9.18).

Remove electrode from storage solution, rinse with distilled water, blot dry with a soft paper, immerse in the first standard buffer solution (pH 4.00 for example) with stirring and start measurement. Never touch the membrane surface with fingers nor scratch the electrode. Avoid high temperature variation.

Remove electrode, rinse and dry it as described above, immerse into the second standard buffer solution (pH 9.18 for example) and start measurement.

Read displayed electrode slope and asymmetry values or zero pH and verify that these values are in the manufacturer's admissible range.

Use the third standard buffer solution with pH value generally close to pH of samples (pH 7.41 for example) to verify the calibration with a measurement.

6 - Determination

Rinse electrode with sample and establish equilibrium between electrode and sample by stirring to insure homogeneity. Stir gently to minimize carbon dioxide entrainment.

For buffered samples or those of high ionic strength, condition electrode after cleaning with sample by dipping it into sample for 1 minute. Blot dry, immerse in a fresh portion of the same sample and read pH after stabilization of displayed value.

With dilute, poorly buffered solutions, equilibrate electrode by immersing in three or four successive portions of sample. Take a fresh sample to measure.

Measure pH on fresh samples or at the opening of bottles. Avoid to work close to contaminated atmosphere (ammonia, acids, gas vapors,….).

- UNITS

pH values are expressed in pH unit at 25 ^{0}C with generally a precision of $\pm$ 0.02 and an accuracy of $\pm$ 0.05 pH unit depending on manufacturer's technical data and ionic strength of samples.

- QUALITY CONTROL

Make initial calibration of pH meter every two months.

Write down electrode slope and asymmetry values or zero pH after each buffer calibration and pH value of the buffer standard solution used for verification.

- TROUBLE SHOOTING AND MAINTENANCE

Glass electrodes can fail because of scratches, deterioration or accumulation of debris on the glass surface causing drifting or instable values. If any problem occurs, rinse with distilled or warm water with detergent or soak in pH 7.00 buffer solution overnight.

Reference electrode troubles are generally traceable to a clogged junction. Interruption of the continuous trickle of electrolyte through the junction causes increase in response time and drift in reading. Follow manufacturer's instructions for clearing the junction.

APPENDIX - B

DETERMINATION OF TOTAL DISSOLVED SOLIDS (TDS)

INSTRUMENT

Total Dissolved Solids Meter :

Conductivity / TDS probe

RANGE

mg/1	0.0 to 199.9
mg/1	0 to 1999
g/1	0.00 to 19.99

ACCURACY : (at 20 ^{0}C)

$\pm$ 1 % Full Scale (excluding probe error)

CALIBRATION

Manual singly point through trimmer (trimmer is on the right hand side)

For best results in calibrating your meter, choose a TDS solution that is closest in value to the sample to be measured.

For accurate calibration, use two beakers for each solution : the first one for rinsing the probe and the second one for calibration. In this way the contamination of the calibration solutions is minimized.

Use plastic beakers wherever possible.

Procedure for calibration :

Fill a beaker with 8 cm (3 ¼") of conductivity calibration solution.

Immerse the probe into the beaker. The level of solution must be higher than the holes on the PVC sleeve.

Turn the instrument ON by pressing the ON/OFF button and press the appropriate range of button (e.g. 1999 mg/1 button).

Tap the probe repeatedly on the bottom of the beaker and stir it to ensure that no air bubbles are trapped inside the sleeve.

When the reading stabilizes, turn the calibration trimmer until the display reads the proper conductivity value at 25 ^{0}C.

The calibration is now complete and the instrument is ready for use.

Calibration solution the TDS are 1382 mg/1 at 25 ^{0}C.

MEASUREMENT

- Switch on the instrument by pressing once the ON /OFF button.
- Press the TDS/TEMP. button to toggle between the TDS display or the temperature display in ^{0}C.
- Adjust the temperature of water sample to 25 ^{0}C.
- Dip the probe into water sample to be tested with the holes completely submerged.

  Tap and stir the probe to remove all air bubbles that may be trapped inside the PVC sleeve.
- Press the button mg/1 to take the TDS (Total dissolved solids) reading.
- After recording the TDS reading, press the ON/OFF button to switch off the instrument.

CLEANING

Wash the cell with distilled water.

STORAGE

Wash the cell with distilled water, and dry after measurements.

Put freely in air. (No need to keep it dipped on water during storage).

PRECAUTIONS

- Put freely in air. (No need to keep it dipped in water during storage).
- Do not use the meter to measure TDS of any liquid / beverage other than water.
- Do not expose the probe to temperature above 60 ^{0}C (do not dip in hot water).

BATTERY CHANGE

The battery is supplied with the instrument.
When the display shows low level..
replace with a new battery of 9 volts (size 9 V).

). PROBE MAINTENANCE

Rinse the probe with tap water after every series of measurements. If more cleaning is required remove the PVC sleeve and clean the probe with a nonabrasive detergent. When reinserting the sleeve always make sure that the four holes are towards the cable end.

After cleaning the probe recalibrate the instrument.

APPENDIX - C.

DETERMINATION OF NITRITE

SCOPE AND APPLICATION

Nitrite (NO_2) is an intermediate oxidation state of nitrogen, both in the oxidation of ammonia to nitrate (NO_3) and in the reduction of nitrate. Such oxidation may occur in wastewater treatment, water distribution systems, and natural waters. Originating from the decomposition of living materials or bacterial oxidative chain, nitrite is a contaminant or an incompleted nitrification process indicator.

PRINCIPLE

After a colour reaction where nitrite is converted into a violet-red dye molecule (magneta azo dye), measurement of nitrite concentration is based on a measure of this dye with a pronounced absorbance maximum at 525 nm.

Reaction of nitrite with sulfanilic acid forms the 4-diazobenzenesulfonic acid which subsequently condenses with N-1-naphtylethylenediamine dihydrochloride to produce the magenta azo dye. The analytical chemical grade reagent NO_2-AN is the combined mix of the sulfanilic acid and N-1-naphtylethylenediamine dihydrochloride compounds.

REAGENT

Potassium nitrite (KNO_2)

Spectroquant nitrite test containing a reagent NO_2 - AN.

APPARATUS

- Photometer with cells corresponding to specific measuring range :

0.015 - 0.65 mg/l NO_2	50 mm cell
0.1 - 3.0 mg/l NO_2	10 mm cell

- Pipette 10 ml
- Test tubes

- PROCEDURE

1 - Calibration

Follow manufacturer's instructions for putting into operation the spectrophotometer.

Preprogrammed method is generally used but you can check or correct the performance of the apparatus with a blank and a reference standard like potassium nitrite (KNO_2) as an adapted dilution of a daily prepared 100 mg/l standard solution (0.185 g/litre) kept in a brown-glass bottle filled to the brim and tightly closed.

2 - Sample measurement

Sample pH must be between 2 and 10.

Wherever possible, samples should be analysed soon after being taken.

The aliquot amounts of sample (5, 10 or 20 ml) determine the quantity of reagent NO_2 – 1AN to be added. For a 10 ml sample :

- Pipette 10 ml of the sample into a test tube.
- Add 2 blue microspoonful of reagent NO_2 – 1 AN and mix.
- Check the pH, specified range : pH 2.0 – 2.5 : If required (for mineral water for example), add dilute sodium hydroxide solution or sulfuric acid drop to adjust the pH.
- Set aside for 10 min.
- Filter turbid sample.
- Transfer the solution into a corresponding cell.
- Select method with autoselector
- Place the cell into the cell compartment

- UNITS

Nitrite concentration values are expressed in N or NO_2 mg/l with at least one decimal depending on the measuring range.

- QUALITY CONTROL

To check the measurement system (test reagents, measurement device and handling), a ready-for-use nitrite standard solution (potassium nitrite for example) can be used after diluting accordingly.

- TROUBLESHOOTING AND MAINTENANCE

Follow manufacturer's instructions for maintenance and selectivity of the kit.

Avoid measurement of samples at very different temperatures below or higher than 25 ^{0}C.

Use the same vessels clean only with distilled water without cleaning agents,

APPENDIX - D.
DETERMINATION OF CHLORIDE

- SCOPE AND FIELD OF APPLICATION

Chloride, in the form of chloride Cl^- ion is one of the major anions in water.

This method is applied for drinking water.

- PRINCIPLE

In a neutral or slighty 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.

- CHEMICALS

- a potassium chromate indicator solution : Prepare by dissolving 50 g K_2CrO_4 distilled water.
- A standard silver nitrate titrant 0.0282 M (0.0282 N) : Prepare by dissolving 4,791 g $AgNO_3$ in distilled water. Store in a brown bottle.

- APPARATUS

- Erlenmeyer flask 250 ml.
- Burette 25 ml
- Pipette 1 ml

- PROCEDURE

- Titration for a 100 ml blank.

  Use a 100 ml distilled water.

  Add 1 ml K_2CrO_4.

  Add standard $AgNO_3$ titrant to a pinkish yellow end point. Be consistent in end-point recognition.

  Note down the volume V_B (in ml) of added standard $AgNO_3$.

- Titration for a 100 ml sample (chloride $C1^-$ concentration range : 50 – 150 mg/1)

  Use a 100 ml sample in 250 ml Erlenmeyer flask.

  Add 1 ml K_2CrO_4.

  Add standard $AgNO_3$ titrant to a pinkish yellow end point. Be consistent in end-point recognition.

  Note down the volume V_A (in ml) of added standard $AgNO_3$.

- EXPRESSION OF RESULTS

$$C_{(Cl^-)}, \text{ mg/l} = (V_A - V_B \times (1000/V) \times 0.0282 \times 35.5$$

- V = ml sample
- V_A = $AgNO_3$ titrant for sample
- V_B = ml $AgNO_3$ titrant for blank
- 0.0282 = Normality of $AgNO_3$ titrant
- 35.5 = conversion factor.

APPENDIX - E.

DETERMINATION OF SULPHATE

- SCOPE AND FILED OF APPLICATION

Sulphate ions (SO_4^{2-}) is widely distributed in nature and is a major anion of bottled waters. This method is applied for drinking water.

- PRINCIPLE OF THE METHOD

Sulphate ions (SO_4^{2-}) react with barium ions (barium chloride $BaCl_2$) in hydrochloric acid (HCl) medium to form slightly soluble barium sulphate ($BaSO_4$). The resulting turbidity is determined photometrically at 525 nm.

- CHEMICALS

- A reagent SO_4-1 K with a green dose-metering cap.
- 25 test tubes with alcoholic solution of dilute hydrochloric acid solution
- 1 blank tube
- a sulphate standard solution 1 g/1
- a sodium hydroxide solution 10 %
- an hydrochloric acid solution 25 %

- APPARATUS

- Photometer with a tube compartment corresponding to specific measuring range : 20 – 240 mg/l SO_4^{2-}.
- Pipette 5 ml.

- PROCEDURE

1 - Calibration.

Follow manufacturer's instructions for putting into operation the ectrophotometer.

Preprogrammed method is generally used but you can check or correct the performance of the apparatus with a blank and a reference standard as an adopted dilution of a 1000 mg/l standard solution.

2 - Sample measurement

- Check the pH of the sample, specified range pH 2-10. If required, add dilute sodium hydroxide solution or hydrochloric acid drop by drop to adjust the pH.
- Pipette 5 ml of the sample into a reaction tube and mix.
- Add one dose of reagent SO_4-1 K using the green dose-metering cap, close tightly the tube with the screw cap.
- Shake the tube vigorously for 1 minute until the reagent is completely dissolved.
- Reaction time : 2 minutes precisely.
- Place the tube into compartment with the vertical line facing the observer and measure immediately.

- EXPRESSION OF RESULTS

Sulphate concentration values are expressed in mg/l without decimals.

/ - QUALITY CONTROL

To check the measurement system (test reagents, measurement device and handling), a ready-for-use sulphate standard solution can be used after diluting accordingly.

– TROUBLESHOOTING AND MAINTENANCE

Follow manufacturer's instructions for maintenance of the spectrophotometer and selectivity of the kit.

The barium-sulphate crystals forming partly deposit on the bottom of the tube during the reaction. It is therefore important to shake the tube contents shortly before the measurement to distribute the crystals in the solution uniformly.

Avoid measurement of samples at a temperature below 20 ^{0}C or higher than 40 ^{0}C.

The tubes must be clean. Wipe, if necessary with a clean dry cloth.

APPENDIX - F & G.

DETERMINATION OF SODIUM AND POTASSIUM IN WATER BY FLAME PHOTOMETRY

PRINCIPLE

Flame photometric determination of sodium and potassium in water.

APPARATUS

Flame photometer, with filters for sodium and potassium.

SAFETY PRECAUTIONS

All glassware must be thoroughly washed and rinsed with water to remove all traces of sodium and potassium.

The distilled water used to prepare the solutions must be free from sodium and potassium ions.

CHEMICALS

Description

Potassium standard solution ready for use (optional)
Sodium standard solution ready for use (optional)
Nitric acid, 65 % GR,
Hydrochloric acid fuming, 37 %, for analysis,
Sodium standard, 1000 mg/l. Titrisol concentrate for the preparation of standard sodium solution
Potassium standard, 1000 mg/l. Titrisol concentrate for the preparation of standard sodium and potassium solution.

SOLUTIONS

1 Sodium standard solution, 1000 mg/l

Transfer the contents of an ampoule of sodium standard solution (1000 mg/l) into a 1000 ml volumetric flask. Dilute to the mark with water. Mix well. Transfer to a decontaminated polyethylene bottle with screw cap lid.

This solution is stable for 1 year at room temperature.

Alternatively a sodium solution 1000 mg/l, ready prepared, may be used.

2 Potassium standard solution, 1000 mg/l

Transfer the contents of an ampoule of potassium standards solution (1000 mg/l) into a 1000 ml volumetric flask. Dilute to the mark with water. Mix well. Transfer to a decontaminated polyethylene bottle with screw cap lid.

This solution is stable for 1 year at room temperature.

Alternatively a sodium and potassium solution 1000 mg/l, ready prepared, may be used.

3 Mixed sodium and potassium standard solution, 50 mg/l

Just before use :

Into a 100 ml volumetric flask, pipette 5.0 ml of sodium standard solution and 5 ml potassium standard solution. Make up to the mark with water. Mix well.

4 Sodium and potassium check solution, 5 ug/ml,

Into a 50 ml volumetric flask, pipette 5.0 ml mixed standard solution. Make up to the mark with distilled water.

5 Mixed sodium & Potassium calibration solution :

Just before use :

Into a series of 50 ml volumetric flasks, pipette 0 – 0.5 – 1.0 – 2.5 – 5.0 – 7.5 – and 10.0 ml respectively of "Mixed Potassium & Sodium standards solution, 50 mg/l". Make up to the mark with distilled water. Mix well.

These solutions contain respectively 0 – 0.5 – 1.0 – 2.5 – 5.0 – 7.5 – 10.0 ug sodium and potassium / ml.

PROCEDURE

1 Sodium determination

1.1 Calibration

Select the sodium filter. Auto zero the flame photometer with the 0 calibration solution.

Aspirate the highest concentration sodium calibration solution 10 ug/ml. Set the gain control to a suitable reading. Aspirate all the calibration solutions

Aspirate each calibration solution three times. Calculate the average absorbance of each solution from the three readings. Draw or calculate the calibration line by plotting the absorbance on the x axis and the concentration of sodium in ug/ml on the y axis. Check the linearity of the calibration.

Aspirate a check solution (5.4) containing 5.0 ug/ml sodium immediately after calibration to verify the slope of the calibration curve. A result of 5.0 $\pm$ 0.1 ug/ml should be obtained; if it is not the case, then repeat the calibration.

1.2 Analysis

Aspirate the water sample in triplicate into the flame photometer. Calculate the average of the readings. Ensure that the capillary tube is about 10 mm from the bottom of the sample cup and not touching the bottom.

Analyze a sodium check solution respectively 5.0 ug/ml after every 10 product solutions. The result should be 5.0 $\pm$ 0.1 ug/ml. If not re-calibrate and re-analyze the previous 10 product solutions.

2 Potassium determination

Seclect the Potassium filter. Reset the zero reading and gain for the highest potassium calibration solution, 10 ug/ml. Continue as in paragraph 6.1.1 & 6.1.2

PERFORMANCE CHARACTERISTICS

1 Repeatability

The absolute difference between two independent test results obtained using the same method on identical test material under identical conditions in the same laboratory using the same equipment within a short interval of time should not be greater than 7 mg/100 g for sodium and 18 mg/100 g for potassium.

2 Reproducibility

The absolute difference between two single test results obtained using the same method on identical test-material in different laboratories with different operators should not be greater than 15-mg/100 g for sodium and 40-mg/100 g for potassium.

WASHING OF GLASSWARE

Wash the glassware to remove all traces of organic matter. Place the equipment requiring decontamination; volumetric flask, stoppers etc. into a polyethylene container, containing 15 litres of a mixture of nitric acid : water (1:1). Decontaminate overnight. Rinse thoroughly with water. Dry in a clean drying oven at 80 ^{0}C. Change the nitric acid solution about every three months.

PERFORMANCE CHARACTERISTICS

1 Instrument maintenance

Daily : Inspect the apparatus before use. Check the condition and cleanliness of the burner, spray chamber and nebulizer. Clean if necessary.

Weekly : Check the gas line connections for leaks with a suitable soap solution.

APPENDIX - H & I.

DETERMINATION OF CALCIUM AND MAGNESIUM

Calcium and magnesium contribute to the Total Hardness (TH) of water.

This method is applied for Drinking Waters.

PRINCIPLE OF THE METHOD

When EDTA (ethylenediaminetetra acetic acid or its salts) is added to water containing both calcium and magnesium, it combines first with the calcium. Calcium can be determined directly by titration, with EDTA, when the pH is made sufficiently high that the magnesium is largely precipitated as the hydroxide and an indicator (calcon carboxylic) is used that only combines with calcium. Magnesium is determined by calculation.

CHEMICALS

- sodium hydroxide solution, NaOH 2 mol/1 : Prepare by dissolving 8 g sodium hydroxide in 100 ml water.
- calcium standard solution 0.01 mol/1 : Prepare by adding 20 ml of standard calcium solution at 1 g/1 diluted to 50 ml distilled water.
- A standard EDTA titrant (C_{EDTA} = 0.01 mol/1) :

  Control the EDTA titrant (0.01 mol/1) with calcium standard solution 0.01 mol/1 as follows :

  Add 10 ml calcium standard solution 0.01 mol/1 in a 250 ml Erlenmeyer flask and dilute to 50 ml with distilled water.

  Titrate (according to the procedure 5) with EDTA titrant (0.01 mol/1) to determine real value of C_{EDTA} :

  $$C_{EDTA} = (0.01 \times V_1) / V_2 \text{ expressed in mol/1}$$

  V_1 = volume of standard calcium standard solution (here 10 ml)

V_2 = volume of EDTA titrant expressed in ml

- Indicator : calcon carboxylic acid ([hydroxy-2-(hydroxy-2-sulfo-4-naphtylazo-1) –1 naphtalene carboxylic]acid) ($C_{21}H_{14}N_2O\ S_{7}.2H_2O$)

  Prepare by carefully grinding and mixing together 0.2 g calcon carboxylic acid with 100 g sodium chloride.

APPARATUS

- Erlenmeyer flask 250 ml
- Burette 25 ml
- Pipette 50 ml
- Pipette 2 ml

PROCEDURE

For a 50 ml sample (calcium concentration range 40 – 120 mg/1 :

Add 50.0 ml sample (V_S) in an 250 ml erlenmeyer flask.
Add 2.0 ml NaOH solution or a volume sufficient to produce a pH of 12 to 13.
Add 0.2 g indicator / 2 mol.
Add EDTA titrant while stirring and then slowly add it to the sample at the end of titration: end-point is reached when the colour clearly becomes blue.
Check end-point by adding 1 to 2 drops of titrant in excess to make certain that no further colour change occurs.
Note down the added EDTA volume V_E (in ml).

EXPRESSION OF RESULTS

$C_{(Ca2+),}mg/1 = (1000 \times 40.08 \times V_E \times C_{EDTA})/V_S$

V_E = ml EDTA titrant for sample.

C_{EDTA} = mol/1 EDTA concentration.

V_S = ml sample.

40.08 = moler weight of calcium, in gm / mol.

DETERMINATION OF MAGNESIUM BY CALCULATION :

Concentration of magnesium C (Mg^{2+}) expressed in mg/1 is determined by calculation using values for total hardness (TH) expressed in French degree (^0F)* and calcium concentration $^C(ca^{2+})$, expressed in mg/1 as follows :

$C_{(Mg2+)}$ =[Total hardness (as meq/l) – Calcium and magnissium hardness (as meq/l)] x 12,15

= [(TH/5) – (C_{Ca2+}/20,04)] x 12,15

*For the conversion of Total Hardness (TH), in French degree (^0F) refer to conversion table that follows

			German	English	French	US
		mmol/1	^{0}DH	^{0}Clark	^{0}French	ppm
	mmol/1	1	5.61	7.02	10	100
German	^{0}DH	0.178	1	1.25	1.78	17.8
English	^{0}Clark	0.143	0.80	1	1.43	14.3
French	^{0}French	0.1	0.56	0.70	1	10
US	ppm	0.01	0.056	0.070	0.1	1

APPENDIX - J.

WATER – DETERMINATION OF ACTIVE CHLORINE AND REFERENCE VOLUMETRIC METHOD

FIELD OF APPLICATION

Chlorinated water containing from 0.02 to 0.5 mg/l active Chlorine.

PRINCIPAL

Release iodine by the reaction of active chlorine with potassium iodide; reaction of iodine with diethyl - phenylenediamine (DPD) and formation of red – violet color.

PROCEDURE

1 With the Lovibond comparator provided with Nessler device.

- In a nessler tube, introduce a DPD tablet Lovibond # 4 and 10 ml water sample.
- Once the tablet is dissolved, fill up to mark with the water sample.
- Compare the nessler tube with the test portion to a tube prepared in the same way, but with distilled water. Use the "Chlorine NDP" (NDP = DPD) disc for concentration from 0.05 to 0.5 mg/l active chlorine.

2 With the Lovibond comparator, but without the Nessler device.

- In a 40 mm cell, introduce a DPD tablet Lovibond # 4 (black package) and 5 ml water sample.
- Once the tablet is dissolved, fill up to 2- 3 mm below the rim with the water sample.
- Compare the test sample prepared in the same way, but with distilled water. Use the "Chlorine NDP" disc for concentration from 0.02 to 0.3 mg/l active chlorine.

4. REMARKS

- Although some what less sensitive (0.05 mg/l), the test method with the Nessler tube allows an easier determination than that using the Lovibond comparator alone (0.02 mg/l).

- The dissolution of tablet requires about 7 minutes. The coloration is stable during half an hour.

- If the water to be analyzed has to be diluted, check that the distilled water used for the dilution gives a negative reaction.

- Don’t expose the sample to sunlight or air, and don’t shake the flask.

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APPENDIX - K.

RESEARCH AND COUNT OF TOTAL COLIFORMS

AND THERMOTOLERANT COLIFORMS

L. O.	STEPS	PROCEDURE	CRITICAL CONTROL POINTS
1.	Sample	Non-packed samples are taken with sterile recipients	Make sure this is done in sterile zone within the heat of blow lamp.
2.	Method	Clean the recipient in modified alcohol.	Handle the sample with care so as to avoid all risk of contamination.
3.	Filteration	Filter a volume of the sample (250 ml) onto a sterile membrane. Place this on the surface of the lactosed gelose with TTC and Tergitol 7 contained in a petri dish.	Check that no air bubbles are trapped between the membrane and the gelose.
4.	Incubation	Invert the plates on a tray and put them in an incubator set at 37 ^{0}C +/- 1 ^{0}C, for 48 hours.	Do not stack more than 6 plates. Ensure correct incubation temperature.
5.	Interpretation/count	Examine the membrane after the incubation period. Yellow colonies with orange centers, some times brownish beige, some times pinkish beige, and these may or may not appear to have a metallic aspect, they can be round, convex flat, granular and very mucus, they are capable of producing gases, but some times they do not. The colonies that ferment lactose are marked by a subjacent yellow halo. - Identify the different types of suspect colonies with a letter symbol. - Count the colonies of each type.	

		Not all yellow colonies are coliforms : Other germs can simulate this aspect on TTC gelose. These can be cocci; Gram + bacilfus, Gram –ve Oxidase +ve bacillus. Isolation is than necessary for identification purposes	
5. 7.	Isolation Incubation	Sow the suspect TTC medium colonies; on EMB gelose, Incubate at 37 ^{0}C (or preferably at 30 ^{0}C if an incubator is available at this temperature) for 24 hours.	Ensure correct incubation temperature.
3.	Confirmation	Using a well-isolated colony on EMB, two mediums are inoculated simultaneously : -Kligler medium : by means of a rib on the slopping surface and a pinprick in the bwer third part of the base, incubator in an incubator at 37 ^{0}C (or preferably at 30 ^{0}C if an incubator is available at this temperature) for 18 to 24 hours. -Nutritive PCA gelose without glucose by means of a rib on the slopping surface. Incubate in an incubator at 37 ^{0}C (or preferably at 30 ^{0}C if an incubator is available at this temperature) for 18 to 24 hours.	
9.	Reading	Kligler medium : In the base :- The gelose is always fermented and induce acidity (yellow). - The fermentation of glucose can be accompanied by the production of gas (by lifting the medium or pocket of gas). - Black precipitate of Fas. PCA gelose : The fermentation of lactose will acidity the medium (yellow colouring).	
0.	Oxidase test/Gram test	The coliforms are oxidase –ve (no coluration) In case of double perform gram test. Thermotolerant coliforms : If colonies of coliforms are present at 44 ^{0}C and have been confirmed. Than transplant each colony on to a schubbert medium.	

1.	Incubation	Incubate at 44 ^{0}C +/- 0.5 ^{0}C for 24 to 48 hours. All colonies which produce gas are thermotolerant coliforms.	
2.	E.Coli	Add a few drops of Kovacs reagent to the schubbert medium tube, if a red coloration appears on the surface : there is production of indole.	

Reagents and / or mediums

Mediums

Lactose-gelose with
TTC and tergitol 7
TTC at 0.05 %
Tergitol 7 at 0.2 %
EMB lactose agar
PCA without glucose
Kligler medium
Oxidase sticks
Schubbert medium
Kovacs reagent