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MEASUREMENT UNCERTAINTY IN HARDNESS OF WATER TESTING

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Abstract:

Hardness of water refers to the excess quantity of calcium and magnesium ions present in the water sample. As water is consumed in the form of drinking water continuous intake of such water may lead to health related issues like kidney stone, diabetes, cardiovascular diseases and sometimes cancer. It is necessary to identify the amount of calcium and magnesium in drinking water in order to make it useful for drinking purpose. Water hardness testing is carried out in various NABL accredited testing laboratories to improve the quality of water. This paper deals with the measurement of uncertainty in water hardness testing methods. The performance of total hardness of water testing is affected by various factors like purity of CaCo3, molecular weight etc.

Keywords: Quality of water, Hardness, Purity, CaCo3, Molecular Weight, Uncertainty of measurement.

1. INTRODUCTION

Water is essential for life as hydration is one of the basic requirements of human body. Not just that it is also very important for food preparation, sanitation and number of such uses. Drinking water is consumed by the body in one or the other forms and hence it is required to supply the safe drinking water in sufficient quantity in order to protect human health. Due to lack of natural water resources and shortage of clean water, now a day's potable water is obtained from saline water, rainwater harvesting etc. but this water is not much safe to consume. Hard water is defined as the water containing more amount of calcium and magnesium than the prescribed limit and higher concentration of mineral which is dangerous to health.

There is huge concern about the quality of drinking water as it is directly affects the human health and indirectly the environmental quality. Hence the water quality testing is done by laboratories authorized and approved by the government agencies. Uttam Saha (2013) et. al. in their study listed the types of water quality tests like bacteriological test for detection of bacteria, mineral test for detection of quantities of minerals like calcium, magnesium, copper, zinc a high concentration of thee mineral cause water hardness and organic chemical test for detection of pesticides, radiological impurities.

Various researchers have conducted experiments on determination of water hardness. Yuguo Zhuo (2012) et al in the study, mentioned hardness as a key factor in deciding the quality of water. Total hardness in drinking water sample was obtained by newly introduced micro titration method and conventional titration method separately and results were compared. The results of micro titration were more accurate and reliable. The study resulted in considerable reduction in the use of chemical reagents used in the titration method that can reduce pollution and protects environment, and meets the requirements of green chemistry.

Chen-Chang Chang (1998) etal, developed a method for checking water quality along with deriving calcium hardness and M alkalinity also designed and patented a multiuse and low-cost automatic water quality monitoring apparatus which can be used in cooling towers, Swimming pools, and boilers etc.

P. Ramya (2015) et al estimated of hardness of ground water samples by using EDTA tritrimetric method. In all 120 samples of ground water samples were collected from a town and two villages. After EDTA tritrimetrictest it was observed that 39 samples were moderately hard, 76 samples were hard water and 5 samples were very hard water.

1.1. What is Uncertainty of Measurement?

The measurement process has achieved huge importance worldwide as measurement provides the information about the unknown quantity known as measurand. Measurement is a process of comparison between the unknown quantity and a universally accepted standard. Every Measurand has a true value but it cannot be completely determined. As far as accuracy in measurement is concerned, hundred percent perfection in results is not possible and that small amount of imperfection or doubt present in the result is known as uncertainty. Actually it is different from errors in measurements as by applying corrections to the results error can be removed but when the value of error is unknown it is termed as uncertainty. Various internal as and external factors such as operator, instruments, method or procedure and environmental conditions are responsible for the presence of uncertainty in measurements

Uncertainty of measurement has been defined differently by different researchers such as uncertainty of measurement is a doubt about the result of any measurement. Even in the case of careful measurements - there can be a margin of doubt [7][8][9]. The uncertainty of measurement defined as "a non-negative parameter characterizing the dispersion of quantity values being attributed to a measurand, based on the information used" [9][10].

1.2. Need of Evaluation of Uncertainty of Measurement

It is mandatory for all the accredited calibration laboratories to describe the uncertainty associated with the results reported on calibration certificate. Evaluation of uncertainty is suggested for the test laboratories to know and understand which factors of the test procedure have the considerable effects on the results so that such aspects may be closely controlled or monitored [10].

1.3. Importance of Evaluation of Uncertainty [13][14][10]

1. To compute the quality of a measured value
2. To equate different measured values, e.g., from different measuring systems
3. To link a measured value with theory
4. To match a measured value with a tolerance.

1.4. Sources of Errors and Uncertainties

Many things may affect the quality of measurement. As it is not possible to make actual measurements under perfect conditions, errors and uncertainties may occur from the sources like [7][10]:

1. The measuring instrument - instruments can produce incorrect results due to bias, ageing, wear, or drift, poor readability etc.
2. The quantity being measured – unstable nature of the measurand.
3. The measurement process - The measurement procedure may be difficult to follow.
4. Operator's skill – Sometimes quality of the measurements depend on the operator's skill.
5. Sampling issues - The homogeneity of the sample must be maintained while choosing samples from a production line.
6. The environment – environmental conditions like temperature, air pressure, humidity and many can affect the measuring instrument or measurand.

2. MEASUREMENT PROCEDURE:

Water hardness determination study was carried out by the laboratory by using EDTA titration method. This study basically deals with the uncertainty determination in the test procedure. The eight factors identified are listed below that are considered as the sources of uncertainty. Factor are categorized on the basis of their responsibility for the Type A and Type B uncertainty. The uncertainty estimation is carried out using analytical approach and uncertainty contribution for each factor is obtained separately.

3. IDENTIFICATION OF UNCERTAINTY SOURCES

The uncertainty in measurement of total hardness in water testing is represented in Figure 1

3.1. Sources of uncertainty

1. Purity of CaCo3
2. Mass
3. Volume
4. Repeatability

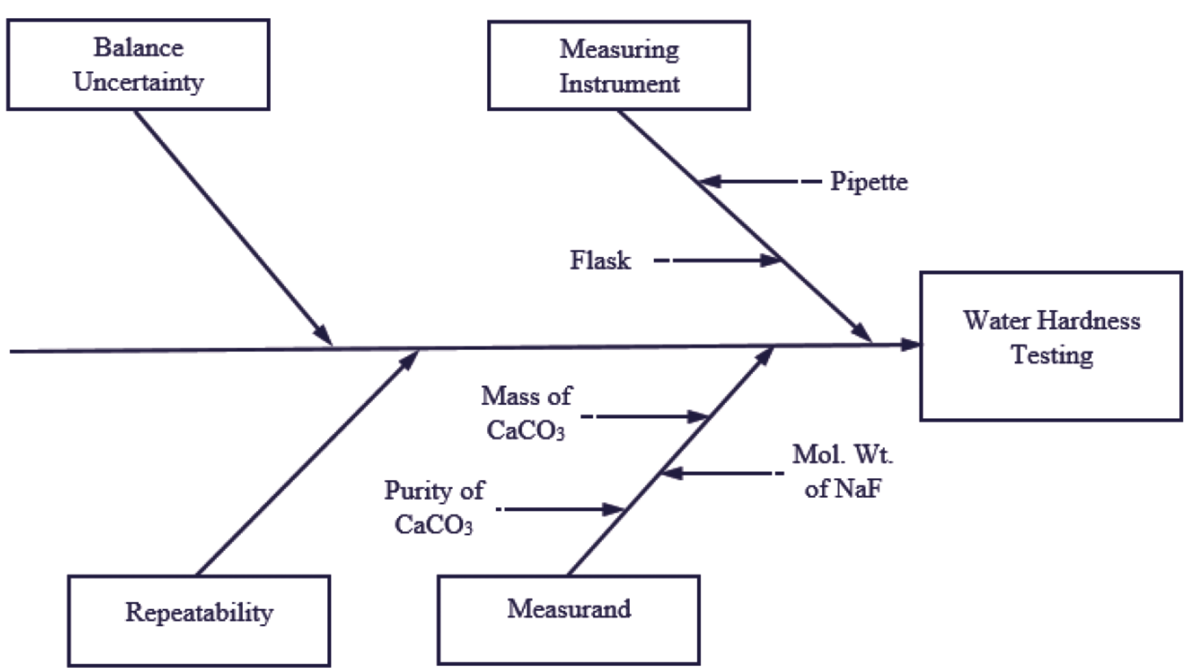

Figure 1: Sources of Uncertainty in Water Hardness Testing Method

3.2. Calculation:

$$\text{Hardness (EDTA) as mg } CaCO_3/L = \frac{A \times B \times 1000}{\text{mL of sample}}$$

Where,
A = mL titration for sample &
B = mg $CaCO_3$ equivalent to 1.00 mL EDTA titrant

4. QUANTIFICATION OF UNCERTAINTY COMPONENTS

4.1. Type A Uncertainty

The following test results were obtained for the sample Type A Uncertainty given in Table 1.

Table 1. Test Results

Sr.No.	Xi	$(X-X_0)$	$(X-X_0)^2$
1	132.000	1.7143	2.93878
2	130.000	-0.2857	0.08163
3	130.000	-0.2857	0.08163
4	130.000	-0.2857	0.08163
5	130.000	-0.2857	0.08163
6	130.000	-0.2857	0.08163
7	130.000	-0.2857	0.08163

Average = X_0 =130.286

$\sum (X-X_0)^2$= 3.42857

$$\text{Standard Deviation = STD = } S = \sqrt{\frac{\sum_{i=1}^{i=N} (x - x_0)^2}{N - 1}}$$

= **0.7559**

Standard deviation is 0.7559 assuming a normal distribution.

Standard uncertainty for type A is Ui= Standard Deviation / √N = 0.7559 / √7 = **0.2857**

4.2. Type B Uncertainty

4.2.1. Purity: The purity of CaCo3 is 0.1g. The distribution factor is rectangular. Hence the standard uncertainty of CaCo3 is **U CaCo3.** By default rectangular distribution is assumed

Uncertainty value is U (P1) = 0.1 / √3 = **0.0577350**

4.2.2. Mass: The uncertainty associated with the mass of the calcium carbonate is estimated using the data from calibration certificate and manufacturer's recommendations on uncertainty estimations as 0.126 mg

4.2.3. Volume (V) of 0.50 ml flask: The volume has three major influences **calibration, repeatability and temperature effects.**

4.2.3.1. Calibration: A volume of standard flask of 50 ±0.5 ml measured at temperature 27°C.

Standard uncertainty is calculated assuming a triangular distribution.

Uc= Standard uncertainty = 0.5 /Sqrt (6) = **0.20412**

4.2.3.2. Repeatability: The uncertainty due to variations in filling flask can be estimated from a Repeatability experiment on a typical example of standard flask used. A series of six filled flasks gave standard deviations of 0.074 ml. This can be directly used as standard uncertainty.

4.2.3.3. Temperature: The flask has been calibrated at a temperature of 27°C, whereas the laboratory temperature varies between the limits of ± 5°C (25+5).The uncertainty from this effect can be calculated from the estimates of the temperature range and co-efficient of volume expansion. The volume expansion of water is considerably larger than that of glass flask. So only the former needs to be considered. The coefficient of volume expansion is 2.1 $*10^{-4}$°C-1which leads to a volume variation of± $(50*5*2.1*10^{-4})$ = 0.0525 ml for the std flask.

The standard uncertainty is calculated using the assumption of rectangular distribution for the temperature variation = 0.0525 / Sqrt (3) = 0.0303 ml for the flask.

The three contributions are combined to get the standard uncertainty Uv of the volume:

$U(v_3)$ = √ (0.20412+0.074+0.0303) = ± 0.2192

4.2.4. Volume (V)1 ml pipette: The volume has three major influences **calibration, repeatability and temperature effects.**

4.2.4.1. Calibration: A volume of pipette 1±0.006 ml measured at temperature 27°C.

Standard uncertainty is calculated assuming a triangular distribution.

Uc= Standard uncertainty = 0.006 /Sqrt (6) = **0.00245**

4.2.4.2. Repeatability: The uncertainty due to variations in filling pipette can be estimated from a repeatability experiment on a typical example of standard flask used. A series of six filled pipette gave standard deviations of 0.055 ml. This can be directly used as standard uncertainty.

4.2.4.3. Temperature: The flask has been calibrated at a temperature of 27°C, whereas the laboratory temperature varies between the limits of ± 5°C (25+5).The uncertainty from this effect can be calculated from the estimates of the temperature range and co-efficient of volume expansion. The volume expansion of water is considerably larger than that of glass flask. So only the former needs to be considered. The coefficient of volume expansion is 2.1 $*10^{-4}$°C-1 which leads to a volume variation of ± $(1*5*2.1*10^{-4})$ = 0.0011 ml for the std pipette.

The standard uncertainty is calculated using the assumption of rectangular distribution for the temperature variation = 0.0011 / Sqrt(3) = **0.0006** ml for the pipette.

The three contributions are combined to get the standard uncertainty Uv of the volume:

$U(v_4) = \sqrt{(0.00245)^2+(0.055)^2+(0.0006)^2}$ = ± **0.05505**

4.2.5. Volume (V) : 2 ml pipette: The pipette has three major influences **calibration, repeatability and temperature effects.**

4.2.5.1. Calibration: A volume of standard flask of 2±0.01 ml measured at temperature 27°C.

Standard uncertainty is calculated assuming a triangular distribution.

Uc= Standard uncertainty = 0.01 /Sqrt(6) = **0.00408**

4.2.5.2. Repeatability: The uncertainty due to variations in filling pipette can be estimated from a Repeatability experiment on a typical example of standard pipette used. A series of six filled pipette gave standard deviations of 0.055 ml. This can be directly used as standard uncertainty.

4.2.5.3. Temperature: The pipette has been calibrated at a temperature of 27°C, whereas the laboratory temperature varies between the limits of ± 5°C (25+5).The uncertainty from this effect can be calculated from the estimates of the temperature range and co-efficient of volume expansion. The volume expansion of water is considerably larger than that of glass flask. So only the former needs to be considered. The coefficient of volume expansion is $2.1 * 10^{-4}$°C-1 which leads to a volume variation of ± $(2*5*2.1*10^{-4})$ = 0.021 ml for the std pipette.

The standard uncertainty is calculated using the assumption of rectangular distribution for the temperature variation = 0.021 / Sqrt(3) = 0.0012 ml for the pipette.

The three contributions are combined to get the standard uncertainty Uv of the volume:

$U(v_5) = \sqrt{(0.00408)^2+(0.055)^2+(0.0012)^2}$ = ± 0.05516

4.3. Weighing Balance

4.3.1. Calibration uncertainty: The certificate of the balance quotes ±0.126 mg for the uncertainty.

The coverage factor is given as K=2 from calibration certificate.

So weight balance uncertainty = 0.126/2 = 0.063 mg

This contribution has to counted twice, once for the tare and once for the gross weight, because each is an independent observation and the linearity effects are not calculated.

So, $U_6 = SQRT(0.063^2+0.063^2)$ = 0.0890955 mg

4.4. Molecular Weight of CaCo3: As this expression is a sum independent values, the standard uncertainty $U(M_{NaF})$ is asimple square root of the sum of the squares of the contributions.

Molecular weight of CaCo3 (Molar mass M CaCo3): The uncertainty of the molar mass of Calcium Carbonate is calculated from IUPAC uncertainties of atomic mass in Table 2.

Table 2. Uncertainty of the Molar Mass

Element	Atomic weight	Quoted uncertainlyu(e)	Standard Uncertaintyu(e) / √3
Ca	40.078	0.00004	0.000023
C	12.0107	±0.00008	0.000046
O_3	15.9994	±0.00003	0.000017

M_{NaF} = **52.089**

$\mathbf{U_{(M)}} = \sqrt{(0.000023)^2+(0.000046)^2+(0.000017)^2}$

$\mathbf{U_{(M)}}$ = **0.0005**

Table 3- Values and Uncertainties

Description	**No. of Times**	**Value X**	**u(X)**	**RSD =U(X)*Sensitivity/X**
Repeatability	1	1	**0.285700**	**0.285700**
Purity of Caco3	1	1	**0.05774**	**0.05774**
Mass of Caco3	1	1	**0.126000**	**0.126000**
Volume of flask 50 ml	1	50	**0.219200**	**0.004384**
Volume of pipette 1 in ml	7	1	**0.055050**	**0.05505**
Volume of pipette 2 in ml	1	2	**0.055160**	**0.027580**
Balance uncertainty	1	41.988	**0.089090**	**0.002122**
Mol. Weight of NaF	1	1	**0.00050**	**0.00050**

Calculating the combined uncertainty
$= \sqrt{(0.2857)^2+(0.05774)^2+(0.126)^2+(0.004384)^2+(0.055050)^2+(0.027580)^2+(0.002122)^2+(0.00050)^2}$
= 0.3234

Expanded Uncertainty: Expanded uncertainty is obtained by multiplying the combined standard uncertainty with a coverage factor K of 1.96

U = Uc x K
= 0.3234x 1.96
± 0.63405 at Confidence level of 95 %

Expanded Uncertainty U = 130.286 ± 0.63405 mg/l

The uncertainty contribution and budget is given in Figure 2 and Table 3.

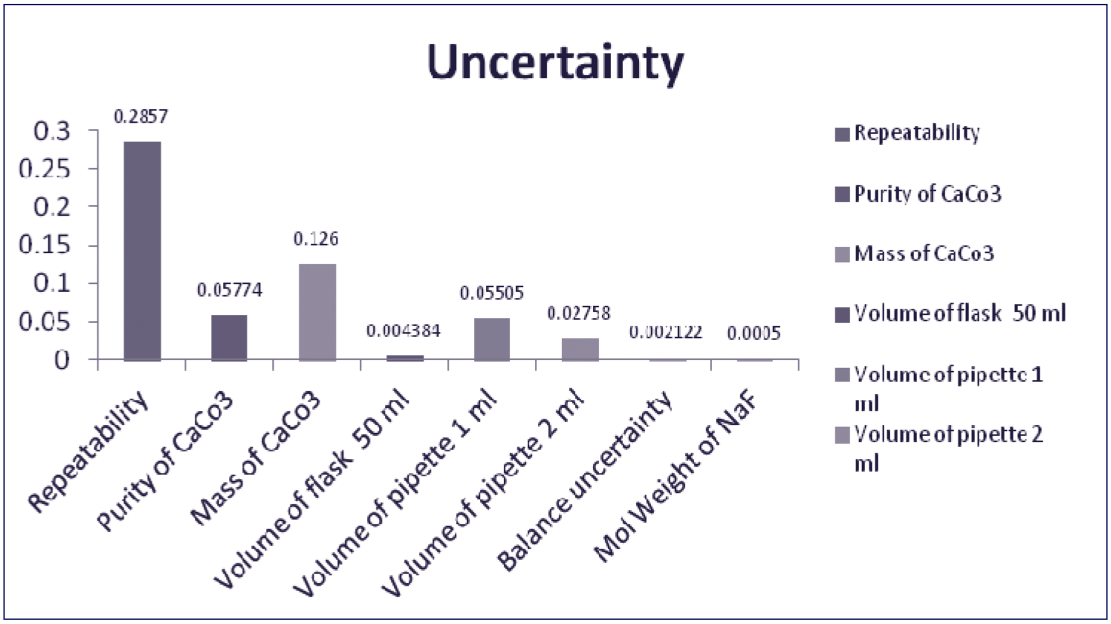

Figure 2. Values and Uncertainties

Suggestions- Total uncertainty is very less which represents the accuracy of the result is quite good. In calculation for uncertainty of measurement in total hardness of water, eight factors affect the performance of system. We can again minimize the uncertainty value though recalibration of 50 ml volumetric flask. Mass of CaCo3 is also more sensitive factor in total uncertainty.

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