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Calcium Hardness Analysis of Water Samples Using EDXRF Technique

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Abstract: Calcium hardness of water samples has been determined using a method based upon the Energy Dispersive X-ray fluorescence (EDXRF) technique for elemental analysis. The minimum detection limit for Ca has been found in the range 0.1-100ppm. The experimental approach and analytical method for calcium studies seem satisfactory for the purpose and can be utilized for similar investigations.

Keywords: Calcium; Water; Water Hardness; Energy Dispersive X-Ray Fluorescence

1. INTRODUCTION

An ecosystem comprises a community of living (biotic) organisms in association with the non living (abiotic) components of their environment, all interacting as a system. The health of an ecosystem is well described from the constitution of its non living components and water is one of the most important abiotic constituents of the human environment. The major desirable uses of water are water supply (domestic and industrial), recreation (swimming, boating), fishing (commercial and sport), irrigation, navigation, power production etc. Each use has its own requirements for the composition and purity of water and to ensure quality control, each body of water under use needs analysis on a regular basis. Therefore, it is vital to obtain accurate qualitative and quantitative information on the distribution of essential and potentially toxic elements in the water bodies.

Several factors need consideration while selecting an analytical method to be used for water quality monitoring such as rapidness of analysis,

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reliability, precision and accuracy (better than 10%), high selectivity and low cost. Generally, the most popular methods used for this purpose at present are atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). The need for exhaustive sample preparation for AAS and ICP-AES has led to increasing interest towards X-ray fluorescence in environmental investigations [1]. X-ray fluorescence (XRF) is non-destructive method. It has multi-element capability, ease of operation, high speed and can be applied to any kind of environmental sample [2, 3].

In the present work, water samples were analyzed for calcium amounts employing the EDXRF set-up in the laboratory [4]. The water is a good solvent; it dissolves minerals with which it comes in contact. Calcium in the form of Ca^{2+} ion is one of major inorganic minerals found in water. While evaluating quality of water, Ca^{2+} amount plays a pivotal role from health as well as economic use viewpoint. As waterborne minerals are in ionic form and are easily absorbed by the gastrointestinal tract, therefore, water is an important source of Ca^{2+} mineral uptake [5, 6]. Moreover, calcium accounts for the major hardness of water and hard water can be a nuisance within the home during laundering, bathing, dish washing, etc. Hence, from health viewpoint and for economic use of water, quantification of hardness of water (in terms of calcium) can be effectual. The details of the experiment, measurements and results have been given in the following sections.

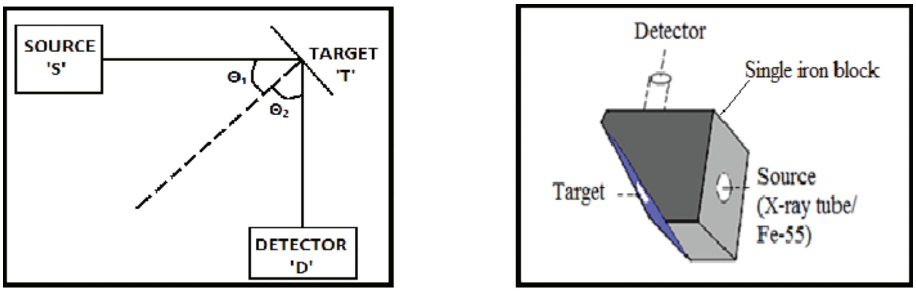
2. EXPERIMENT AND MEASUREMENTS

To use the existing EDXRF set-up for calcium determinations in different water samples, the sensitivity of the set-up was established for calcium X-rays in the samples. For this, standard solutions of 1mM $CaCO_3$, 0.01M $CaCO_3$, 0.1M$CaCO_3$, 0.5M $CaCO_3$ and 1M $CaCO_3$ were prepared and irradiated in thin polythene bags using low power X-ray tube operated at different anode voltages and filament currents in a 90° single reflection geometrical set-up (figures 1a & 1b).

The spectra were recorded with Amptek X-123 spectrometer comprising Si-PIN detector having 0.5mil Be window and of dimensions $6mm^2/500\mu m$ with resolution of 145eV at 5.959keV. The figure 2 shows the spectra of the five solutions at 6kV/0.2mA tube conditions.

The minimum detection limits (MDL) for Ca K X-rays were calculated from the obtained spectra using the formulation [7]:

$$\mathrm{MDL}=\frac{3\mathrm{C_i}}{\left(\mathrm{I_p}-I_b\right)}\sqrt{\frac{I_b}{T_b}} \qquad (1)$$



(a)

(b)

Figure 1: **(a)** Ray diagram for 90° single reflection geometry set-up. **(b)** Single reflection geometry for photon irradiations from single iron block. Distances in the diagram are not according to the scale. (*Size of collimation between; X-ray tube window and target = 0.8cm, target and detector = 1.0cm, Distance between; X-ray tube window and target = 3.5cm, target and detector =0.5cm*).

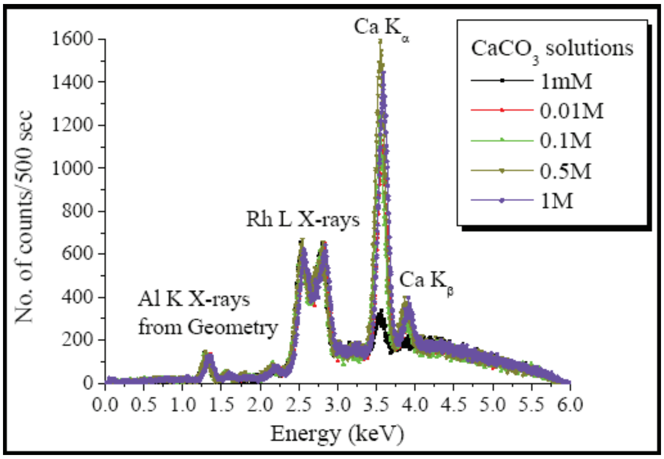


Figure 2: Spectra of 1mM/0.01M/0.1M/0.5M/1M $CaCO_3$ solutions at 6kV/0.2mA in single reflection geometry set-up.

where,

C_i, concentration of analyte i
I_p, peak intensity
I_b, background intensity
T_b, time of background measurement

Table 1: Minimum Detection Limit (MDL) for Ca K X-rays at different anode voltages and filament currents.

$CaCO_3$ Solution	X-ray line analyzed	Voltage (kV)	Current (mA)	MDL (ppm)
1mM	K_α	6/7	0.2	0.28/0.21
0.01M	K_α	6/7	0.2	0.57/0.45
		6	0.1/0.15/0.2/0.25/0.3	0.77/0.72/0.57/0.55/0.53
0.1M	K_α	6/7	0.2	9/6
0.5M	K_α	6/7	0.2	38/23
1M	K_α	6/7	0.2	53/32

The MDL evaluated for Ca K X-rays in water samples has been tabulated in table 1 and is found to be in the range 0.1-100μg/L in water, thereby, establishing the appreciable sensitivity of the set-up for calcium determinations in water samples.

For the present experiment, nine different water samples; (i) aqua guard water (ii) bathing soap mix water (iii) distilled water (iv) pond water (v) rain water (vi) detergent mix water (vii) mixture of oil & water (viii) tap water (ix) dish bar mix water were taken.

The different water samples in equal amounts in thin polythene bags were, in turn, mounted on sample holders and irradiated with photons from low power X-ray tube with operating voltage 6kV/0.2mA just above the K-edge energy of calcium in single reflection geometrical set-up [4]. The fluorescent X-rays were recorded with Amptek X-123 spectrometer. To account for scattering of incident photons from the sample targets, a spectrum with blank polythene bag was recorded at the same tube conditions and subtracted from each of the sample spectrum. A typical net background subtracted spectrum for aqua guard water sample has been shown in figure 3 with appreciable calcium.

The method employed for calcium quantification is the well established method in the laboratory [8]. It just requires selective excitation of characteristic X-rays of analyte *x* in the sample *S* and its two references where one of the references is the analyte itself or its known compound *X* with *n* atoms of *x* and the second reference material *Sp* is obtained by mixing known fraction δ' of first reference in the sample. The analyte concentration δ is evaluated simply from the known fraction of the first reference material δ' added to the sample material for second reference and *x* X-ray counts; $N_x^S(i_x)$, $N_x^X(i_x)$ and $N_x^{Sp}(i_x)$ from sample *S* and two reference materials *X* and *Sp*; using relation:

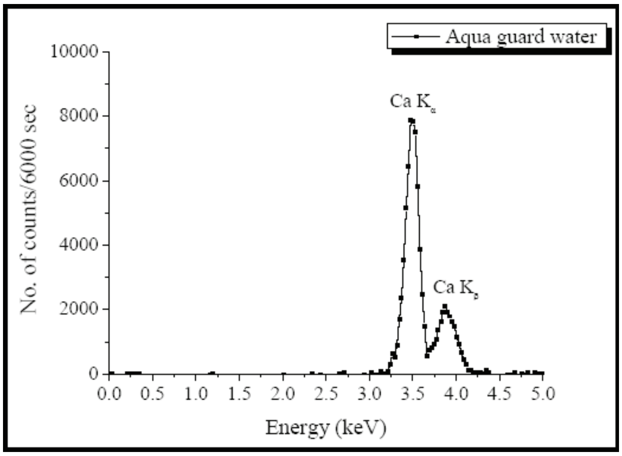


Figure 3: Background subtracted net spectrum of aqua guard water at 6kV/0.2mA.

$$\delta = \frac{nM_x}{M_X}\delta' \frac{\left[\dfrac{N_x^X(i_x)}{N_x^{Sp}(i_x)} - 1\right]}{\left\{\left[\dfrac{N_x^X(i_x)}{N_x^S(i_x)}\right] - \left[\dfrac{N_x^X(i_x)}{N_x^{Sp}(i_x)}\right]\right\}} \tag{2}$$

where, M_x is atomic weight of analyte x; M_X is molecular weight of analyte compound X, i_x is incident energy for selective excitation of x.

For calcium determination in water samples, the first reference was 1M $CaCO_3$ solution and second reference was mixture of water and first reference in known ratios. The two references were irradiated, in turn, in the same set-up and under same tube conditions. The counts under the x photo peaks were recorded for sufficient time to obtain the counting statistics <1%. The spectrum for first reference i.e. 1M $CaCO_3$ solution is shown in figure 4.

The fractional amounts of calcium in water samples were evaluated with formulation (2) and the obtained amounts are listed in table 2. The reported errors in the determined amounts are <7%.

3. RESULTS AND DISCUSSION

The reproducibility of the set-up was checked with five sets of 'S' and 'Sp' samples of pond water irradiated at the same tube conditions. The %age variance ~6 (table 3) was found, well within the error limits, thereby, establishing the reproducibility of the measurements.

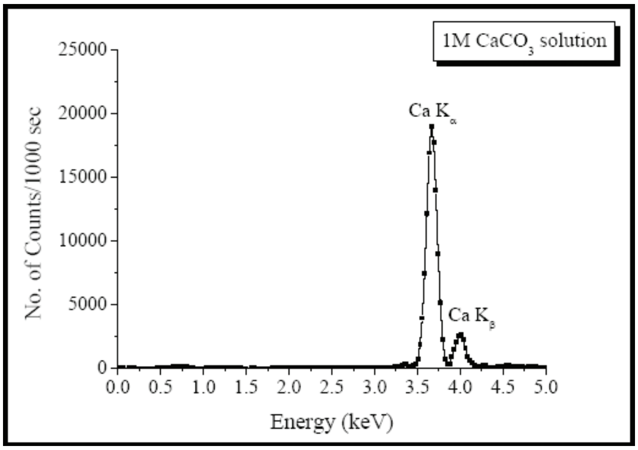


Figure 4: Background subtracted net spectrum of 1M $CaCO_3$ at 6kV/0.2mA.

The calcium amounts, thus determined, were used to classify hardness of various water samples. The amounts were compared with the values quoted by Skipton and Dvorak [9]. The inferences drawn from table 2 are as follows:

(1) The distilled and rain waters are the most soft forms of water.
(2) The tap water is found slightly hard.
(3) The hardness of tap water decreases when fed to an aqua guard because it involves the softening process in which the water is passed through a medium of sulfonated polystyrene beads which are super saturated with sodium. The ion exchange takes place replacing calcium ions with sodium when water passes through the medium, thus, making it softer.
(4) The outcomes predict that softness of tap water enhances further with addition of soaps and detergents. Soaps and detergents contain sequestering ingredients (e.g sodium tripolyphosphate, tetrasodium pyrophosphate) which act as softening agents.
(5) The presence of oil in water doesn’t affect its hardness as it is immiscible in water.
(6) Water collected from a pond is found hard thereby ruling out its use in activities within the home.

Hence, for economical use of water in household activities; tap, aqua guard, distilled and rain waters are suitable except the pond water.

Apart from this, from health viewpoint, calcium-rich mineral water offers effective alternative to calcium supplementation from milk and dairy products because of comparable or possibly even better bioavailability of calcium [10] which is found clinically relevant for patients with osteoporosis

Table 2: Determined calcium contents in water samples.

S.No.	Water Sample	Ca content (mg/L)
1	Aqua guard water	13.45±0.94
2	Dettol soap water	14.18±0.99
3	Distilled water	0.00±0
4	Pond water	58.97±4.13
5	Rain water	0.14±0.01
6	Surf Excel water	13.87±0.97
7	Surf+Oil+Tap water	15.29±1.07
8	Tap water	22.54±1.58
9	Vim soap water	13.73±0.96

Table 3: Determined calcium contents in five sets of pond water samples.

Pond water set no.	Ca content (mg/L)
1	54.023±3.80
2	57.813±4.04
3	55.086±3.86
4	58.008±4.06
5	54.931±3.84
%age Variance w.r.t mean	5.89

as it affects the absorption and efficacy of the bisphosphonate group of drugs used in osteoporosis treatment [11] and is potentially effective in controlling cardiovascular causes [12].

Further, the amount of calcium in water reflects the toxicity of water as the solubility of potentially toxic metal ions is poor in hard water [13]. Hence, it appears that the pond water being rich in calcium can be less toxic.

In a nutshell, if both toxicity and calcium bioavailability factors are concerned, then it can be found that the tap water is much suitable for drinking (provided no other impurities and harmful bacteria are there) as compared to the distilled and aqua guard water. This holds the old concept that tap water after boiling is good for drinking as boiling only kills the harmful bacteria without softening the water.

4. CONCLUSIONS

The calcium variation in different samples follows the general trend so it can be said the current EDXRF method is suitable for liquid analysis. The present EDXRF method is less laborious as compared to the pre-concentration techniques employed for liquid analysis which increase the time required for analysis and may also involve risks of contamination [3]. Moreover, the methodology adopted has the advantage that it can also account for compensation of matrix effects [14] which disturb the linearity between the concentration of an element and its intensity. So, it can be concluded that the approach followed can be efficiently exploited for similar studies in liquids. Moreover, present findings predict the tap water after boiling most suitable for drinking as compared to the distilled and aqua guard waters as it provides calcium bioavailability to intakers free from harmful bacteria.

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REFERENCES

[1] X. Hou, and B.T. Jones, Microchemical Journal **66**, 115 (2000). http://dx.doi.org/10.1016/S0026-265X(00)00058-8

[2] F.L. Melquiades, and C.R. Appoloni, Journal of Radioanalytical and Nuclear Chemistry **262** (2), 533 (2004). http://dx.doi.org/10.1023/B:JRNC.0000046792.52385.b2

[3] E. Margui, R. Van Grieken, C. Fontas, M. Hidalgo, and I. Queralt, Applied Spectroscopy Reviews **45**, 179 (2010). http://dx.doi.org/10.1080/05704920903584198

[4] S. Gupta, K. Deep, L. Jain, M. A. Ansari, V. K. Mittal, and R. Mittal, Applied Radiation and Isotopes **68**, 1922 (2010). http://dx.doi.org/10.1016/j.apradiso.2010.05.001

[5] R.S. Gibson, P.S. Vanderkooy, C.E. McLennan, and N.M. Mercer, Archives of Environmental Health **42**, 165 (1987). http://dx.doi.org/10.1080/00039896.1987.9935816

[6] R.P. Heany, and M.S. Dowell, Osteoporosis International **4**, 323 (1994). http://dx.doi.org/10.1007/BF01622191

[7] R.M. Rousseau, The Rigaku Journal **18**, 33 (2001).

[8] R. Mittal, K.L. Allawadhi, and B.S. Sood, X-Ray Spectrometry **16**, 37 (1987). http://dx.doi.org/10.1002/xrs.1300160109

[9] S.O. Skipton, and B.I. Dvorak, NebGuide G1274, (2009).

[10] H. Bohmer, H. Muller, and K.L. Resch, Osteoporosis International **11**, 938 (2000). http://dx.doi.org/10.1007/s001980070032

[11] S. Morr, E. Cuartas, B. Alwattar, and J. M. Lane, Hospital for Special Surgery Journal **2**, 130 (2006).

[12] S. Marque, H. Jacqmin-Gadda, J.F. Dartigues, and D. Commenges, European Journal of Epidemiology **18**(4), 305 (2003). http://dx.doi.org/10.1023/A:1023618728056

[13] U. Borgmann, Y. Couillard, P. Doyle, and D.G. Dixon, Environmental Toxicology and Chemistry **24** (3), 641 (2005). http://dx.doi.org/10.1897/04-177R.1

[14] M. Bansal, K. Deep, and R. Mittal, Applied Radiation and Isotopes **70**, 2525 (2012). http://dx.doi.org/10.1016/j.apradiso.2012.07.011