Determination of Potassium and Magnesium in the Glass Sample by Neutron Activation Technique

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Abstract- **Elemental analysis of potassium and magnesium in the glass sample with reference to IAEA standard has been carried out simultaneously by using neutron activation and off-line gamma ray spectrometric technique. The amount of potassium and magnesium in the glass sample was also obtained from the composition of glass sample given by the supplier and compared with the experimental value of the present work. It was found that the experimental value for magnesium is in good agreement with the theoretical value. However, in the case of potassium the experimental value is around ten times higher than the theoretical value. Reason for this discrepancy has been investigated.**

Keywords- Neutron Activation Analysis; off Line Gamma-Ray Spectrometry; Float Glass Sample; Potassium and Magnesium Estimation; IAEA Reference Standard

I. INTRODUCTION

The main constituent of glass is SiO_2 and oxides of other elements like Na, K, Mg, Ca, Al, Li, B and so on. Based on the percentage of these elements, glasses are categorizes in different types. As for example boron silicate glass has the composition of 60% SiO_2, 20% B_2O_3, 5% Na_2O, 5% Li_2O, 2% K_2O. Pyrex glass has the compositions of 80.6% SiO_2, 13% B_2O_3, 4% Na_2O, 2.3% Al_2O_3 and 0.1% other trace element oxide. Similarly, lead glass has the composition of 62.9% SiO_2, 13.6% B_2O_3, 2.6% Al_2O_3, 10.3% MgO, 2.1% ZrO_2 and 8.5% PbO. Different constituents of glasses of different types are important from the point of their applications in various fields. As for example Pyrex glass is used in chemical environment in chemistry laboratory, lead glass in radioactive fields and float glass for Resistive Plate Chambers (RPCs) to be deployed in 50 kilo ton Indian Neutrino Observatory (INO) detectors [1]. RPCs are parallel glass plates gas detectors, which record signals of passage of charged particle through the active gas medium. Thus it is important to estimate the different elements in a glass sample in quantitative way. Various destructive methods such as gravimetric method [2, 3], flame spectrometry [4-6], and x-ray microanalysis [7, 8] are used to estimate the composition of glass. In both gravimetric and flame

spectrometry method, glass has to be dissolved and then chemical separation is carried out. In gravimetric method the element of interest to be estimated has to be brought into its oxide, carbonate or in other compound form for its estimation. In flame spectrometric method also the element of interest in particular alkali earth metals has to be separated for its analysis. Thus the above two methods are destructive and are time-consuming. In x-ray micro analysis, the element to be taken for x-ray analysis is compared with a standard for its estimation. On the other hand, non-destructive method such as neutron activation analysis has been used by various authors [9-11] for the estimation of different elements of glass samples such as Si, Na, K, Al, Mg and Ca etc. Similarly, other non-destructive technique such as photon activation analysis [12] was also used for the estimation of multi-elements in glass sample. The neutron and photon activation techniques are not only non-destructive but also less time-consuming. Among these two techniques, neutron activation analysis is used by Penov et.al [11] for the estimation of various elements in samples other than glass like rock and pottery. In the present work, we have determined the potassium and magnesium in the float glass sample using neutron activation and off-line gamma ray spectrometric technique.

II. EXPERIMENTAL METHOD

Glass sample of about 49.42 mg and IAEA standard sample of 44.96 mg having sizes of about 6 mm^2 area and 3 mm thick were separately sealed in two alkathene bags. Additionally they were sealed together in an alkathene bag and mounted into an irradiation capsule. The sealed sample was irradiated for one minute at a neutron flux of 5×10^{13} n cm^{-2} s^{-1} using pneumatic carrier facility of the heavy water moderated natural uranium fueled reactor DHRUVA [13]. Separate irradiations were done for different samples. After irradiation the samples were opened and the alkathene covers were cut opened to take out the samples. Then the irradiated glass sample and IAEA standard were mounted separately on two different Perpex plates and taken for gamma-ray spectrometry. The direct gamma-ray counting of the irradiated samples were done using energy and efficiency calibrated 120 cm^3 HPGe

detector coupled to a PC based 4096 channel analyzer. The resolution of the detector system was 2.0 keV at 1332.0 keV of [60]Co. The energy and efficiency calibration of the detector system was done by counting the γ-ray energies of standard [152]Eu source keeping the same geometry, where the summation error was negligible. This was checked by comparing the efficiency obtained from γ-ray counting of standards such as [241]Am (59.54 keV), [133]Ba (80.997, 276.4, 302.9, 356.02 & 383.82 keV), [137]Cs (661.66 keV), [54]Mn (834.55 keV), [60]Co (1173.23 & 1332.5 keV). The efficiency of the HPGe detector used was 25% at 1332.5 keV relative to 3" diameter x 3" length NaI(Tl) detector. The uncertainty in the efficiency was 2-3%. The gamma-ray counting was done in live time mode and the dead time of the counting was kept less than 10% by placing the sample at a suitable distance from the detector to avoid pile up effect. Both the irradiated glass sample and standard are counted alternatively for 300 sec in the beginning for [27]Mg. Then long counting of few hours for the glass sample and standard were also done alternatively for [42]K. Several sets of counting for both sample and standard were done. A typical γ-ray spectrum of the irradiated glass sample and IAEA standard from short and long counting are shown in Fig. 1 and Fig. 2, respectively. In Fig. 1 the gamma-ray energy of 1014.4 keV for [27]Mg is clearly seen. On the other hand, in the gamma ray spectrum (Fig 2) of the long counting sample, the gamma-ray of [27]Mg is absent but 1524.7 keV gamma lines of [42]K are clearly visible.
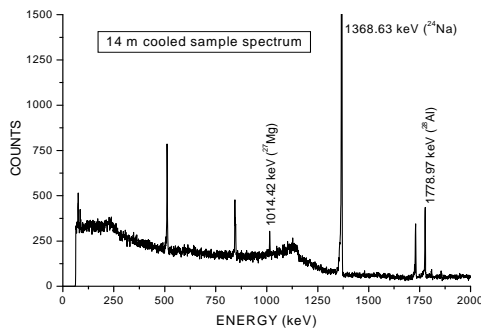

Fig. 1 Gamma ray spectrum of irradiated glass sample showing the γ-lines of [24]Na, [27]Mg and [28]Al
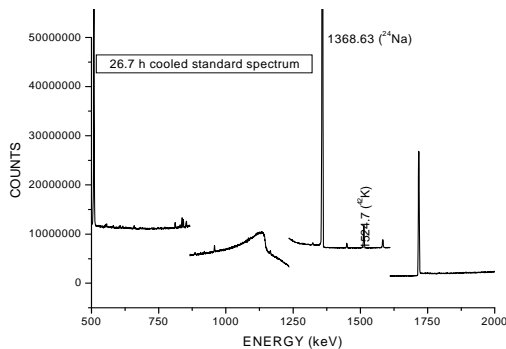

Fig. 2 Gamma ray spectrum of irradiated IAEA standard showing the γ-lines of [24]Na and [42]K

III. CALCULATION AND RESULTS

The photo peak areas of different gamma-rays of reaction products of interest of nuclide such as [42]K and [27]Mg were calculated by subtracting the linear Compton background from their total net peak areas. The number of detected gamma-rays (A_{obs}) under the photo peak of individual nuclide is related to the (n, γ) reaction cross-section (σ_R) as [14].

$$A_{obs}(CL/LT) = n\sigma_R \varphi I_\gamma \varepsilon\, b(1-e^{-\lambda t})\, e^{-\lambda T}(1-e^{-\lambda CL})/\lambda \qquad (1)$$

where n is the number of target atoms with isotopic abundance b and φ is the neutron flux. The measurands t and T are the irradiation time and cooling time, whereas CL and LT are the real time and live time respectively, "λ" is the decay constant of the isotope of interest and I_γ is the abundance or branching intensity of the chosen γ-rays of the reaction products. The γ-rays energies and nuclear spectroscopic data such as half-lives and branching intensity of the reaction products are taken from reference [15, 16], which are shown in Table 1.

TABLE I NUCLEAR SPECTROSCOPIC DATA FROM REFS. [15, 16]

Nuclides	Isotopic Abundance (%)	(n, γ) Product of Nuclide	Half-Life	γ-ray Energy (keV)	γ-ray Abundance (%)
[41]K	6.71	[42]K	12.36 h	1524.7	18.3
[26]Mg	11.01	[27]Mg	9.458 m	1014.4	28.0

The detector efficiency "ε" for the γ-ray energy at a fixed geometry was calculated as follows

$$Ln\varepsilon = \sum C_n\, lnE \qquad (2)$$

where C_n represents the fitting parameters and E is the γ-ray energies for [152]Eu standard source used in the present work.

The numbers of detected γ-rays under the photo-peak of nuclide of the irradiated sample (A_{sample}) and the IAEA standard (A_{std}) are related as:

$$\frac{A_{sample}}{A_{std}} = \frac{n_{sample}\sigma_R\, \varphi I_\gamma \varepsilon b(1-e^{-\lambda t})e^{-\lambda T(sample)}(1-e^{-\lambda CL(sample)})/\lambda}{n_{std}\sigma_R\, \varphi I_\gamma \varepsilon b(1-e^{-\lambda t})e^{-\lambda T(std)}(1-e^{-\lambda CL(std)})/\lambda}$$

$$= \frac{n_{sample}\, e^{-\lambda T(sample)}(1-e^{-\lambda CL(sample)})}{n_{std}\, e^{-\lambda T(std)}(1-e^{-\lambda CL(std)})}$$

$$n_{sample}$$

$$= \frac{n_{std} A_{sample} e^{\lambda T(sample)}(1-e^{-\lambda CL(std)})}{A_{std}\, e^{\lambda T(std)}(1-e^{-\lambda CL(sample)})} \qquad (3)$$

where n_{sample} and n_{std} are the amount of element in the sample and IAEA standard. The n_{std} for 44.96 mg of IAEA standard sample was obtained by using the Eq. (4)

n_{std} = Conc. of the element in IAEA standard x Wt. of the standard (4)

The concentration of the element in the IAEA standard sample is shown in Table 2.

TABLE II ENVIRONMENTAL REFERENCE MATERIALS MEASURED FOR TRACE ELEMENT, WHICH WAS SORTED BY MANUFACTURER CODE (THE CONCENTRATIONS ARE GIVEN IN MG PER ONE KG OF STANDARD.)

MEASURED	CONC mg/kg
K	87400
Mg	27000

After knowing the value of n_{std}, the amount (n_{sample}) of particular element (K and Mg) in the sample per 100 g of glass were determined using Eq. (3) and are given in the second column of Table 3.

TABLE III COMPARISON OF EXPERIMENTAL VALUE OF K AND MG WITH THE THEORETICAL VALUE

Element	Experimental (g in 100g of Glass)	Manufacturer Specification (g in 100g of Glass)
K	0.40119±0.03086	0.02604
Mg	2.473±0.241	2.283

The amount of K and Mg in the float glass sample was also calculated using manufacturer specification given in molar percentages and standard molar to weight conversion factor (Table 4). The value of K and Mg calculated from manufacturer specification using above technique is given in third column of the Table 3 for comparison.

TABLE IV FLOAT GLASS AND TYPICAL CONTAINER GLASS COMPOSITION, MOL% AND CONVERSION FACTORS

	Float Glass	Typical Container Glass	Mol%	Wt%
K_2O	0.02	0.19	0.32	0.50
MgO	5.64	0.30	1.49	1.00

IV. RESULT AND DISCUSSION

The amount of Mg and K per gram of sample obtained experimentally in the present work based on neutron activation and off-line gamma-ray spectrometric technique are given in the second column of Table 3. The uncertainties shown in the measured value are the precision from two determinations. The overall uncertainty represents contribution from random and systematic errors. The random error in the observed activity is due to counting statistics and is estimated to be 5-10% which can be determined by accumulating the data for an optimum time period that depends on the half line of nuclide of interest. On the other hand the systematic errors are due to uncertainties' in the irradiation time (~2%), the detection efficiency calibration (~3%), the half life of nuclides of interest and the γ-ray abundance (~1%), which are the largest variation in the Literatures [15, 16]. The overall systematic error is about 4%. An upper limit of 6.5-11% has been carried out for the amount of K and Mg in the glass sample based on 5-10% random error and 4% systematic error.

The values of K and Mg in the glass sample were also calculated from manufacturer specification given in molar percentages and standard molar to weight conversion factor (Table 4). The calculated value based on manufacturer specification for Mg and K is given third column of Table 3 for comparison. It can be seen from Table 3 that the experimental value for Mg is in good agreement with the calculated value based on manufacturer specification, which shows the correctness of the present approach. However, in the case of K, the experimental value is fifteen times higher than the calculated value based on manufacturer specification. This discrepancy may be due to the inaccurate estimates of K in the glass by manufacturer. This is most probably, the estimates given by manufacturer is based on chemical analysis, which is not so accurate. However, the present method of neutron activation is very accurate for determining the trace levels of quantity of different isotopes of elements present in the glass samples.

During the irradiation, radioactive ^{42}K is usually formed from the following reactions [11] as shown in Table 5.

TABLE V PRODUCTION ROUTES OF ^{42}K FROM DIFFERENT REACTIONS CHANNELS

a (%)	Reactions	$E_{th}(MeV)$	$\sigma(mb)$
6.71	$^{41}K(n, \gamma)^{42}K$	-	1460
0.647	$^{42}Ca(n, p)^{42}K$	2.81	230
100	$^{45}Sc(n, \alpha)^{42}K$	0.41	75

Similarly, in the case of Mg the radioactive nuclide ^{27}Mg is usually formed from the reactions as shown in Table 6.

TABLE VI PRODUCTION ROUTES OF ^{27}MG FROM DIFFERENT REACTIONS CHANNELS

a%	Reactions	$E_{th}(MeV)$	$\sigma (mb)$
100	$^{26}Mg(n, \gamma)^{27}Mg$	-	38
100	$^{27}Al(n, p)^{27}Mg$	1.896	110
3.1	$^{30}Si(n, \alpha)^{27}Mg$	4.0	120

From the above reactions, it can be seen that ^{42}K can form from ^{42}Ca (n, p) reaction besides ^{41}K (n, γ) reaction. However, from these reactions it can be inferred that the formation probability of ^{42}K from the ^{42}Ca (n, p) reaction is insignificant due to higher reaction threshold value. On the other hand, the contribution of ^{42}K from ^{45}Sc (n, α) reaction is not possible

due to the absence of Sc in the float glass sample. Thus the lower evaluated value of K may be due to the incorrect specification of 0.02 mol% of K_2O quoted for float glass compared to the value of 0.19% for typical container glass. Thus the estimation of different elements based on the activation and off-line gamma-ray spectrometric technique will help glass industry to classify the glass composition accurately. In particular estimation of K in float glass is important as the glass is used in RPC detector [1]. In this ^{40}K isotope can contribute to the background radiation.

V. CONCLUSION

1. In the present work, the amount Mg and K per 100 gram of glass sample was estimated using neutron activation and off-line gamma-ray spectrometric technique.

2. The experimentally determined value for Mg per 100 gram of glass sample from present work is in agreement with the value calculated based on the quoted data of composition, which shows the correctness of the present approach. However, in the case of K the experimental value per 100 gram of glass sample is about 15 times higher than the estimated value based on the quoted data of composition.

3. The estimation of different elements in glass sample by neutron activation and off-line gamma-ray spectrometric technique will help glass industry to classify the glass and their composition accurately.

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