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Study on Photon Activation Analysis of Carbon in Glasses for Fiber Amplifiers by Using the Flow Method for the Rapid Separation of ^{11}C

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We have studied nuclear interference from a matrix produced by (γ, n) , $(\gamma, 2n)$, (γ, p) and (n, γ) reactions and a flow method for ^{11}C separation in order to develop an approach for the photon activation analysis of carbon in InF_3 -based fluoride, chalcogenide and tellurite glasses for fiber amplifiers. We found that seventeen radionuclides are produced from these glasses and chemical separation is necessary to determine carbon. For the flow method, which involves the fusion of an irradiated sample with an oxidizer, the conversion of ^{11}C into $^{11}\text{CO}_2$ and the absorption of ^{11}C in ethanolamine solution, we used a mixture of Pb_3O_4 and B_2O_3 as the oxidizer. We also found that the reaction between $^{19}\text{F}(\gamma, n)$ and $^{23}\text{Na}(\gamma, \alpha n)$ in the ethanolamine solution produced ^{18}F contamination with fluoride and chalcogenide glasses and that this flow method can only be applied to tellurite glasses. We confirmed that the chemical yield of the flow method was close to 100 % when determining carbon in standard steel samples by using lithium carbonate as a standard sample. We determined that the carbon concentrations in two kinds of tellurite glass were 8 to 13 and 21 to 28 ppm, respectively.

§ 1. Introduction

Rare-earth element-doped fluoride, chalcogenide and tellurite glasses are expected to be important materials as host glasses for fiber lasers and optical fiber amplifiers [1,2]. It is important to determine the trace amounts of light elements such as carbon and oxygen in these glasses because impurities affect their optical properties.

Charged particle activation analysis (CPAA) is one of the most sensitive, precise and accurate methods for analyzing light elements such as boron, carbon, nitrogen, and oxygen and we have used this technique to determine the light elements in highly pure materials such as rare metals and semiconductor crystals [3-5]. We have also determined the oxygen concentration in Pr^{3+} -doped InF_3 -based fluoride and Ga-Na-S (GNS) glasses by charged particle activation analysis using the $^{18}\text{O}(\text{p}, \text{n})$ ^{18}F reaction. As a result, we found that the oxygen concentration in fluoride glasses is reduced when chemically produced strontium fluoride is used as a material. Moreover, GNS glass produced in a conventional process contained about 0.1% - 0.2% of oxygen, whereas the oxygen content decreased to 0.04% - 0.08% when we added magnesium to the glass melt as a deoxidizer and this oxygen was related to the optical properties [6].

However, CPAA has a disadvantage in that it requires standardization to correct the difference in stopping power between test and standard samples for accurate determination.

By contrast, it is well-known that carbon, nitrogen, and fluorine can be determined by photon activation analysis (PAA) and that correction, such as the standardization needed for CPAA, is unnecessary with PAA. Therefore, we believe PAA to be useful for the determination of carbon.

However, we recently proposed a flow method for the rapid separation of ^{11}C produced by such nuclear reactions as $^{12}\text{C}(\gamma, n)^{11}\text{C}$, $^{12}\text{C}(^3\text{He}, \alpha)^{11}\text{C}$, $^{10}\text{B}(\text{d}, n)^{11}\text{C}$ [7]. With this technique an irradiated sample is heated by an oxidizer in an O_2 gas flow and ^{11}C in the sample is oxidized into CO_2 and carried to an absorption column by the O_2 gas flow. In the column, $^{11}\text{CO}_2$ is adsorbed in a 750 % ethanolamine solution supplied at a rate of 3 cc/min and transferred to the detection part. Then, the radioactivity of ^{11}C in the solution is measured in the form of a radiochromatogram with a coincidence counting system. However, it is difficult to determine chemical yields for ^{11}C with the proposed method and this flow method has not been used to determine carbon by activation analysis.

This paper describes an analytical method for determining carbon in InF_3 -based fluoride, chalcogenide and tellurite glasses by using the $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction and the flow method for the chemical separation of ^{11}C . First, we studied the nuclear interference from the matrix elements. Then, we investigated the chemical separation of ^{11}C using the flow method and we attempted to determine the chemical yield in the separation by using standard steel samples. Finally, we determined the carbon in these glasses by a comparison method using lithium carbonate as a standard sample. We compared the results with results estimated by using radiochromatograms obtained from glass and steel samples.

§ 2. Experimental Procedure

2.1 Reagents

We used InF_3 - GaF_3 - PbF_2 - BaF_2 - SrF_2 - ZnF_2 - LaF_3 - YF_3 - LiF - NaF glass [InF_3 -based glass], Ga - Na - S glass [GNS glass] and a glass prepared by using highly pure TeO_2 [tellurite glass] as analytical samples. We doped these glasses with 1000 ppm of praseodymium. We fabricated the InF_3 -based glasses in the same way as described in refs. [6, 8, 9] and prepared the GNS glasses by a melt-quenching method. We fabricated tellurite glasses in the same way as described in ref.[10]. We also analyzed a standard steel sample (JSS1201-1, certified value of 5 ppm) in this experiment to determine chemical yields. We used a mixture of Pb_3O_4 and B_2O_3 as an oxidizer for fusion and oxidation.

We used lithium carbonate as a standard sample and Cu film $5\text{ mm} \times 5\text{ mm}$ in size and $30\text{ }\mu\text{m}$ thick as a flux monitor.

2.2 Irradiation

The samples and Cu flux monitors were wrapped in aluminum foil ($8\text{ }\mu\text{m}$ thick). Bremsstrahlung irradiation was undertaken with the linear electron accelerator of Tohoku University at less than 30 MeV for 20 min at $100\text{ }\mu\text{A}$. A graphite block was placed between a converter and the samples, and the samples were cooled in a water bath during irradiation to avoid heating the sample.

To remove contamination from the surface of the irradiated samples, we etched the InF_3 -based fluoride with 0.4 M $\text{ZrOCl} \cdot 8\text{H}_2\text{O}$ solution and the other glasses with diluted hydrofluoric acid. We

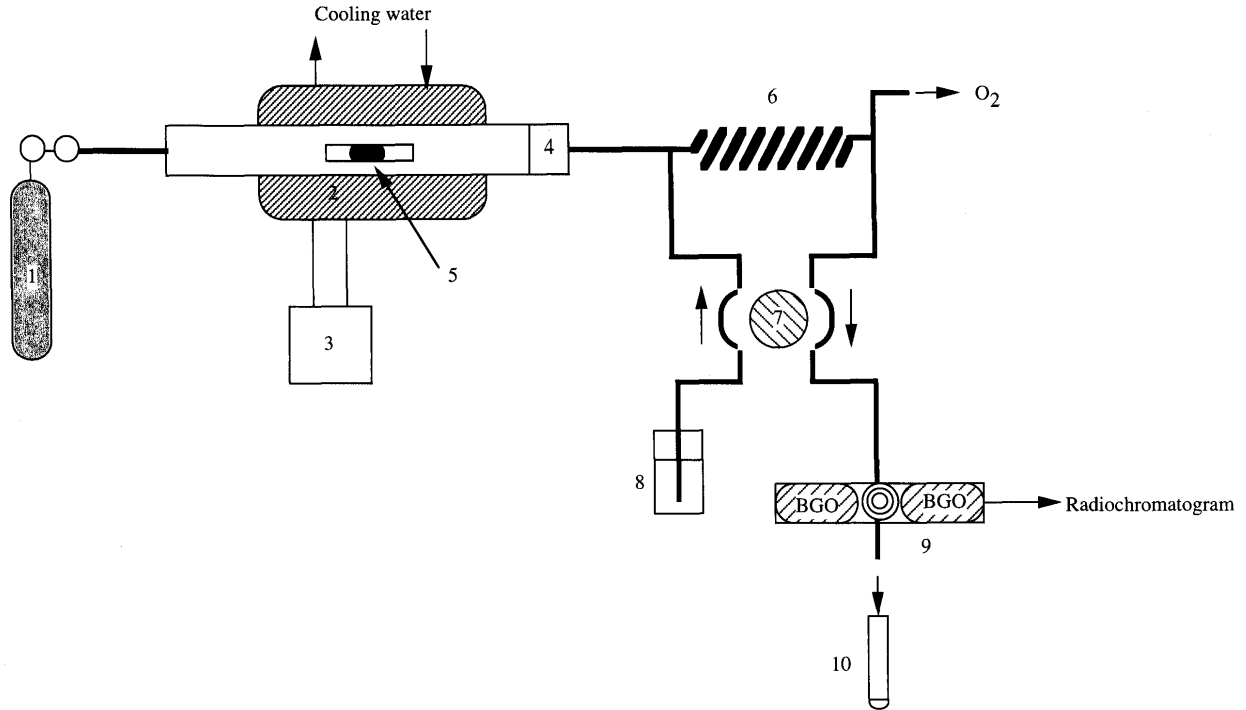


Fig.1. Set-up for separation of ^{11}C and radiochromatography; 1: carrier gas (O_2), 2: infrared heating furnace, 3: controller, 4: quartz wool, 5: sample and oxidizer, 6: adsorption column, 7: pump, 8: 75% ethanolamine solution, 9: coincidence counting system, 10: test tube for collecting ethanolamine.

etched the steel sample with a mixture of hydrofluoric acid and hydrogen peroxide.

2.3 Separation and radioactivity measurement of ^{11}C

Figure 1 shows the flow method set-up for the separation and radiochromatogram measurement of ^{11}C . We mounted the sample in a quartz boat with the oxidizer and then placed the boat in an infrared heating furnace. The sample was heated and fused with an oxidizer in an O_2 gas flow. The ^{11}C in the samples was oxidized to $^{11}\text{CO}_2$ in the furnace and transferred to an absorption column with O_2 gas. Then, $^{11}\text{CO}_2$ was absorbed in a 75% ethanolamine solution and measured to obtain a radiochromatogram by using a coincidence counting system consisting of a pair of bismuth germanium oxide (BGO) detectors installed downstream of the absorption column. We collected the solution containing the absorbed $^{11}\text{CO}_2$ in a test tube and then measured it with the coincidence counting system connected to two NaI(Tl) detectors to obtain decay curves. Irradiated lithium carbonate was dissolved in water and measured in the same way as the ethanolamine collected in the test tube. We analyzed the decay curve with a multiple least-squares computer program.

We also measured the nuclear interference produced from the matrix by the (γ, n) reaction using a Ge detector with a 4096 channel pulse height analyzer. The relative efficiency and FWHM of the Ge detector were 20% and 2.0 keV for a ^{60}Co 1332 keV γ -ray.

2.4 Calculation of carbon concentration

We calculated the carbon concentration (C_x) using Eq.(1).

$$C_x = (A_x/A_s) (M_s/W_x) k, \quad (1)$$

where A_x and A_s indicate the radioactivity of ^{11}C at the end of irradiation, M_s is the amount of carbon in

a standard sample, W_x is the weight of the test sample, and k is the relative flux.

§ 3. Results and Discussion

3.1 Nuclear interference

Table 1 shows the nuclear reaction of carbon and radionuclides produced from glasses with photon bombardment. We found that eleven radionuclides (^{63}Zn , ^{68}Ga , ^{70}Ga , $^{85\text{m}}\text{Sr}$, $^{87\text{m}}\text{Sr}$, ^{111}In , ^{112}In , $^{114\text{m}}\text{In}$ and $^{116\text{m}}\text{In}$) and four radionuclides (^{67}Ga , ^{68}Ga , ^{70}Ga and ^{72}Ga) were produced by (γ, n) , (n, γ) and $(\gamma, 2n)$ reactions of InF_3 -based fluoride and GNS glasses, respectively. ^{127}Te and ^{129}Te were also produced by the (γ, n) reaction of tellurite glasses. Some of these radionuclides were the same positron emitter as ^{11}C produced from carbon. Therefore, we found that the chemical separation of ^{11}C is required for the determination of carbon in these glasses.

Table 1. Nuclear reaction of carbon and nuclear interference produced from the matrix by Bremsstrahlung bombardment.

Nuclear reaction	Half-life	Decay mode	E γ , keV(%)
$^{12}\text{C}(\gamma, n)^{11}\text{C}$	20.38 m	β^+	511(99.76)
$^{64}\text{Zn}(\gamma, n)^{63}\text{Zn}$	38.1 m	β^+ , EC	511(185.6), 669.6(8.4)
$^{66}\text{Zn}(\gamma, n)^{65}\text{Zn}$	244.1 d	EC, β^+	511(2.92), 1115.5(50.8)
$^{69}\text{Ga}(\gamma, 2n)^{67}\text{Ga}$	78.2 h	EC	184.6(22.9)
$^{69}\text{Ga}(\gamma, n)^{68}\text{Ga}$	68.0 m	β^+ , EC	511(178.2), 1077.4(3.2)
$^{71}\text{Ga}(\gamma, n)^{70}\text{Ga}$	21.1 m	β^-	1039.2(0.7)
$^{71}\text{Ga}(n, \gamma)^{72}\text{Ga}$	14.1 h	β^-	834.0(95.6)
$^{86}\text{Sr}(\gamma, n)^{85\text{m}}\text{Sr}$	68.0 m	IT, EC	231.7(85.0)
$^{88}\text{Sr}(\gamma, n)^{87\text{m}}\text{Sr}$	2.806 h	IT, EC	388.4(82.3)
$^{113}\text{In}(\gamma, 2n)^{111}\text{In}$	2.83 d	EC	245.4(94.0)
$^{113}\text{In}(\gamma, n)^{112}\text{In}$	14.4 m	β^\pm , EC	511(42.8), 618.2(5.3)
$^{115}\text{In}(\gamma, n)^{114\text{m}}\text{In}$	49.5 d	IT, EC	190.2(18.4)
$^{115}\text{In}(n, \gamma)^{116\text{m}}\text{In}$	54.15 m	β^-	1293.5(84.4)
$^{122}\text{Te}(\gamma, n)^{121}\text{Te}$	16.78 d	EC	573.1(80.3)
$^{128}\text{Te}(\gamma, n)^{127}\text{Te}$	9.35 h	β^-	417.9(1.0)
$^{130}\text{Te}(\gamma, n)^{129}\text{Te}$	69.6 m	β^-	459.6(7.4)
$^{130}\text{Te}(\gamma, p)^{129}\text{Sb}$	4.41 h	β^-	812.8(43.5)
$^{204}\text{Pb}(\gamma, n)^{203}\text{Sb}$	52.0 h	EC	279.2(80.1)

3.2 Chemical separation of ^{11}C

To enable us to fuse glass samples rapidly and oxidize ^{11}C to $^{11}\text{CO}_2$ completely, we studied the fusion of these glasses using three kinds of oxidizers (a mixture of Pb_3O_4 and B_2O_3 , CuO , and NaCl). As a result, we selected the mixture of Pb_3O_4 and B_2O_3 as the oxidizer because the ^{11}C yield in the radiochromatogram was the highest and ethanolamine was uncontaminated by other nuclides. In contrast, ^{63}Zn and ^{68}Ga was detected in the solution because their chlorides became volatile when NaCl was used.

Figure 2 shows radiochromatograms we obtained from InF_3 -based fluoride, GNS, and tellurite glasses that were not chemically etched after irradiation. As shown in the figure, we found that the greatest amount of radionuclides such as ^{11}C or other positron emitters were produced by fluoride and the least amount by tellurite. Figure 3 shows the decay curve of a 511 keV γ -ray obtained from the

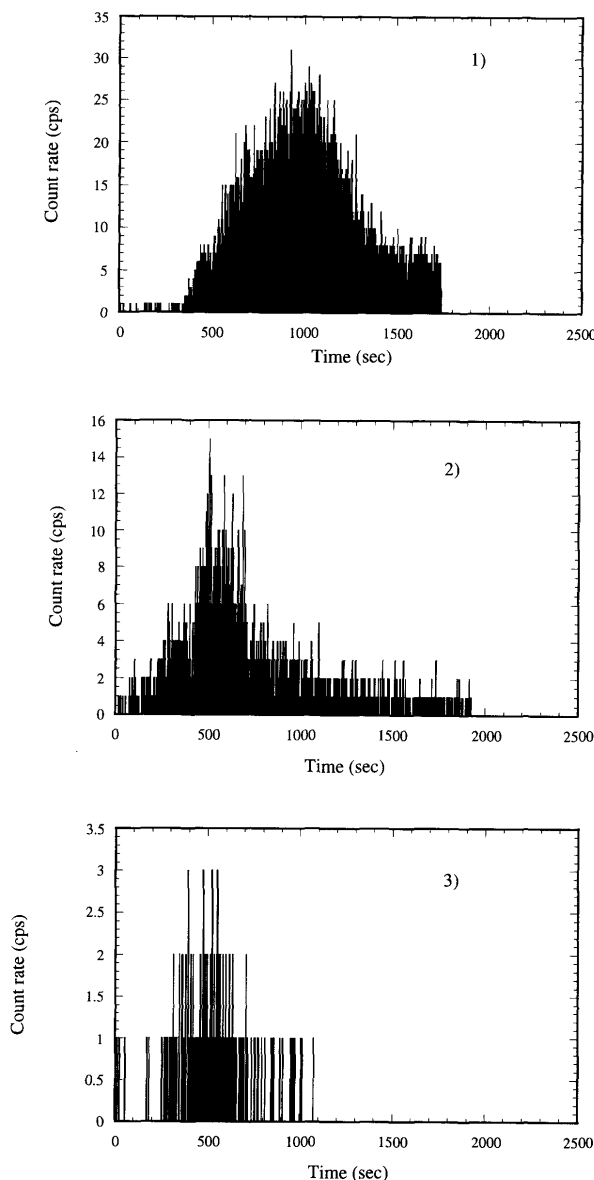


Fig.2. Radiochromatograms obtained from three glasses;
1) InF₃-based fluoride glass, 2) GNS glass, 3) tellurite glass.

absorption solution collected in the test tube. As shown in the figure, we found that there are long half-life nuclides in the decay curves of the InF₃-based and GNS glasses. Our analysis of their half-life showed these nuclides to be ¹⁸F. We believe that ¹⁸F is produced from the fluoride and GNS glasses by ¹⁹F(γ , n)¹⁸F and ²³Na(γ , α n)¹⁸F reactions and volatilized. It then contaminates the ethanolamine solution used for absorbing ¹¹CO₂. Therefore, we concluded that it is difficult to employ the chemical separation of ¹¹C by the flow method for the determination of carbon in fluoride and GNS glasses because of large radioactivity of ¹⁸F compared with that of ¹¹C after etching. However, this method can be used to determine carbon in tellurite glasses.

3.3 Determination of chemical yield for ¹¹C

Steel samples were fused in the same way described in ref.[7]. Figure 4 shows the radiochromatogram and decay curve of the steel sample. We found that only ¹¹C can be separated by the flow method from this decay curve. Table 2 shows the analytical results for carbon in steel. As

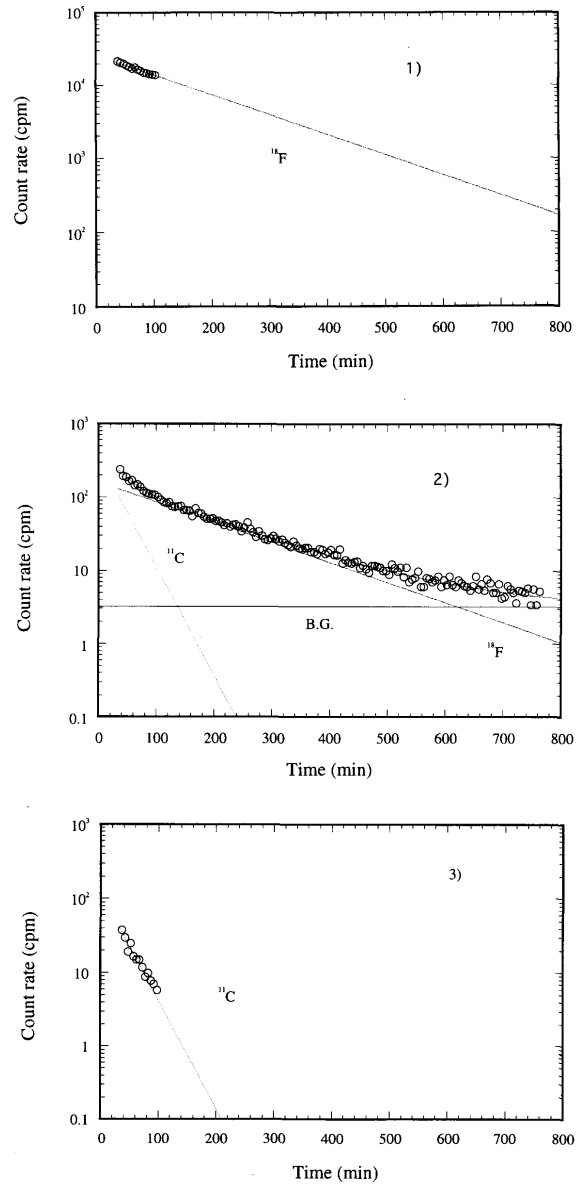


Fig.3. Decay curves of 511 keV γ -ray obtained from three glasses;
1) InF₃-based fluoride glass, 2) GNS glass, 3) tellurite glass.

shown in the table, the carbon concentration is 5.0 ± 1.0 ppm and in good agreement with the certified value but the relative deviation is large at 20%. It seems that ^{11}C in the steel sample is converted to $^{11}\text{CO}_2$ and all the $^{11}\text{CO}_2$ is completely absorbed in the ethanolamine solution, although the concentration is widely dispersed. Therefore, we concluded that the chemical yield with the flow method is close to 100%.

3.4 Determination of carbon in tellurite glasses

Table 2 shows analytical results for carbon in two kinds of tellurite glass. As shown in the table, their carbon concentrations were respectively 8 to 13 and 21 to 28 ppm and the relative deviation was 14 to 24% in both samples. Table 2 also shows the carbon concentration in the tellurite glasses calculated by using their radiochromatograms and the certified carbon concentration (5 ppm) in the steel samples. The carbon concentrations were 7 to 14 and 22 to 33 ppm in the two kinds of tellurite glass (Tellurite-1, 2). The concentration in Tellurite-1 is in good agreement with the above values but that in Tellurite-2 is a little larger than earlier values. Therefore, we found that the radioactivity of ^{11}C measured from

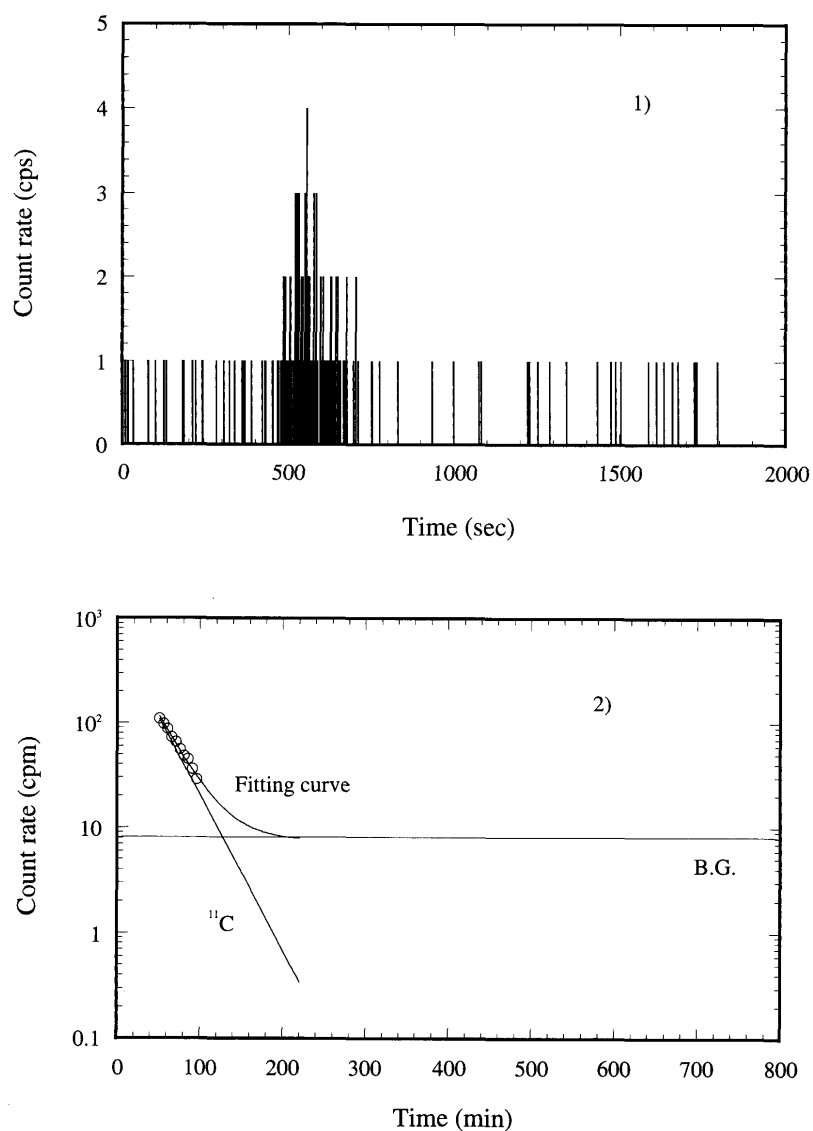


Fig.4. Radiochromatogram 1) and decay curve 2) of steel sample (JSS 1201-1).

Table 2. Analytical results for carbon in steel sample and tellurite glasses.

Sample	Concentration* (ppm)	Concentration** (ppm)
Steel JSS1201-1-1	5	
-2	6	
-3	4	
Average value	5.0 ± 1.0	
Tellurite-1-1	8	7
-2	13	14
Tellurite-2-1	21	22
-2	28	33

* Calculation by using lithium carbonate as a standard sample.

** Calculation by using steel (JSS1201-1) as a standard sample.

radiochromatograms and decay curves can be used for the determination of carbon, and the precision and accuracy of this analytical method can be improved when there is no contamination in the radiochromatogram.

In conclusion, our proposed analytical method is a simple, rapid and accurate way to determine the carbon in these glasses. This is because we can confirm the chemical condition using radiochromatograms and detect any contamination by other positron emitted nuclides such as ^{18}F from the decay curve. Moreover, we can exactly correct the radioactivity of ^{11}C by analyzing the half-life of the decay curve.

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