Bull. Chem. Soc. Jpn., *58*, *1273—1278 (1985)*

Studies of Quenching Processes in NE-213 and Insta-Gel Liquid Scintillators by Using Pulse Shape Discrimination Technique

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(Received September 12, 1984)

Quenching processes for different excitation sources such as alpha-particles and electrons in NE-213 and Insta-Gel were studied by the use of the pulse shape discrimination technique and pulse height analysis. The dependence on electron energies of time spectra due to the difference in pulse shape was observed for NE-213 by setting energy windows to Compton scattered electrons. The results were interpreted on the basis of the linear energy transfer of electrons in liquid scintillator solution. The chemical and oxygen quenchings in Insta-Gel were compared with each other by using conversion electrons and alpha-particles. Quenching constants for those particles were found to be the same for each organo halogen compound used, irrespective of the excitation sources used. Paramagnetic quenchings were also examined for such agents as oxygen, Gd^{3+} ($4f^7$), and Yb^{3+} ($4f^{13}$) by using the above two excitation sources in Insta-Gel. Possible mechanisms of their effects on the quenching processes were discussed in terms of the spin conversion between the paramagnetic quencher and the excited solvent.

The liquid scintillation counting technique has been widely used for the determination of soft beta-emitting nuclides such as tritium, carbon-14 and calcium-45 because of its excellent detection efficiency and of its simplicity in sample preparation.[1—5] In addition, this technique has been found to be very useful for the determination of low level radon in the environment.[6—10] However, quenching phenomena caused by various impurities often make the observable pulse heights lower. On the other hand, several studies have been made on quenching mechanisms in liquid scintillation systems by using monochromatic photons in the UV region,[11,12] but only a few by using radioactive nuclides for excitation of the scintillation system.[13—15]

Quenching effects have so far been classified into three categories; chemical quenching, color quenching, and oxygen quenching. The chemical quenching is caused by some energy transfer reactions between solvents or between the solvent and fluorescent molecules that do not take part in the emission of fluorescence. The color quenching is the process due to the absorption of fluorescence by quenching molecules. This process is caused by the superposition of the emission spectrum of the scintillator and the absorption spectrum of the quenching molecules. The oxygen quenching is considered to be the process related to the strong electron affinity and paramagnetism of oxygen, but details remain unknown.

It is known that the mean life time of fluorescence emission is affected by the chemical and oxygen quenchings. Hence, the pulse shape discrimination is a useful technique to get information regarding variation of such life times. The technique has been successfully applied to neutron spectroscopy, separating gamma-rays and recoil protons in inorganic[16—19] and organic scintillation countings.[20—21] Recently, this has been also effectively applied to alpha- and beta-countings by using liquid scintillator solution.[22—24]

In the present work, we studied the chemical and oxygen quenching processes in NE-213 (a product of Nuclear Enterprises) and Insta-Gel (a trade name of Packard Co., Inc.), using the pulse shape discrimination technique and pulse height analysis, and laid stress on the following points. Firstly, the relative resolving power of pulse shape discrimination between alpha-particles and electrons was examined as a function of electron energy. Secondly, the oxygen quenchings for different excitation sources such as alpha-particles and electrons were compared with each other by using the pulse shape discrimination technique. Thirdly, the effects of these different excitation sources on the chemical and oxygen quenching were studied by means of pulse height analysis. Lastly, the paramagnetic effects of oxygen, Gd^{3+} ($4f^7$), and Yb^{3+} ($4f^{13}$) were studied in order to clarify their quenching processes by the pulse shape discrimination technique. Among lanthanoid ions, Gd^{3+} shows high paramagnetic moments whereas Yb^{3+} does the least. The comparative study by the use of such ions as quenchers will make the quenching mechanism clear. The results will be discussed in terms of possible spin conversion mechanisms. In the present study, the alpha-particles from ^{210}Po and the conversion electrons from ^{139}Ce were used in order to compare the quenching effects for their excitation sources. It is expected that the quenching reactions involved will be simple for the electrons with a simple energy spectrum.

Experimental

Chemicals. *a) Sources for Insta-Gel.* For an alpha-ray source, ^{210}Po in 1 M[†] hydrochloric acid solution was used, and for a conversion electron source, ^{139}Ce in the cerium(III) chloride form was used. The 1 M hydrochloric acid solution (1 ml) of these radioisotopes was put into a standard vial containing Insta-Gel (15 ml). The content was deoxygenated by argon gas bubbling, unless otherwise stated.

Gadolinium and ytterbium chlorides were prepared from their oxides. After dissolving the oxides into small amounts of nitric acid, their salts were converted to chlorides by repeated addition of hydrochloric acid and heating. Finally, the chlorides were obtained by evaporating the solution to

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[†] 1 M=1 mol dm^{-3}.

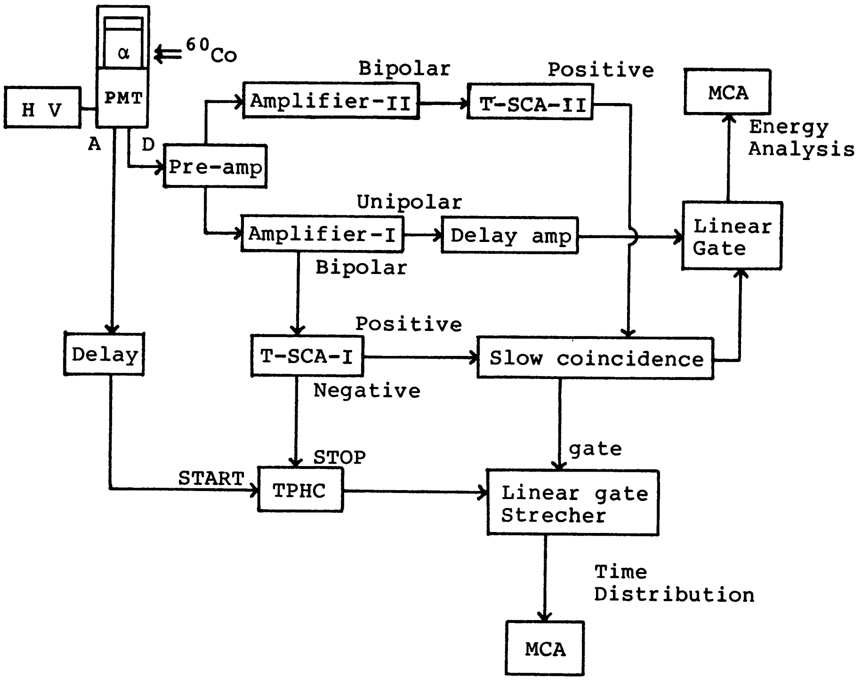

Fig. 1. A block diagram of a zero-crossing pulse shape discrimination system.

dryness.

b) Sources for NE-213. Polonium-210 and cerium-139 were extracted from each 1 M hydrochloric acid solution with a toluene solution of di(2-ethylhexyl)phosphoric acid (volume ratio of 1:1). For investigation of the electron energy dependence on the zero-crossing time, a vial containing the ^{210}Po source (the extracted solution, 1 ml) and 15 ml of NE-213 was externally irradiated with gamma-rays of ^{60}Co. The alpha-ray source was used to generate a standard zero-crossing time of alpha-rays on a time spectrum.

Measurements of Dissolved Oxygen. An oxygen analyzer manufactured by Beckman Instrument Inc. was used to measure the partial pressure of oxygen dissolved in Insta-Gel. We used the value for the partial pressure of oxygen in atmosphere, *i.e.*, 21% as the standard partial pressure of oxygen dissolved in Insta-Gel, assuming that the oxygen in solution is in equilibrium with that in air. In the case of oxygen quenching experiments, the gel was bubbled by oxygen through a glass capillary and the oxygen contents were measured before and after the pulse height and pulse shape measurements.

Measurement System. The schematic counting system used in this experiment is shown in Fig. 1. The vial was surrounded by an aluminium foil and directly connected at the bottom with optical greese to a RCA 8575 photomultiplier. All the electric instruments used were ORTEC NIM modules. In order to measure normal pulse shape distributions of alpha-particles and electrons, we used a simple system of a time pick-off at the zero-crossing point of slow bipolar signals. Anode pulses shaped with the constant fraction discriminator inside the ORTEC 270 photomultiplier base were used as start signals for a time-to-pulse height convertor (TPHC). The voltage signals from the dynode were passed through the pre-amplifier, and shaped with the main amplifier-I. The resulting bipolar signals were fed to a timing SCA-I and the fast negative signals were used as stop signals for the TPHC. In order to reduce the shifts of zero-crossing time due to pulse height variation, the range of the pulse height to be measured was kept constant by timing SCA-I and -II. The lower level of the pulse height range was selected with the timing SCA-I. For selecting the upper level of the specified range, the upper level discriminator of the timing SCA-II was used, and the lower level discriminator was set to be zero. The gain of the amplifier-I was changed to adjust the pulse height of a given electron energy to the window selected by the above two SCA.

Results and Discussion

Dependence of Zero-crossing Time Distribution on Electron Energy. Dependence of the time spectrum on the energy of electrons was examined by using Compton scattered electrons of various energies and alpha-particles of ^{210}Po in NE-213. The latter was used as a standard source for the time distribution of alpha-particles. The time spectrum of the alpha-particles from ^{210}Po and the Compton scattered electrons from ^{60}Co in NE-213 is shown in Fig. 2. The resolving power of zero-crossing time distribution between the electrons and alpha-particles was analyzed by a figure of merit, $M_{\alpha,e}$, defined as

$$M_{\alpha,e}=\frac{\Delta S}{T_1+T_2}$$

where ΔS is the separation between two peaks, T_1 and T_2 are the full widths at half maximum (fwhm) of electrons and alpha-particles, respectively. For the present experiment, the T_2 value was constant for alpha-particles of ^{210}Po. The $M_{\alpha,e}$ values for the electrons of selected energy ranges were evaluated from the observed ΔS, T_1, and T_2 values as shown in Fig. 3. As the electron energy decreases, the $M_{\alpha,e}$ value becomes smaller. A similar trend has been reported

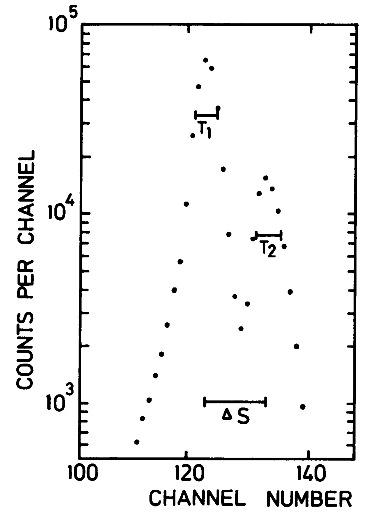

Fig. 2. Time spectrum of alpha-particles from ^{210}Po and of Compton scattered electrons in oxygen-free NE-213 irradiated with gamma-rays of ^{60}Co. T_1 and T_2 indicate the full widths at half maximum of electrons and alpha-particles, respectively.

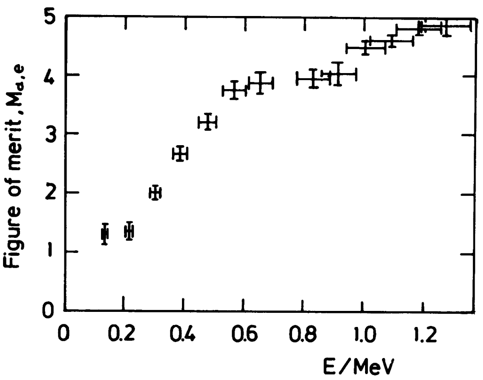

Fig. 3. Figure of merit, $M_{\alpha,e}$, of alpha-particles from ^{210}Po and of Compton scattered electrons in oxygen-free NE-213 irradiated with gamma-rays of ^{60}Co as a function of electron energy.

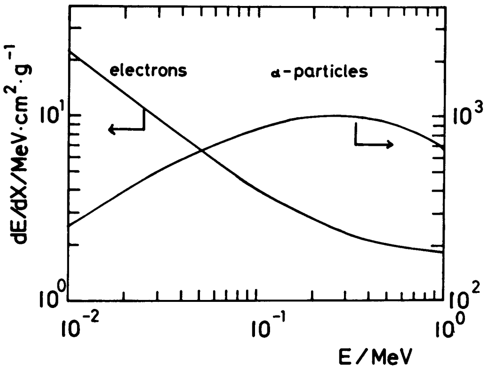

Fig. 4. Stopping powers of alpha-particles and electrons calculated by using Bethe's equation in a system of PPO (4 g), POPOP (0.1 g), and toluene (10^3 ml).

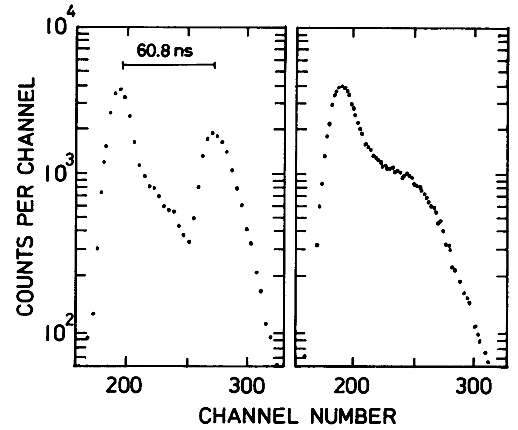

Fig. 5. Time spectra of conversion electrons from ^{139}Ce and alpha-particles from ^{210}Po in NE-213 liquid scintillator under oxygen-free (left side) and oxygen-saturated (right side) conditions.

for neutron and gamma-ray separation.[19,27] The energy loss of electrons can be calculated by using Bethe's equation.[28] Although the exact chemical composition of NE-213 is not available, the energy loss of electron for an analogous material, toluene-PPO system, is shown in Fig. 4, together with that of alpha-particles.[29] The chemical compositions used for calculation are 4 g of PPO ($C_{15}H_{11}NO$, 2,5-diphenyloxazole), 0.1 g of POPOP ($C_{24}H_{16}N_2O_2$, 1,4-bis-2-(5-phenyloxazole)-benzene), and 10^3 ml of toluene. The stopping power becomes greater as the electron energy decreases. On the other hand, the value corresponding to the 5.3 MeV alpha-particles of ^{210}Po is calculated to be 2.20×10^2 MeV/cm^{2}g^{-1} in the system by using Bethe's equation,[29] which is at least two order of magnitude greater than that of electrons of the same energy. The high linear energy transfer causes localized ionization, molecular damages, and free radical formation along the path, which are closely related to the overall fluorescence conversion efficiency. The highly ionized species in a small limited spur recombine with electrons, resulting in the excited triplet state of a neutral molecule in the absence of spin correlation between the ion and an electron. The neutralization into a triplet state is favored by spin statistics. The present results of the $M_{\alpha,e}$ dependence on electron energy suggest that the energy loss processes of electrons in liquid scintillation system is similar to those of alpha-particles as the electron energy decreases.

Effects of Oxygen for Pulse Shape Discrimination. Since the time spectra of electrons were found to be dependent upon the energy in the preceding section, we used conversion electrons from ^{139}Ce as an electron source of simple energy spectrum. The time spectra of the conversion electrons and the alpha-particles from ^{210}Po in NE-213 are shown in Fig. 5. Although the center of the pulse shape distribution due to conversion electrons was not affected by oxygen, that of alpha-particles was shifted to shorter direction. The time difference of peaks was found to be 60.8 ns for oxygen-free NE-213, and to be 42 ns for oxygen saturated one. Diamagnetic compounds such as chloroform, carbon tetrachloride, bromoform, dibromomethane, and aniline did not cause variations in the time spectrum for alpha-particles and electrons within the experimental errors, compared with those of NE-213 containing no quenching agents. The results obtained on Insta-Gel were similar to those on NE-213, except that the separation of two peaks on the time spectrum was inferior to that of the latter.

It is known in radiation chemistry that a large number of excited molecules generated through decomposition or ionization, followed by recombination of an ion and an electron, are in a triplet state as described in the preceding section. Such a triplet state will subsequently be quenched through the spin conversion process between the excited solvent and paramagnetic oxygen to the singlet state, which results in a shortening of the decay time of scintillation. The excited molecules due to the recombination of an ion and an electron will be produced in much larger quantities by alpha-particles than electrons because of the greater linear energy transfer of the former.

Shifts of the Pulse Height by Chemical and Oxygen Quenchers. The chemical and oxygen quenchings were examined by means of the pulse height analysis. Relative pulse heights (I_0/I) are plotted in Fig. 6 against the concentration of each quencher, where I and I_0 are the peak channels of the pulse height spectra observed with a given quencher and without the quencher, respectively. The linear relationship between I_0/I and the concentration was observed for each quencher. Hence, the relation can be analyzed by the following equation:

$$I_0/I = 1 + \gamma[\mathrm{C}]$$

where γ is the quenching constant, and [C] the quencher concentration. The quenching constant was evaluated from the slope in Fig. 6, and the results are listed in Table 1. The constants were the same for alpha-particles and conversion electrons for given halogeno compounds. This would suggest that there are no remarkable differences between the chemical reactions due to the halo methanes and the excited solvents produced through the energy loss processes of alpha-particles and electrons.

Takiue and Ishikawa reported quenching constants for a series of organo halogen compounds in the toluene-PPO system using conversion electrons from ^{113}Sn.[14] For the same quencher, the quenching constant for the Insta-Gel system was found to be roughly one-half of the value in the toluene-PPO system as seen in Table 1. The quenching constant should be inversely proportional to the viscosities of the solvent from the bimolecular reaction theory.[30] The observed values, however, are not consistent with this. The discrepancy seems to be ascribed to the reasons that the scintillator solution is a mixtured solution containing PPO and a surface-active agent.

Effects of Paramagnetic Species on Time Spectrum. In order to examine in greater details the effects of paramagnetic species revealed in the time spectrum of alpha-particles and conversion electrons, we studied the effects of $GdCl_3$ ($4f^7$, S=7/2) and $YbCl_3$ ($4f^{13}$, S=1/2) in Insta-Gel. The time spectra of alpha-rays of ^{210}Po and conversion electrons of ^{139}Ce in Insta-Gel (containing 50 mM $GdCl_3$ used as a quenching agent) are shown in Fig. 7a, and the time difference between the peak channels was plotted against the concentration of $GdCl_3$ as shown in Fig. 7b. The results on $YbCl_3$ used as a quenching agent were the same as those obtained on $GdCl_3$. The oxygen effect in the foregoing arguments raises an expectation that a time spectrum of alpha-particles from ^{210}Po would be affected by the lanthanoid ions through spin conversion process. The experimental results, however, failed to show this. Unlike oxygen, paramagnetic lanthanoid ions did not shift the time spectrum for alpha-particles and conversion electrons. In order to find a reasonable explanation, the shortening process of the time distribution by paramagnetic quenchers may be considered as follows.

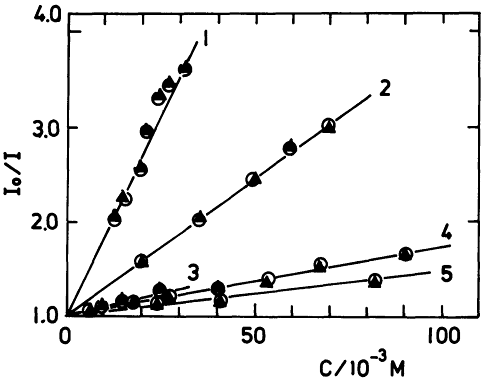

Fig. 6. Values of I_0/I plotted against the quencher concentration; 1: CBr_4, 2: $CHBr_4$, 3: CCl_4, 4: CH_2Br_2, 5: $CHCl_3$. ○: alpha-particles, ▲: electrons.

Table 1. Quenching constants of halomethanes and oxygen observed in Insta-Gel excited with conversion electrons from ^{139}Ce and alpha-particles from ^{210}Po

Compound	Quenching constant $10^3\gamma_1/M^{-1}$ (in Insta-Gel)	 $10^3\gamma_2/M^{-1}$[a)] (in toluene-PPO)	(γ_1/γ_2)
CBr_4	88.7	164.0	0.54
$CHBr_3$	30.2	57.0	0.53
CCl_4	26.3	50.8	0.52
CH_2Br_2	7.39	13.3	0.56
$CHCl_3$	3.95	6.83	0.58
O_2	57.8[b)]	—	—

a) The data of toluene-PPO system were cited from Ref. 14. b) In the case of oxygen, the value was obtained by the least squares method on seven data points (up to 8 mM).

When the spin conversion process takes place between an unpaired electron of a paramagnetic quencher and the excited triplet state of a solvent molecule, a spin pairing will occur in the paramagnetic quencher if the partly filled electron shell has more than one electron or hole. Therefore, for the spin

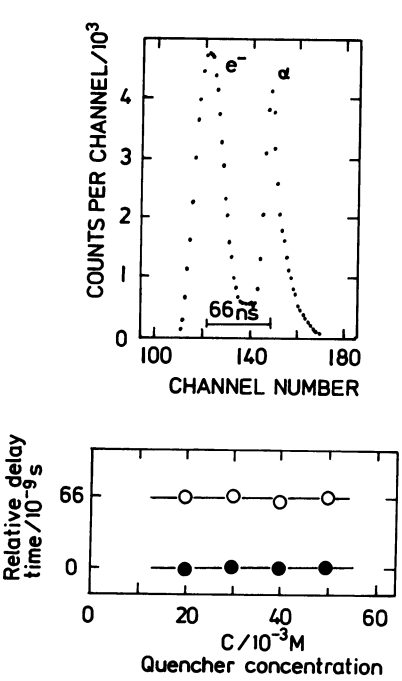

Fig. 7. (a) Time spectra of conversion electrons from ^{139}Ce and alpha-particles from ^{210}Po in oxygen-free Insta-Gel containing 50 mM $GdCl_3$. (b) Relative peak delay on the time spectra of conversion electrons and alpha-particles against the concentration of $GdCl_3$; open and full circles show the peak positions due to alpha-particles and conversion electrons, respectively.

conversion to occur, the spin pairing energy of the quenching molecule or ion must be at least lower than the energy of the lowest excited triplet state of the solvent molecule. The spin pairing energies of low lying states of oxygen are reported to be 1.46 and 0.98 eV.[31] The lowest excited triplet states of such solvents as xylene, toluene, and benzene are reported to be 3.49, 3.57, and 3,65 eV, respectively.[32–34] Thus, the spin conversion process is energetically allowed for the oxygen quencher. However, the energy balance between the solvent molecule and the paramagnetic quencher is not a sole dominant factor for the process. The lowest spin pairing energy of trivalent gadolinium ions is estimated to be 3.9 eV ($^6P_{7/2}\leftarrow{}^8S_{7/2}$), while trivalent ytterbium ions require no spin pairing energy with the electric confiration of $4f^{13}$,[35] so that the latter would be expected to act as a good paramagnetic quencher. However, no meaningful difference in quenching effect was found between the above two lanthanoid ions. This observation may be explained if we recall that trivalent lanthanoid ions have unpaired electrons of 4f-orbitals inside the filled 5s–5p orbitals, and probably have little overlap with an orbital of an unpaired electron of an excited solvent molecule. The spin conversion in the scintillation process is, therefore, forbidden for lanthanoid ions not only because of the energy balance but also because of the inertness of 4f-electrons. These results may lead us to conclude that the spin conversion process for oxygen is allowed from two reasons of the energy balance and the overlap of orbitals.

Conclusion. 1) The time spectra of electrons were affected by electron energies. The results may be explained in terms of the energy loss of electrons in liquid scintillator solutions as follows. As the electron energy decrease, the stopping power increases. The increased energy loss per unit length causes localized ionizations, radiation decompositions, and radical formations. The ionized species recombine in a short time with electrons, and subsequently lead to the formation of an excited triplet state in the absence of spin correlation between a positive ion and an electron. The energy transfer from the decay of a long-lived triplet state and the subsequent fluorescence of PPO will result in the delayed distribution on the time spectrum.

2) The chemical quenching constants for alpha-particle and electron excitations were found to be identical with the same organo halogen compound. The results suggest that the chemical reactions of organo halogen compounds with the excited solvents lead to practically the same reduction of the fluorescence yields for alpha-particles and electrons.

3) The time spectra of alpha-particles were shifted by oxygen, whereas those of electrons were not. In addition, they were not also affected by lanthanoid ions. The facts may be explained in terms of spin conversion mechanism. For the spin conversion to occur, the molecule must be excited at least to an excited state whose spin multiplicity is smaller by two than that of the ground state. In the case of spin doublet state, the process is expected to be allowed energetically. However, the results on the lanthanoid ions showed that the overlap of an unpaired electron of the paramagnetic quencher and that of the excited solvent is also important for the process.

The authors are grateful to Dr. H. Ishikawa of Radioisotope Nuclear Reactor School at Japan Isotope Research Institute for the use of an oxygen analyzer, and to Prof. Y. Murakami at Kitasato University for kind suggestions throughout this work.

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