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Radio-Gas Chromatographic Measurement of Separation Factors in Laser Isotope Separation of Tritium

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Abstract

A new method is proposed for the evaluation of the separation factors in laser isotope separation of tritium using radio-gas chromatograph technique, when the radioactivity detection is severely affected by the quenching effect. It is shown mathematically that the overall efficiency of radioactivity measurement with a proportional counter (internal gas flow type) can be described as functions of the intrinsic detection efficiency and the shape of the elution curve. This mathematical treatment is shown to be useful for the experimental determination of the separation factors for the system of CF_3CTBrF/CF_3CHBrF which is an excellent working substance for tritium isotope separation.

INTRODUCTION

Molecular laser isotope separation (MLIS) has been studied intensively in the last 10 years for such practical goals as uranium enrichment (*1*), heavy water production (*2*), and tritium isotope separation (*3–8*).

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For hydrogen isotope (deuterium or tritium) separation, highly efficient infrared lasers (especially pulsed CO_2 laser) are used, and working substances are searched which have selective absorption of deuterated or tritiated molecules in the wavenumber region where the CO_2 laser lines are available. In the industrialized stage the working substance for hydrogen isotope separation is assumed to be circulated in a closed loop consisting of the isotope exchange process, the selective photodissociation process, and the photoproduct separation process (*9–10*). High separation factor (isotopic selectivity of infrared-laser induced multiphoton dissociation), high operating pressure, and low dissociation threshold fluence are required for the working substance in the laser isotope separation of tritium, and these conditions have been successfully investigated in small-scale batch experiments by analyzing the concentration changes of the protonated and tritiated substances between before and after laser irradiation using a radio-gas chromatographic technique (*3–5*). For trifluoromethane (CTF_3/CHF_3) (*4*) and pentafluoroethane (*6*), the separation factor measurement is straightforward since the radioactivities of tritiated substances detected in the chromatographic peaks are linearly dependent on the amount of tritiated substances and independent of the amount of protonated substances. For such molecules as 2-bromo-1,1,1,2-tetrafluoroethane (CF_3CTBrF/CF_3CHBrF) and trichloromethane ($CTCl_3/CHCl_3$), however, the radioactivity measurement of tritiated forms with an internal gas flow type proportional counter is severely distorted due to the quenching effect of the corresponding protonated molecules. The total radioactivity counts in the elution curve of tritiated substances are, therefore, dependent on the amount of protonated substance as well as of the tritiated substance.

In Fig. 1 the quenching effects of radioactivity measurement are illustrated for comparison. Figure 1(a) shows the chromatograms for the CTF_3/CHF_3 system with no quenching, where the shapes of the elution curves detected by a thermal conductivity detector (TCD) for the protonated component and those by a proportional counter (PC) for the tritiated component are proportional. In Fig. 1(b) the chromatograms for CF_3CTBrF/CF_3CHBrF are shown. It illustrates that the quenching effect for the measurement of CF_3CTBrF is dependent on the local concentration of CF_3CHBrF in the proportional counter; the peak top is more severely suppressed by quenching than the leading and tailing regions of the chromatogram. In an extreme case, the radio-gas chromatogram gives two peaks.

In this paper a mathematical method for treating such distortion is presented. The proposed method is experimentally investigated for the CF_3CTBrF/CF_3CHBrF system and the premises are validated.

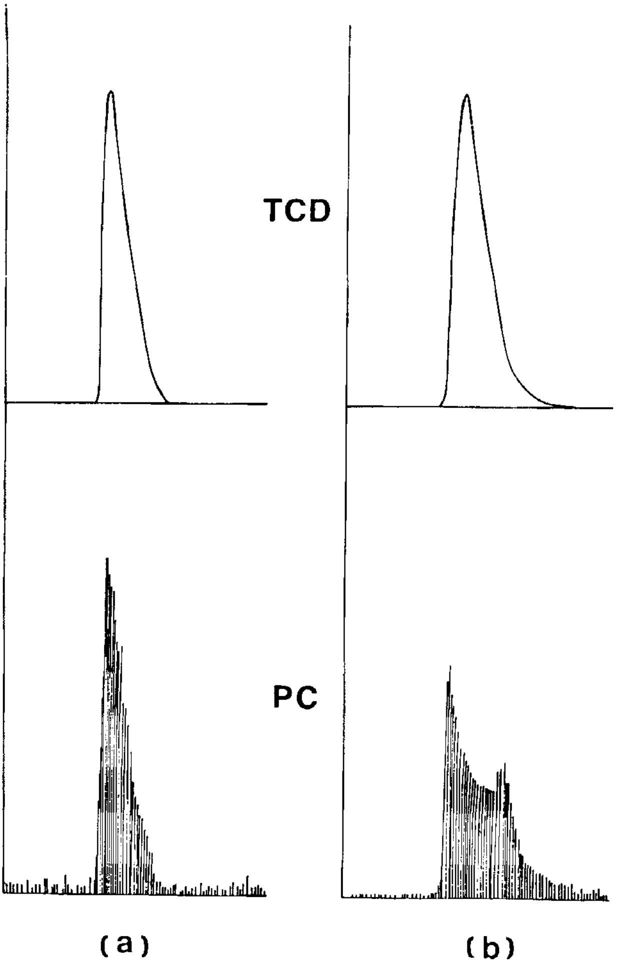

FIG. 1. Chromatograms for (a) CTF_3/CHF_3 and (b) CF_3CTBrF/CF_3CHBrF.

MATHEMATICAL TREATMENT

Let C_T and C_H denote the concentrations of CF_3CTBrF and CF_3CHBrF in the detector.

The total radioactivity count A (counts) is related to the time-dependent radioactivity counting rate a (counts per minute) as

$$\int a d\theta = A \tag{1}$$

The quantity a is proportional to the time-dependent concentration of tritiated molecules C_T expressed as

$$a = \alpha Q C_T \tag{2}$$

where α is a counting coefficient and Q is the volumetric flow rate of the carrier gas. Without quenching, α is constant (independent of both C_T and C_H) and the total amount of tritiated molecules M_T is related to A simply by

$$A = \alpha Q \int C_T d\theta \propto M_T \qquad \text{(no quenching)} \tag{3}$$

When the quenching effect is present, α is dependent on C_H but not on C_T as long as C_T is low: $\alpha = \alpha(C_H)$. When C_H is decreased, α approaches a limiting value α_0 under the condition of no quenching.

In this paper as a first-order approximation, α is assumed to decrease linearly with C_H as given by

$$\alpha = \alpha_0(1 - C_H/C_{H_0}) \tag{4}$$

where C_{H_0} is a characteristic concentration. This assumption is checked later.

When the time-dependent radioactivity detection efficiency η is defined by α/α_0, η is dependent only on C_H:

$$\eta(C_H) = \alpha(C_H)/\alpha_0 = 1 - C_H/C_{H_0} \tag{5}$$

The overall detection efficiency $\bar{\eta}$ is defined by

$$\bar{\eta} = \frac{\int C_H(\theta)\eta(C_H)d\theta}{\int C_H(\theta)d\theta} = 1 - \frac{1}{C_{H_0}} \frac{\int C_H{}^2 d\theta}{\int C_H d\theta} \tag{6}$$

where Eq. (5) is substituted in the latter half.

When the elution curve of the protonated sample is normalized by the concentration at the peak $C_{H_{pk}}$, Eq. (6) is rewritten as

$$\bar{\eta} = 1 - \frac{C_{H_{pk}} \int f^2 d\theta}{C_{H_0} \int f d\theta} = 1 - (1 - \eta_{pk}) \frac{\int f^2 d\theta}{\int f d\theta} \tag{7}$$

where η_{pk} is the detection efficiency at the peak (see Eq. 5) and f is the dimensionless concentration normalized by the concentration at the peak $C_{\mathrm{H}_{\mathrm{pk}}}$. The value of f is equal to unity at the peak.

The quantities $(1 - \bar{\eta})$ and $(1 - \eta_{\mathrm{pk}})$ correspond to the degree of overall quenching for an elution curve and to the degree of quenching at the peak top, respectively. Equation (7) simply indicates that $(1 - \bar{\eta})$ and $(1 - \eta_{\mathrm{pk}})$ are proportional:

$$(1 - \bar{\eta}) = \frac{\int f^2 d\theta}{\int f d\theta}(1 - \eta_{\mathrm{pk}}) \tag{8}$$

where the proportionality constant Ψ ($\equiv \int f^2 d\theta / \int f d\theta$) is between 0 and 1 and only dependent on the shape of the elution curve. Then the mathematical treatment of the quenching is now reduced to the evaluation of Ψ ($\equiv \int f^2 d\theta / \int f d\theta$) for different elution curves.

Triangular Pulse

For symmetrical triangular pulses, $f(\theta)$ is written by

$$f(\theta) = 0 \text{ for } \theta < \theta_1 \text{ and } \theta > \theta_2 \tag{9a}$$

$$f(\theta) = k(\theta - \theta_1) \text{ for } \theta_1 < \theta \leqslant \tfrac{1}{2}(\theta_1 + \theta_2) \tag{9b}$$

$$f(\theta) = -k(\theta - \theta_2) \text{ for } \tfrac{1}{2}(\theta_1 + \theta_2) \leqslant \theta < \theta_2 \tag{9c}$$

The value of $(\int f^2 d\theta)/(\int f d\theta)$ is $\frac{2}{3}$. That is, the total quenching for one elution curve is $\frac{2}{3}$ times less than the quenching at the peak top.

Rectangular Pulse

For a rectangular elution curve, $f(\theta)$ is written by

$$f(\theta) = 1 \text{ for } \theta_1 \leqslant \theta \leqslant \theta_2 \tag{10a}$$

$$f(\theta) = 0 \text{ for } \theta < \theta_1 \text{ or } \theta > \theta_2 \tag{10b}$$

In this case, Ψ is unity.

Gaussian Distribution Curve

A Gaussian elution curve in which the peak height is normalized to unity is expressed as

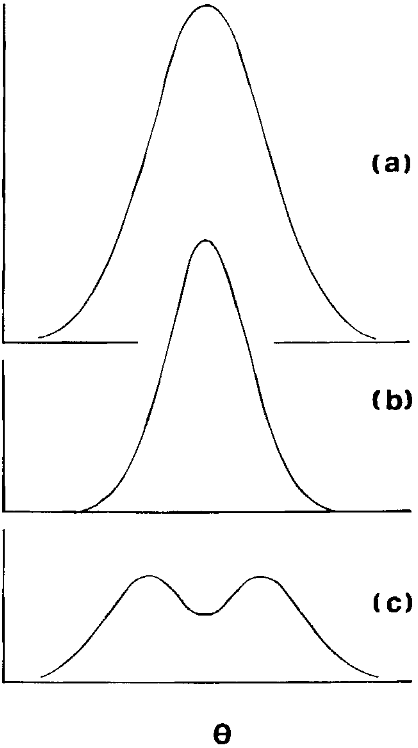

FIG. 2. Synthesis of chromatogram under quenching conditions.

$$f(\theta) = \exp\{-(\theta - \mu_1)^2/2\sigma^2\} \tag{11}$$

where μ_1 is the mean residence time and σ is the standard deviation. Since $\int f d\theta$ and $\int f^2 d\theta$ are equal to $\sqrt{2\pi}\sigma$ and $\sqrt{\pi}\sigma$, respectively, Ψ is equal to $1/\sqrt{2}$ for this case.

From the viewpoint of the quenching effect in proportional counter measurement, the Gaussian elution curve is situated between the rectangular and triangular elution curves.

In Fig. 2 the elution curve under the quenching condition for this case is shown to be obtained as Curve (c) by subtracting Curve (b), which is proportional to $f^2(\theta)$, from elution Curve (a) without quenching.

Poisson Distribution Curve

When the elution curve is skewed, it is customary to describe it with a Poisson distribution curve (*11*) given by

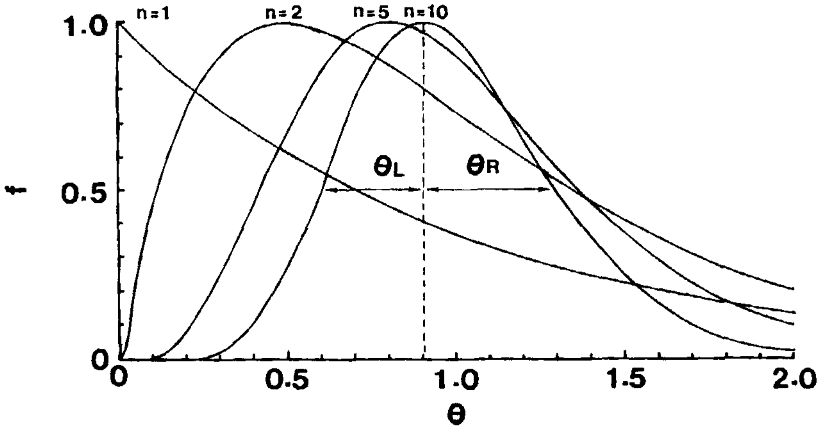

FIG. 3. Residence time distributions in continuous stirred tanks in series.

$$g(\theta) = \frac{n^n \theta^{n-1} e^{-n}}{(n-1)!} \tag{12}$$

Since $g(\theta)$ is maximum when $\theta = (n - 1)/n$, the elution curve whose peak height is normalized to unity is given by

$$f(\theta) = g(\theta)/g\left(\frac{n-1}{n}\right) \tag{13}$$

The parameter n of the Poisson distribution curve corresponds to the number of cells of the "continuous stirred cells in series" model for the description of the elution curve. The shape of the curve is changed as shown in Fig. 3 with increasing n. The degree of skewness is most conveniently evaluated as the ratio

$$\frac{(\text{right-hand side half width at half maximum } \theta_R)}{(\text{left-hand side half width at half maximum } \theta_L)}$$

as illustrated in Fig. 3.

The values of Ψ and θ_R/θ_L are 0.5 and infinity, respectively, when $n = 1$. As the value of n increases, the degree of skewness θ_R/θ_L decreases toward unity (no skewness) and Ψ approaches the value of Ψ for a Gaussian distribution curve.

TABLE 1
The Values of Ψ for Different Elution Curves

Elution curve		Ψ	Skewness factor θ_R/θ_L
Rectangular		1.0	1.0
Triangular		⅔	Arbitrary
Gaussian distribution		$1/\sqrt{2} = 0.707$	1.0
Poisson distribution:	$n = 1$	0.500	∞
	$n = 2$	0.680	2.18
	$n = 3$	0.693	1.74
	$n = 4$	0.698	1.57
	$n = 5$	0.700	1.48
	$n = 10$	0.704	1.30
	$n = 20$	0.706	1.20
	$n = \infty$	0.707	1.0

The values of Ψ for different shapes of the elution curves are summarized in Table 1. It shows that the value of Ψ in a Poisson distribution curve is close to that of the Gaussian distribution curve for *n* values as small as 2, although the curves are appreciably skewed ($\theta_R/\theta_L = 1.3$) even when *n* is as large as 10.

EXPERIMENTAL

The sample gas CF_3CHBrF was synthesized by fluorination of bromodifluoroethylene (CF_2CHBr) with cobalt trifluoride (CoF_3) for 30 min at 30°C in a way similar to that reported in the literature (*12*). The crude product containing 40% CF_3CHBrF was purified via bulb-to-bulb distillation followed by preparative gas chromatographic separation to yield 99% CF_3CHBrF. The sample gas thus prepared was contacted with tritiated water (1 mCi/mL) for a few minutes at room temperature in the presence of sodium hydroxide and dimethylsulfoxide. The CF_3CTBrF/CF_3CHBrF gas obtained was diluted with CF_3CHBrF to give a specific radioactivity of 0.6 μCi/mL. The level of radioactivity in the proportional counter was lower than the saturation level. No product originating from hydrolysis of the sample was observed in the radio-gas chromatogram.

The CF_3CTBrF/CF_3CHBrF gas mixture was sampled in a glass loop and injected into the radio-gas chromatograph. The amount injected was typically between 1 and 3 μmol. The injected sample was separated from such impurities as air with a Porapak-Q column (4ϕ × 200 cm) at 130°C.

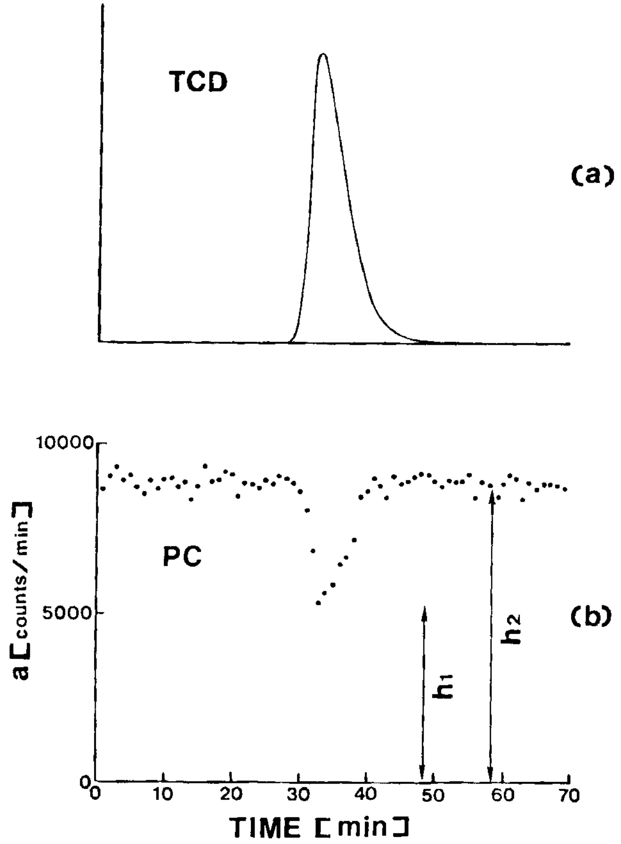

Fig. 4. Temporal decrease of *a* at the elution of CF$_3$CHBrF.

The amount of CF$_3$CHBrF was measured with a thermal conductivity detector (TCD) with reproducibility within 1%. Radioactivity of CF$_3$CTBrF was measured with an internal gas flow type proportional counter (Aloka FC2003) with a reproducibility of 3% with propane (30 mL/min) added just prior to the counter as a make-up gas to the helium carrier gas (90 mL/min). The radioactivity counting system consisted of a high voltage source (Ortec 759, 0-5 kV), a preamplifier (Camberra 2006E), an amplifier (Ortec 570), a single channel analyzer (Ortec 770), and a counter (Ortec 770/77x-01) with a timer (Ortec 719) and a printer (Ortec 777A). When an external radiation source was used for preliminary assessment of the quenching effect, a ^{22}Na standard source was placed at the center of the proportional counter.

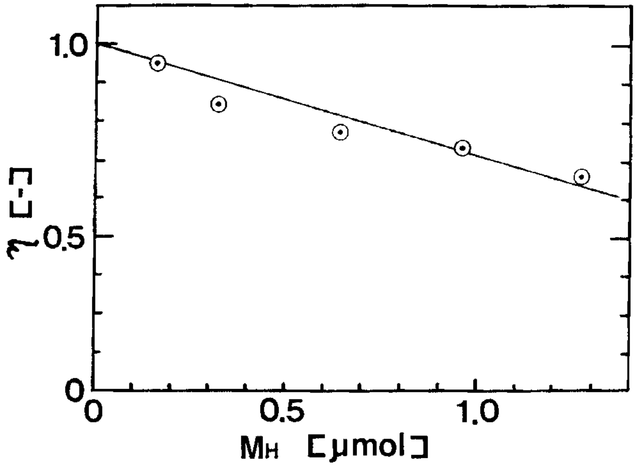

FIG. 5. η vs M_H in the experiment with ^{22}Na as the standard source.

RESULTS AND DISCUSSION

Figure 4 illustrates an example of the radio-gas chromatogram with the external radiation source, ^{22}Na. When the sample of CF_3CHBrF (without CF_3CTBrF) was introduced into the proportional counter, a dip due to quenching was observed as shown in Fig. 4(b).

When the volumetric flow rate of the carrier gas and the FWHM pulse width are kept constant the CF_3CHBrF concentration at the peak is usually proportional to the total amount of the injected sample. The radioactivity detection efficiency η was obtained as the ratio h_1/h_2 as shown in Fig. 4(b). The amount of sample injected, M_H, was varied systematically, and the relation between η and M_H was obtained (plotted in Fig. 5). It was confirmed that the linear relation as assumed in Eq. (5) held for this case. Such an experiment with an external radiation source is very convenient in estimating the overall detection efficiency, since it is obtained as the product of the detection efficiency η at the peak ($= h_1/h_2$ in Fig. 4b) and the value of Ψ in Table 1 that depends on the shape of the elution curve.

As the next step, the mixture of CF_3CTBrF/CF_3CHBrF was introduced into the radio-gas chromatograph. When the amount of mixture injected was varied with the specific radioactivity (or T/H ratio) unchanged, the total radioactivity A was found to level off with an increasing amount of injected CF_3CHBrF, M_H. The value A/M_H corresponds to the overall specific radioactivity averaged over the elution curve. When M_H is

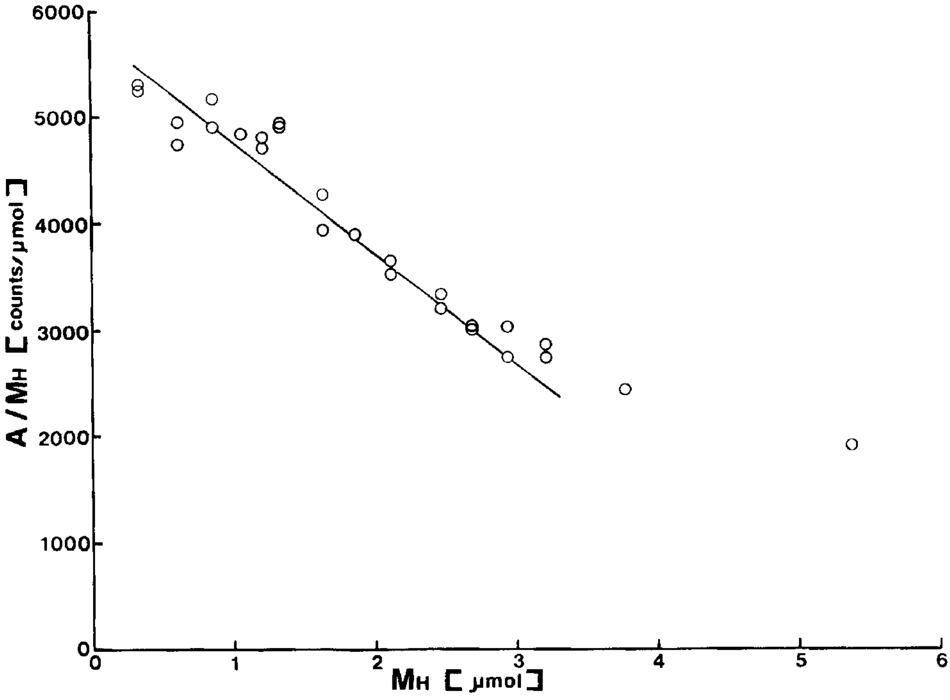

FIG. 6. Decrease of the specific activity A/M_H with increasing M_H.

decreased, A/M_H approaches the specific radioactivity $(A/M_H)_0$ where there is no quenching.

In Fig. 6 the overall specific radioactivity A/M_H is plotted against M_H. The value of $(A/M_H)_0$ was obtained as 5800 counts/μmol by extrapolating the linear relation between A/M_H and M_H when M_H is below 3 μmol. The overall counting efficiency $\bar{\eta}$ is obtained as $(A/M_H)/(A/M_H)_0$, which decreases linearly with increasing M_H when the quenching effect is not extremely serious. The deviation from the linear relation between M_H and (A/M_H) in the high M_H region presumably indicates that the simple assumption of Eq. (4) no longer holds in this region.

An Example of Application

In batch laser isotope separation, the specific dissociation rate b is defined as $-\ln(1 - X)/t$, where X is the fraction dissociated after t-pulse irradiation (*13*). The separation factor (selectivity) of laser isotope separation of tritium is obtained as the ratio b_T/b_H by using the relation

$$S = \frac{b_T}{b_H} = \frac{-\ln (M_{T2}/M_{T1})/t}{-\ln (M_{H2}/M_{H1})/t} \tag{14}$$

where M_T and M_H are the amounts of the tritiated and protonated substances, respectively, and the subscripts 1 and 2 correspond to before and after irradiation, respectively.

When there is no quenching, M_T is proportional to A_T. When the effect of quenching is not negligible, M_T is related to A_T as follows:

$$M_T \propto A_T\bar{\eta}(M_H) \tag{15}$$

where $\bar{\eta}$ is dependent only on M_H under the same gas chromatographic conditions. Consequently, the specific dissociation rate b_T for tritiated substance is obtained as

$$b_T = -\ln \left\{\frac{A_{T2}\bar{\eta}(M_{H2})}{A_{T1}\bar{\eta}(M_{H1})}\right\}/t \tag{16}$$

The value of $\bar{\eta}$ as a function of M_H can be obtained directly from Fig. 6.

A typical example of measurements with a proportional counter and a thermal conductivity detector is discussed next. Under irradiation conditions the radioactivity of CF_3CTBrF seemingly decreased by 15.1% (or $A_{T2}/A_{T1} = 0.849$), while the amount of CF_3CHBrF decreased by 15.7% after 10^4 pulse irradiation. The value of b_H was calculated as 1.71×10^{-6}. The value of b_T is obtained as 16.3×10^{-6} if there is no quenching effect. From Fig. 6, $\bar{\eta}(M_{H2})/\bar{\eta}(M_{H1})$ was obtained as 0.75. After the effect of quenching is evaluated, the value of b_T is corrected from 16.3×10^{-6} to 21.9×10^{-6}. Consequently, the apparent value of S (= $16.3 \times 10^{-6}/17.1 \times 10^{-6} = 0.95$) was found to be underestimated compared with the corrected S value of 1.28 in this case.

CONCLUDING REMARKS

Radio-gas chromatography is a very useful method to determine the separation factor in laser isotope separation of tritium. However, when the protonated sample quenches the radioactivity measurement of a tritiated sample with a proportional counter of the internal gas flow type, the measurement of the separation factor is seriously biased. In this report, theoretical analysis of radio-gas chromatography with quenching was performed, and it was shown that quantitative evaluation of radioactivity quenching was possible; the quenching is dependent on the elution curve and the amount of the sample.

Experimentally, it was found that the radioactivity detection efficiency is linearly dependent on the sample amount, and a method for the correction of the bias on the measurement of the separation factor was proposed.

SYMBOLS

A	total radioactivity count of the tritiated peak (counts)
a	time-dependent counting rate (counts/min)
C_H	concentration of protonated molecules (mol/cm^3)
C_{H_0}	characteristic concentration in Eq. (4) (mol/cm^3)
C_T	concentration of tritiated molecules (mol/cm^3)
f	$C_H/C_{H_{pk}}$ = dimensionless concentration
M_H	amount of protonated sample (mol)
M_T	amount of tritiated sample (mol)
n	number of tanks in the continuous-stirred-tanks-in-series model
Q	volumetric flow rate of the carrier gas (cm^3/min)
t	number of pulses
α	proportionality constant in Eq. (3) (counts cm^3 s^{-1} mol^{-1})
α_0	limiting value of α without quenching (counts cm^3 s^{-1} mol^{-1})
η	α/α_0 = time-dependent radioactivity detection efficiency
$\bar{\eta}$	overall radioactivity detection efficiency
η_{pk}	radioactivity detection efficiency at the peak
θ	time (min)

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