=단 신=

중수소 핵자기 공명을 이용한 외국 술과 국산 술의 비교 분석

한기정 · 이석근*†
한국화학연구소
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Application of Deuterium NMR Analysis for the Differentiation of Korean and Foreign Liquors

Gee-Chung Han and Sueg-Geun Lee*†

Korea Research Institute of Chemical Technology, P.O. Box 107, Yusung, Taejon 305-606, Korea

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Abstract: The ^2H NMR analysis was used to determine the relative deuterium contents at the position of methyl and methylene in ethyl alcohols. Four different liquors manufactured in Korea clearly showed different **R** values from those of foreign liquors. These **R** values for the Korean liquors could be used to distinguish adulteration.

Key words: ^2H NMR, SNIF NMR, alcohol

1. INTRODUCTION

Since the ^2H NMR was used to show large differences in the distribution of natural abundance at individual sites in ethanol derivatives in 1981,[1] quantitative ^2H NMR at the natural abundance level provides a new and efficient tool for investigating the origin of ethanols in various spirits and beverages.[2,3] Although ^2H NMR analysis was used in the restricted area, the recent NMR technology, high field magnet and new electronic development, has made possible the use of ^2H NMR as a routine work at the natural abundance level. Generally, the ^2H NMR analysis of alcohol was used in terms of the relative contributions of different monodeuterated molecules.[4,5]:

$$CH_2DCH_2OH(I):CH_3CHDOH(II) : CH_3CH_2OD(III).$$

In order to compare the quantity of the deuterated species (II) to that of (I), which is normalized to the statistical value of 3, we used the parameter, $R(II) = 3 \times S(II)/S(I)$, was defined by G. J. Martin.[5-10] Thus, the

parameter **R** generally represents the relative enrichment of the methylene site with respect to the methyl group and provides a means of distinguishing alcohol origins. Here we report preliminary result of the **R** values of Korean liquors.

2. EXPERIMENTAL

2.1. NMR experiment

^1H (500.13 MHz) spectrum was obtained using 5 mm QNP probe. ^2H(76.77 MHz) spectrum was obtained using 10 mm broad band probe. All spectra were recorded on Bruker AMX-500 spectrometer. Deuterium spectra requiring about 3 k scans (signal to noise ratio : over 120) were collected with 3 s relaxation delay and 1 k data points over a 415 Hz spectral width using a 30° pulse (acquisition time : 1.23 s). All ^2H spectra were observed under proton decoupling conditions and without lock. For the instrument shimming, the FID area was used in the acquisition mode. Data were processed using exponential multiplication with a 2.5 Hz line broadening and 5 degree of polynomial baseline correction. Internal isotopic ration, **R**(II), were calculated according to the formula, **R**(II) = 3 × S(II)/

†Corresponding author
Phone: 042-860-7710 Fax: 042-860-7704
E-mail: leesg@pado.krict.re.kr

S(I), where S(I) is the integrated area of methyl and S(II) is methylene group. The relative deuterium enrichment of each site was based on the integration of each deuterium peak. In order to determine whether saturation effects may be ignored for our pulse angles and repetition time (30° pulse and 4.23 s repetition time), the same pulse angles and a pulse repetition rate of 9.23 s was applied to the samples using the CH_3CN as an internal standard. Each deuterium peak was compared with that of CD_3CN for the two different repetition times. The negligible ratio change of the intensities in two sites suggests that the saturation effect is not important in this pulse conditions.

2.2. material

KA1-KA4 of samples are Korean liquors manu-factured in Korea. FA1-FA4 of samples are foreign liquors directly imported. All the samples were used directly without further purification.

3. RESULTS AND DISCUSSION

All experiments have been performed on alcohols manufactured in Korea (KA1-KA4) and foreign alcohols (FA1-FA4) imported. For the illustration pur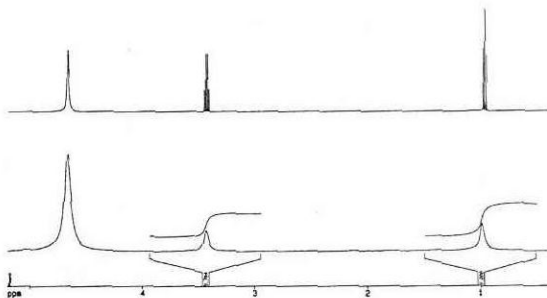pose, typical ^1H and ^2H spectra of alcohol are shown on Fig. 1. While ^1H NMR line half-width was 0.3 Hz and ^2H NMR line half-width was 2.5 Hz. As can be seen in Fig. 1, 2.5 Hz line half-width of deuterium NMR is narrow enough to distinguish the individual isotopomer on 76.77 MHz deuterium NMR. ^2H NMR spectrum has clearly been divided in three regions defining different groups of isotopomers as ^1H spectrum: CH_3, CH_2, and H_2O. Fig. 2 shows representative ^2H NMR spectra of Korean and foreign alcohols. The integrals of the deuterium NMR signal in Fig. 2 indicate the relative proportions of each of the chemically distinct monodeuterated species. The standard deviations of integration in ^2H NMR spectrum was within 0.01 which represents good repeatability of the NMR measurement. The results obtained by 10 determinations corresponding to each alcohols are shown in Table 1. Table 1 shows that the significant differences of R values exist between Korean and foreign liquors. The R values of the Korean alcohols were in the range of 2.33 to 2.41. However, the R values of foreign alcohols were in the range of 2.20 to 2.25. Thus, the natural deuteration of methylene site of Korean alcohols is higher than that of foreign alcohols. This interesting result indicates that the high field
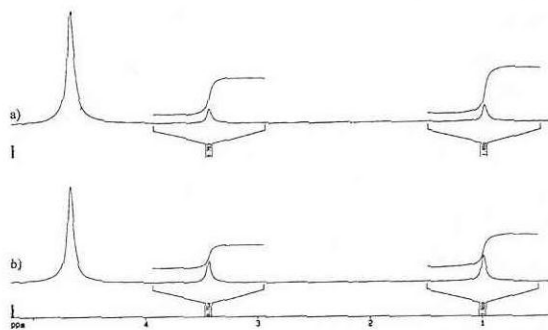

Fig. 1. ^1H NMR spectrum and natural abundance corres-ponding ^2H NMR spectrum of alcohol.

Fig. 2. Representative ^2H NMR spectra of Korean and foreign alcohols.
a) Korean alcohol b) foreign alcohol.

Table 1. Internal distribution of deuterium in alcohols. $R = 3 \times S(II)/S(I)$, where S the integrated area of signal I, II. (The value of the parameter (R) are averaged over 10 determinations and the standard deviations are within 0.01.)

	Korean alcohols				Foreign alcohols			
SAMPLE	KA1	KA2	KA3	KA4	FA1	FA2	FA3	FA4
R	2.36	2.34	2.33	2.41	2.24	2.25	2.20	2.20

quantitative ^{2}H NMR method may provide a simple and rapid way for adulteration and identifying Korean alcohols from foreign alcohols.

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