Quantitative Elemental Analysis of Sodium(^{23}Na) by NMR Spectroscopy

Heon-Sung Lim, Gee-Chung Han, and Sueg-Geun Lee*

Chemical Analysis Laboratory, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusung, Daejon 305-606, Korea
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One of the most useful components in NMR spectroscopy is the application of the peak area for the quantitative analysis. Although the use of proton NMR has been applied for the determination of trace components such as the residual hydrogen in D_2O,[1] the mixtures of dinitrotoluene,[2] and the mixtures of drugs,[3] its great merits have been ignored in the field of quantitative analysis because NMR method is inherently less sensitive than many other spectroscopic methods. The quantitative analysis using NMR spectroscopy, however, has been increased significantly during the last few years because of the development of new techniques including high-field NMR. Its applications are generally limited to the use of hydrogen nucleus.[4]

In our previous study, we reported that the accuracy and precision of the ^{31}P-NMR method are either comparable or superior to that of the conventional method (ASTM D 515).[5] In continuing study of heteronucleus NMR application in quantitative analysis, we attempted the analysis of sodium (^{23}Na) in solution. The sodium is one of the most abundant and the most frequently analyzed elements and its analysis methods are well established. In modern laboratory, the concentration of sodium in the solution is generally analyzed by AAS or ICP methods using an external standard.[6] These classical methods, however, could have factors, which disturb correct analysis, such as spectral, physical, chemical, and ionizational interference. Thus, these matrix effects, which could repress or enhance the radiation of the element to be determined to derive considerable error, are well documented.[7] Therefore, if the composition of sample is known, the error can be compensated by using calibrating solution through the time consuming procedures. On the other hand, the unknown matrix sample could not be calibrated by this procedure and could produce a result containing significant error.

In this study we report a new preferred alternative NMR method for the quantitative analysis of sodium in solution. Because of the natural abundance (100%) and quadrupole relaxation (I=3/2), sodium is a very amenable nucleus for NMR study.[8] Two case studies, which are the most extreme cases containing cobalt(Co) and silver(Ag) ion in the sample, are employed to show that this NMR method is comparable or superior to that of the conventional flame or ICP method in the analysis of sodium. The representative ^{23}Na-NMR spectra obtained on a Bruker DRX-300 spectrometer at 79.3 MHz equipped with 10 mm broad band probe are shown in the Figure 1. A singlet peak (δ 3.2 ppm) shown with same

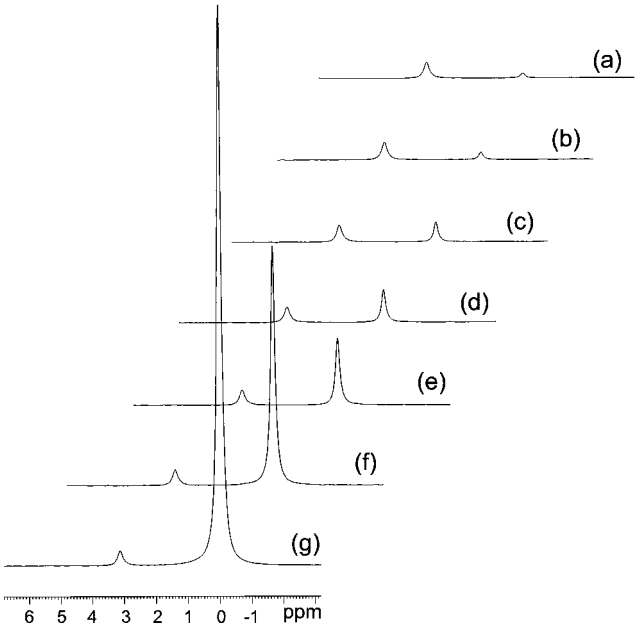

Figure 1. A stack plot of ^{23}Na-NMR spectra at various concentrations with 50 μg/mL Na and 7.7 mM Dy(TTHA) as reference. The concentrations (a-g) are 0.2, 1.0, 10, 20, 50, 200, and 500 μg/mL sodium.

intensity in all spectrum (a-g) is the peak of the 50 μg/mL sodium[9] which is contained with 7.7 mM of $Dy(TTHA)^{3-}$ at a 5 mm NMR tube[10] and placed co-axially in a 10 mm NMR tube containing various concentrations of sodium. The complex of dysprosium used here was a shift reagent and was made by the literature procedure.[11] This complex is widely used as a reagent to differentiate the content of intracellular and extracellular sodium in *in vivo* study.[11a,12]

The spectra were collected with 0.01 s relaxation delay, 0.9 s acquisition time, and 4 k data points over a 1,500 Hz spectral width using a 90° pulse. Because of the fast pulsing due to the quadrupole relaxation of sodium, the total acquisition time of each experiment was only about 10-60 min to get reasonable signal-to-noise ratio depending on the sample concentration. The ^{23}Na integration ratio of individual sample to the 50, 150, and 250 μg/mL sodium with shift reagent as an external standard showed the excellent linear regression coefficient (R^2 = 0.9998) in the range of 0.1 to 500 μg/mL sodium concentration (Figure 2). The different slope of calibration line for sodium concentration by the integration ratio of sample and reference solution clearly indicates that

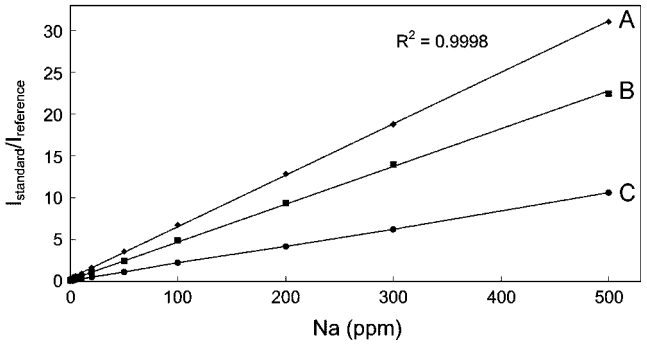

Figure 2. Calibration for 0.1-500 μg/mL sodium on different references and shift reagent concentration from ^{23}Na-NMR spectra {$I_{reference}$ = A: 50 μg/mL Na/7.7 mM Dy(TTHA), B: 150 μg/mL Na/20 mM Dy(TTHA), C: 250 μg/mL Na/20 mM Dy(TTHA)}.

construction of calibration plot is necessary for this analysis. It is possible to analyze for the lower concentration than 0.1 μg/mL when the lower reference concentration is exploited. Furthermore, its high dynamic range between sample and standard could get rid of experimental error followed by the sample dilution procedures in flame or ICP methods.

We applied these calibration results to two samples containing Ag and Co, respectively, which are impossible to analyze accurately by flame or ICP methods because of matrix effect. The results expressed in percent recovery are summarized in the Table 1 with the results obtained by ICP/AES and flame methods in 1 μg/mL of sodium. Relative standard deviations and relative percent accuracy were within 5%.

Table 1. Determination of sodium in silver and cobalt solution (10,000 ppm) by ^{23}Na-NMR [shift reagent and reference: 50 ppm Na with 7.7 mM Dy(TTHA)]

Na (ppm)	Recovery (%)[a]	
	Ag	Co
0.2	120	116
1.0	92 (842)[b]	91 (222)[b]
	(89)[c]	(110)[c]
10	98	97
100	99	99

[a]Average of 3-5 runs. RSD (%) was about 5%.[d] [b]Determined by ICP AES. [c]Determined by Atomic Absorption. [d]RSD (%) could be reduced by increasing the total acquisition time.

In conclusion, the method of sodium analysis by ^{23}Na-NMR is either comparable or superior to that of the conventional flame or ICP methods. Although the total acquisition time is the limiting factor for this analysis, this problem could be improved significantly using high field instrument. Especially, the advantages of this NMR method over the other methods are the selectivity and simplicity of procedure.

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9. KOH, which was used for making complex, contained sodium as impurity and its concentration was determined by AAS. Therefore, the concentrations of sodium ion as reference were made with those amounts in KOH and the addition of Aldrich calibration standard solution.
10. Dy(TTHA)^3 is the complex of dysprosium trichloride with triethylenetetraaminehexaacetic acid. The concentration of shift reagent changes the chemical shift of sodium.
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