Discernment of Chemical Shift in MRMI System Simulation

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Abstract: - This paper describes an industrial magnetic resonance multiple imaging (MRMI) system that measures nuclear magnetic resonance of several kinds of nuclei and functional group simultaneously. We use a new reconstruction principle of CT. Then we reconstruct distribution images of nuclear magnetic resonance (NMR) without using usual gradient coils. We propose an image reconstruction method of a new industrial MRMI for non-destructive test. Finally, we show simulation results for it.

Key-Words: - Magnetic Resonance Multiple Imaging (MRMI), Chemical Shift, Free Induction Decay (FID), Fast Model Reconstruction (FMR), Wavelet

1 Introduction

Since the discovery of NMR in 1946 [1], its technologies have evolved in the chemical field. Recently, MRI is thought to be safe because a radiation is not used as in X-ray CT. Therefore, MRI is anticipated for application in medical fields [2]-[5]. Importantly, industrial MRI must be inexpensive to address demands to reconstruct inner structure of objects in the industrial sector.

In present MRI, a superconductive magnet and a permanent magnet are used for the static magnetic field magnet. The former use a strong magnetic field and are costly; the latter are neither strong nor expensive. We adopt the latter permanent magnet as the static magnet for industrial MRI.

Specifying a substance and the NMR method has been developed in the field of the molecular structure analysis for an organic compound. By the NMR method, the atom and molecule which are contained in an object can be specified using that resonance phenomena happen in specific frequency according to the kind of nuclei, and a chemical shift. Chemical shift is the slight difference in the resonant frequency produced by difference of the character of a nuclear chemical bond [6].

We propose the Fast Model Reconstruction (FMR). It is a new CT technique that can reduce the calculation burden against the back projection method. Using this technique, we can reconstruct images inexpensively and rapidly using a small amount of projection data from a few directions.

In present MRI, several nuclei are not detected simultaneously because occurrence parts of the NMR-signals are specified according to magnetic field strength in the gradient magnetic field. Accordingly, this study is intended to depict magnetic nuclear resonance of several nuclei and functional group simultaneously. This proposed industrial MRI system does not use gradient coils. In addition, we use FMR method to compute simulation of this system.

2 NMR Imaging

2.1 Nuclear Magnetic Resonance

The NMR system has been developed in the field of molecule structure analysis for organic compounds. A magnetic resonance phenomenon occurs at a specified frequency representing each nuclei, corresponding to magnetic field strength. This frequency is called the Zeeman frequency. The example is shown in Table 1. Therefore, we know the type of nuclei contained in the target object. The main detection objects of MRI for medical study are [1]H-nuclei, which offer good detectability and are ubiquitous in living bodies. An applicable object irradiates a RF pulse which contains the resonance frequency of nuclei. Accordingly, a NMR-signal is detected in a form that contains NMR-signals of various nuclei.

Table 1. An example of NMR applicable nuclei

Nuclei	[1]H	[13]C	[15]N	[31]P
v_0 [MHz]	42.58	10.71	4.31	17.24

v_0 is a Zeeman frequency at B=1tesla

2.2 Position Specification by Gradient Magnetic Field

The difference in the frequency spectrum by the existence of a gradient magnetic field is shown in Figure 1. A gradient magnetic field is used to specify the occurrence part of the NMR-signal in usual MRI. Gradient magnetic field(G_x) is used in order to give the difference of a magnetic field. Since magnetic field intensity differs according to each position, the resonance frequency of a nuclei also differs, and with a position, the spectrum obtained appears as a difference in frequency, and can specify the occurrence part of signal. Therefore, it is difficult to reconstruct a density distribution image of several nuclei simultaneously.
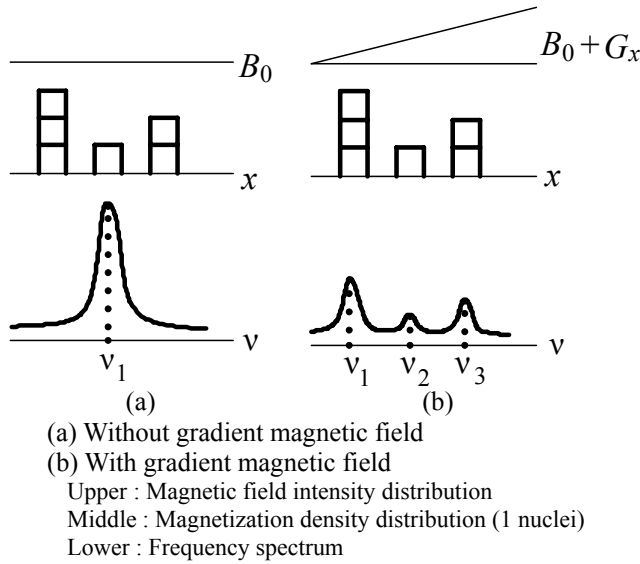

(a) Without gradient magnetic field
(b) With gradient magnetic field
   Upper : Magnetic field intensity distribution
   Middle : Magnetization density distribution (1 nuclei)
   Lower : Frequency spectrum
Fig.1. Specification of signal generating part by gradient magnetic field

2.3 Propose NMR Imaging

It is possible to construct an MRI system that detects several nuclei simultaneously if the occurrence part of the NMR-signal can be specified without using gradient coils. With this perspective, we examine a new industrial MRI system that detects several nuclei without using expensive gradient coils.

By combining a NMR phenomenon and the back projection reconstructing method, the NMR signal of several nuclei is specified, without using a gradient magnetic field.

As shown in Figure 2, without using a gradient magnetic field, the atom and molecule which are contained in the object can be specified. Because the resonance frequency in several nuclei is differing.

We have been proposed a hardware construction of NMR imaging[7]. Industrial MRI systems must have lower unit cost than medical MRI, in general. A permanent magnet is used as a static magnet to reduce cost. The RF pulse has the frequency bandwidth where several numbers of nuclei cause NMR phenomena in the object. The RF pulse is irradiated into the object from the transmitter. The NMR-signals are detected in the receiving part that opposes the transmitting part. They pass through LPF after NMR-signals are multiplied by the reference signal of every nucleus. Therefore, the NMR-signals are separated into signals of each nucleus. Images are reconstructed using those data in each nucleus.

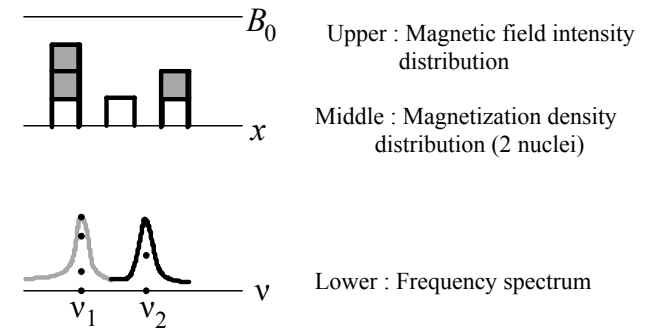The NMR-signals obtained by this hardware construction are transverse relaxation signals.

Upper : Magnetic field intensity distribution
Middle : Magnetization density distribution (2 nuclei)
Lower : Frequency spectrum

Fig.2. Nuclear magnetic Resonance in 2 nuclei

3 Theory

3.1 Detection of NMR-signals

A basic equation in NMR is shown in the following:

$$\omega = 2\pi\nu = \gamma B , \qquad (1)$$

where ω is an angular frequency, ν is a Zeeman frequency, γ is a gyromagnetic ratio, and B is magnetic flux density.

In general, resonance frequency in nuclei changes along the direction of the gradient magnetic field, i.e. an occurrence location of a NMR-signal is specified by introduction of a gradient magnetic field. Here, we suppose that magnetic flux density is fixed only by the permanent magnet. Based on that idea, we attempt to get NMR-signals for several nuclei. The NMR-signal of several nuclei is separable from the detected one because resonance frequencies of respective nuclei are different. Therefore, NMR-signals of several nuclei are detected and their images are reconstructed simultaneously. We

simulate such a process using free induction decay (FID) signals that are NMR signals after a 90° pulse. On the projection line of the RF pulse, a FID signal($s(t)$) is the value at which distribution density of magnetization ($m(x,y)$) was line-integrated along that axis. The FID-signal for several numbers of nuclei is shown in the following.

$$s(t) = \sum_{i=1}^{N} \int_{0}^{L} m_i(x,y) \exp(-i\gamma_i Blt/T_{2(i)}^*) dl \qquad (2)$$

In that equation, L is the distance between the transmitting part and receiving part, $T_{2(i)}$ is a transverse relaxation time, and i means the kind of nucei($i=1,2,\ldots$). A detected NMR signal is shown in the form of the sum of a signal each of nucleus, which decreases by an exponential function. The FID-signal of each nucleus is extracted if the detected one is separated. Therefore, the NMR-image can be reconstructed as well as the method in CT if we detect FID-signals from various directions.

3.2 Chemical Shift

With the character of a nuclear chemical bond, NMR occurs in different resonant frequency. This is called chemical shift. The difference of the resonant frequency(ν_r) of a standard substance and the target resonant frequency(ν) of a nuclear chemical bond is shown in the following:

$$\nu - \nu_r = \frac{\gamma B}{2\pi}(\sigma_r - \sigma) \qquad (3)$$

where σ is shielding constant.

In the case of many nuclei, such as ^{1}H, ^{13}C, and ^{31}P, since it is very small as compared with the resonance frequency of the nuclei, a chemical shift expresses with ppm, applying the 6th power of 10.

$$(\nu - \nu_r)/\nu_r \times 10^6 \qquad (4)$$

By using a chemical shift, magnetization of a specific functional group is extracted from the NMR signal containing several functional groups.

3.3 FMR method

We propose the FMR method[8], which is a method to reconstruct an image from a minimum number of directions by combining the wavelet-sampling model with the singular-valued decomposition. Relations between the projection value (p) and strength value (f) of each frequency element are shown in the following:

$$p = \int_{0}^{L} f(x,y) dl \qquad (5)$$

$$p = \int_{0}^{L} \sum_{i=0}^{n-1} \sum_{j=0}^{n-1} f(x_i, y_j) \cdot W(x-x_i) \cdot W(y-y_j) dl$$

$$= \sum_{i=0}^{n-1} \sum_{j=0}^{n-1} f(x_i, y_j) \cdot \int_{0}^{L} W(x-x_i) \cdot W(y-y_j) dl$$

$$= \sum_{i=0}^{n-1} \sum_{j=0}^{n-1} f(x_i, y_i) \cdot C_{ij} \qquad (6)$$

where $W(x)$ is sampling function. Projection value is computed by line-integrating strength value.

The reconstruct-coefficient matrix multiplied by the projection value is the strength value, which is shown in the following.

$$f = C^+ p \qquad (7)$$

We introduce a two-dimensional projection scanning system to maintain nature to irradiate uniformly (Figure.3).

If the nature irradiated unanimously is held, the row of the reconstruct-coefficient about a series of each beam becomes the same in every pixel.

Computation structure of the reconstruct becomes similar. Furthermore, a good image can be composed of projection data in the extreme minor direction with the projection scanning form that it does like this and the nature irradiated unanimously is held at high speed by the FMR method.
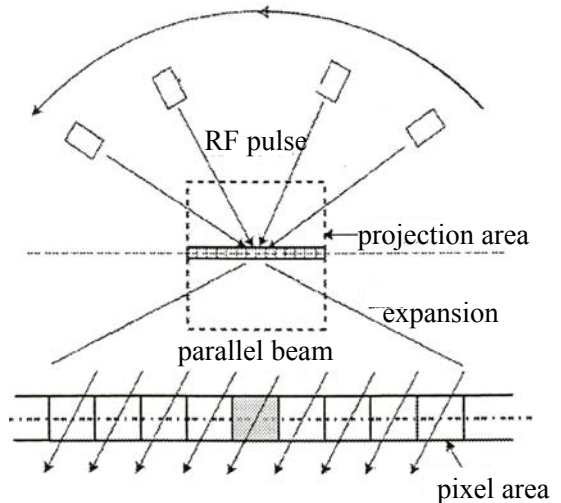

Fig.3. Two-dimensional projection scanning

4 Simulation Result

4.1 Formation of NMR-signals

We presume that four nuclei comprise the target.

- ^{1}H-nuclei: These nuclei are generally used for MRI; they offer good detectability.
- ^{13}C-nuclei: These nuclei, along with hydrogen, specify an organic compound.
- ^{15}N-nuclei: These nuclei are useful in detection of explosives.
- ^{31}P-nuclei: These are important nuclei for the field of physiology.

Moreover, to ^{1}H-nuclei NMR, the simulation is performed by using TMS(Tetramethylsilane) as a standard substance about a possibility of identifying and detecting magnetization of a methyl group(-CH$_3$) and a carboxyl group(-COOH) from acetic acid (CH$_3$COOH).

The static magnetic field is uniform and is set to B=0.611tesla.

The NMR signals are shown in the following:

$$s(t) = \sum_{i=1}^{N} m_i \exp(-i2\pi \nu_i Bt) \exp(-t/T_{2(i)}{}^*)$$

$$= \sum_{i=1}^{N} m_i \exp(-i\omega_i t) \exp(-t/T_{2(i)}{}^*) \qquad (8)$$

I suppose that magnetization (m_i) has an expanse of space. m_i are calculated by using the projection value and the sinc function by the following equation.

$$m(i) = \sum_{j=-n}^{n} p(i+j) \cdot \mathrm{sinc}\,(j) \qquad (9)$$

5.2 Separation of the NMR signal

The NMR-imaging is multiplied by the reference signal of each nucleus; signals are extracted in every nucleus, as indicated in the following expression.

$$\exp(-i\omega t) \cdot \exp(i\omega_{0i}\, t) = \exp\{-i(\omega - \omega_{0i})t\}$$

$$= \cos\{(\omega - \omega_{0i})t\} - i\sin\{(\omega - \omega_{0i})t\} \qquad (10)$$

In those equations, ω is the angular frequency of NMR-signals; ω_{0i} represents the reference signals.

It passes through LPF, and the magnetization of several nuclei is computed by complex FFT.

From the NMR signal in several nuclei, the result which computes magnetization is shown in Figure 4 and Table 2. The chemical shift can be detected and identified.

5.3 Reconstructed Images

Using signals of every nucleus yielded reconstructed images by the FMR method, as shown in Figure.5. All were considered to have the same beam width as X-rays. Then, projection distribution was calculated.

I evaluated the reconstructed images by normalization error dispersion (E) is shown in the following:

$$E = \sqrt{\dfrac{\displaystyle\sum_{n=1}^{N}(F_n - f_n)^2}{\displaystyle\sum_{n=1}^{N}(F_n - F)^2}} \qquad , \qquad (11)$$

where F is an average of original image, F_n is specimen point density of original image, f_n is specimen point density of reconstructed image. E in each image is shown in the Table 3.
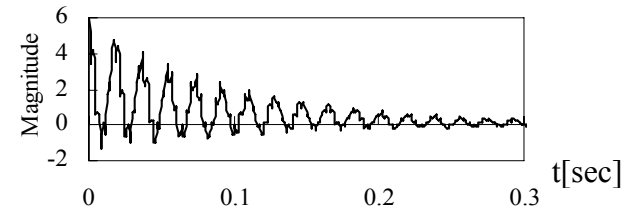
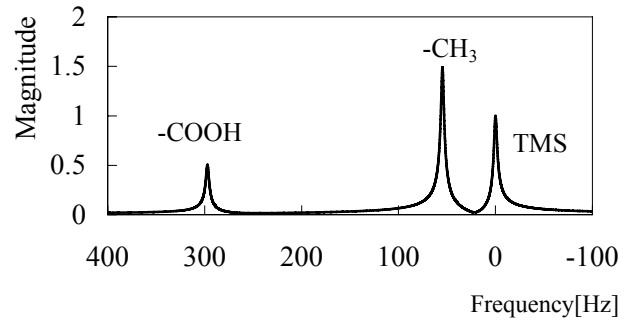I can get good images with small error.
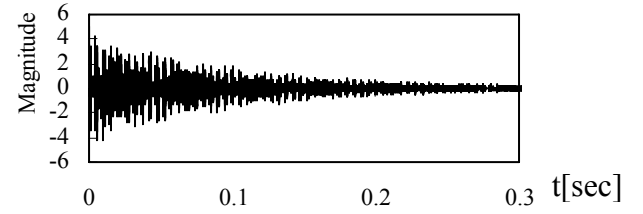
(a) FID-signal(several nuclei are included)
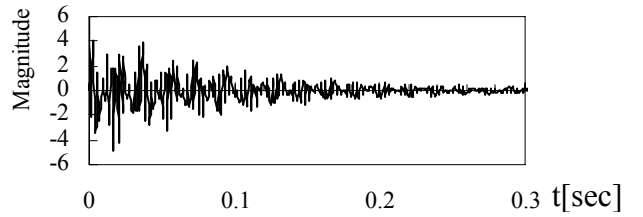
(b) FID-signal(multiple the ^{1}H reference signal)

(c) ^{1}H FID-signal(path through LPF)

(d) ^{1}H spectrum(Resolution: 0.061Hz)

Fig.4. Result of signal processing

Table 2. ^{1}H spectrum data

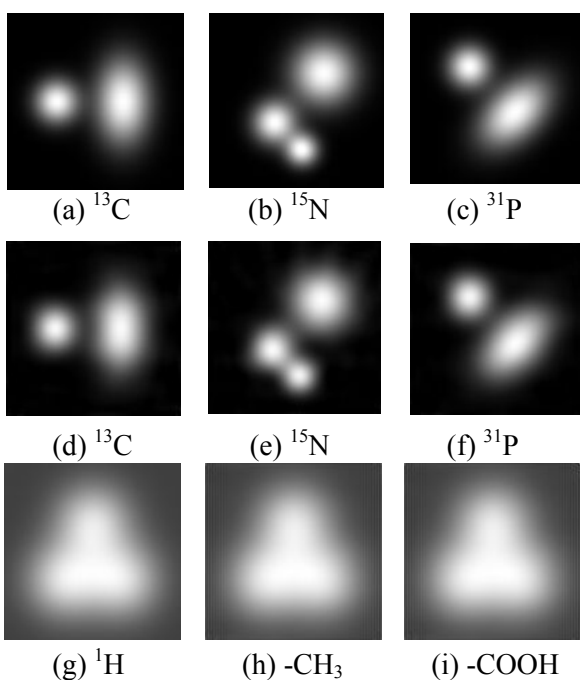|	Lv.	Int.	CS1	CS2	CS3
TMS	2	1	0	0	0
-CH$_3$	3	1.490	54.626	2.100	2.098
-COOH	1	0.507	297.241	11.425	11.42

Lv.: Setting intensity level
Int.: Intensity of a TMS standard
CS1: Chemical Shift[Hz](by Figure 4.(d))
CS2: Chemical Shift[ppm](by Formula 4)
CS3: Chemical Shift[ppm](by Reference[9])

(a) ^{13}C	(b) ^{15}N	(c) ^{31}P

(d) ^{13}C	(e) ^{15}N	(f) ^{31}P

(g) ^{1}H	(h) -CH$_3$	(i) -COOH

Size of Images: 128×128 pixels
Original images: (a)-(c), (g)
Reconstruction images: (d)-(f), (h), (i)
Fig.5. Simulation results (Normalization images)

Table 3. Normalization error dispersion of images

	^{13}C	^{15}N	^{31}P	-CH$_3$	-COOH
$E×10^{-2}$	5.65	5.97	4.77	5.56	5.80

5 Conclusion

This study introduces a new MRI system without gradient coils. In addition, we examined the validity of that system.

Characteristics of this new MRI system are:
- An inexpensive permanent magnet is used to build the static magnet for MRI equipment.
- MRI equipment structure is simplified because gradient coils are not used.

- NMR-signals of several nuclei are each detected simultaneously.
- The chemical shifts of several functional groups are computed from frequency spectrum.
- Nuclei distribution images are reconstructed rapidly and inexpensively using the FMR method.

Dangerous objects in luggage or other packages may be detected by combining organic chemistry analysis with this system. The MRMI system proposed in this paper is under development.

In the future, we will experiment with MRMI system and compute automatically magnetization from the signal containing a noise.

Finally, the new MRI system introduced in this paper may be applied to non-destructive detection equipment for detecting and depicting concealed dangerous objects in mail, parcels, airport luggage, food evaluation, and so on.

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