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JEOL, NMR and ESR: A 65 year evolution

Eguchi Keiji

NM Group SI Sales Promotion Department JEOL Ltd., Otemachi Nomura Bldg. 13F, 2-1-1, Otemachi, Chiyoda, Tokyo 100-0004, Japan

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ABSTRACT

Felix Bloch and Edward Purcell successfully detected NMR signals in 1946, and VARIAN was the first company in the world to complete a commercial product in 1950. JEOL released their first commercial NMR instrument 6 years later. At that time, the magnetic field intensity was 30–40 MHz, so the ability to separate signals was extremely low. The users of NMR wanted higher magnetic fields, and the key issue for NMR manufacturers became how to increase the magnetic field strength. With a permanent magnet, the maximum magnetic field is 90 MHz (2.11 Tesla), and the limit with an electromagnet is 100 MHz (2.4 Tesla). This limitation was removed with the advent of superconducting magnets (SCM). Furthermore, in addition to the Continuous Wave method, which only allowed observation of 1H nuclei, Pulse Fourier Transform (FT) methods were developed, enabling observation and measurement of 13C and other nuclei. The development of SCM and FT was epoch-making for NMR, and the field has flourished since then. Of course, there has been technical innovation that could not be accomplished by the NMR manufacturers alone, such as the development of superconducting materials and winding techniques for SCM, and new algorithm development and the acceleration of computing speeds for FT. This report will relate the story of NMR, including these developments that have provided the background.

1. Introduction

I joined JEOL in 1965 and was assigned to the NMR technology sales promotion team. There were no superconducting magnets, it was the era of electromagnets, and it was the year after 100 MHz JNM 4H100 was released. That was when we tried to improve the reliability of the 60 MHz and 100 MHz excitation power supplies, which utilized vacuum tubes, by adopting transistors (low impedance). In 1970, the Fourier Transform instruments became commercial products, and I was stationed to JEOL (UK) to work on seriously growing the NMR market, and began NMR sales promotion activities not just in England, but throughout Europe. After returning to Japan in 1980, I was involved in the development of NMR devices, including the development of several of the devices described later.

I guess you could say that I have been with NMR throughout the 50 years of tumultuous progress in the hardware, software and applications, from the era of low magnetic fields, CW NMR and the heyday of ^{1}H one-dimensional NMR, to Pulse FT NMR, superconducting magnets, 2D NMR, NMR imaging, and ultra high magnetic field NMR.

Table 1 introduces the technological changes that have occurred over the past 50 years.

2. Back story of NMR development

In 1946 Felix Bloch and Edward Purcell successfully detected NMR signals. In Japan, NMR signals were successfully detected by Shizuo Fujihara and Shoichi Hayashi at the University of Electro-Communications (UEC) in 1950 (See Fig. 1).

At the time that JEOL began paying attention to NMR, the instruments were regarded as extremely specialized devices for research, and there were many people opposed to trying to develop commercial products because of the questionable marketability.

On the other hand, although the marketability was not clear, the fact that no other manufacturers were working on it, and there was an opportunity to develop a unique and distinctive product, after nearly a year of deliberation, JEOL started work on the prototype Unit No. 1 in December 1955.

The initial issue for the development was whether to use a permanent magnet or an electromagnet. At that time it was considered extremely difficult to make an electromagnet with a uniform magnetic field and good stability. With a large electromagnet, not only are there issues with the stabilization of the excitation power supply, there is also a magnetic hysteresis phenomenon, in which the magnetic field distribution changes every time that the power is turned on or off. So, based on the technology at that time, permanent magnets were thought to be better for NMR. With a permanent magnet, if you carefully polish the

E-mail address: eguchi@jeol.co.jp

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Table 1

1949	1949 JEOL Established	
1956	JNM-101	JEOL's first commercial NMR 32 MHz(7000Gauss)
1957	JNM-3-40	40 MHz
1960	JNM-3H40	Super stabilizer, Current Shim, New type probe, Flat bed Recorder.
1962	JNM-3H60	60 MHz, External NMR Control, Spin Decoupler, Integrator
	JNM-C60	60 MHz Compact type NMR
1964	JNM- 4H100	100 MHz, ^{1}H ^{19}F ^{13}C ^{14}N ^{31}P ^{2}H, Internal lock.
1966	JNM-C60H	NSS method, Resolution stabilizer, NMR control.
1967	JNM-MH60	Ease of use high performance (award the IR100)
1968	JNM-C60HL	Low impedance Magnet
1969	JNM-PS100	100 MHz Low impedance magnet ^{2}H lock
1970	JNM-MH100	100 MHz
	JEC-6 High speed computer	
1971	PS/PFT100	FT NMR system
	New Jersey Application center open (Dr. Thomas. C. Farrar)	
1972	JEC-100	Mini computer (Ti 980 CPU, Light pen system)
1973	JNM-PMX60	Permanent magnet
1974	JNM- FX60,	C/H Dual probe
1976	JNM-FX 100	Digital quadrature detection (DQD), Light pen control system auto stacking software, World first multi nuclear probe
1977	World's first triple resonance experiment capability $^{13}C\{^{1}H\}\{^{19}F\}$ 1.7 mm probe for FX-100	
1977	JNM-FX60Q	DQD, solids capability
	World first LC-NMR by FX60Q	
1978	JNM-FX90Q	World first "Omni"probe:1.7 mm 5 mm, 10 mm insert changeable, C/H, Multi nuclear probe module changeable
1979	JNM-FX200, 270, 400	FG/BG, light pen, CH switchable probe, tunable probe, solid state CPMAS
1981	JNM-GX series	World first full Automatic spectrometer
1985	Auto tune probe	World first Automatic Probe
1986	Automatic sample changer	
1988	Delivery of LCNMR for supercon system	
	Micro NMR Imaging system 270WB SCM	
1990	Lagrange shim	World first 44ch Shim
	High pressure NMR probe for 270WB (2000 atm)	
	World first liquid Nitrogen refill system	
1991	Alpha series	DEC VMS industry std computing shaped pulse World first Work Station
1994	Lambda Unix, Eclips	Delta software Using SGI computer
1996	AL series	World first WINDOWS® PC NMR
1997	Eclips+	Upgrade of Eclips
1999	^{2}H Gradient shimming using homospoil	
2002	ECX ECA series	World first Multi sequencser NMR
2003	World First 920 MHz delivered	
2004	World First 930 MHz delivered	
2005	Delta software PC linux Mac free software	
	World first Mac software	
2014	World First over 1 GHz NMR (1020 MHz)	
2014	ECZ series	Newly developed technology of smart transceiver system
2015	World First 120 kHz sample spinning	

magnetic pole surfaces, and use the portions with good uniformity, it is possible to obtain a relatively stable magnetic field. In those days there were several companies in Japan capable of producing large permanent magnets that could be used for NMR, but there had to be a reexamination of the magnet structure to be suitable for use in a high resolution instrument. In addition, even after buying a magnet product, it was still necessary to perform the additional polishing mentioned above.

As a result, it was eventually decided to adopt a large electromagnet, based on the foundation of the technologies for manufacturing the stable excitation power supplies that were used for the electron microscopes. There was also a strong desire to be able to vary the value of the magnetic field, and a need to improve the

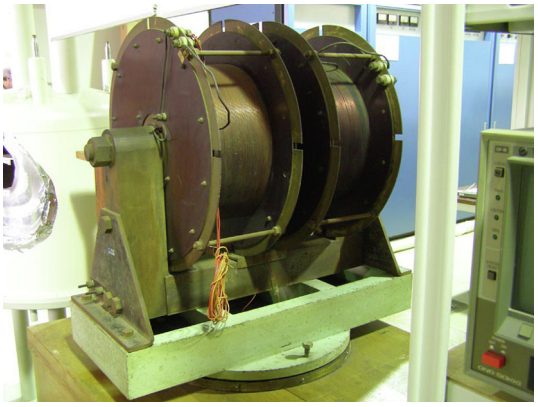

Fig. 1. First NMR instrument produced in Japan (exhibit at the UEC Communication Museum).

machining precision of the magnet poles in order to obtain a magnetic field with good uniformity, so that was another reason that it was better to have a structure to rework the finish of the surfaces. However, there were a lot of problems that had to be solved, such as the development of an excitation power supply with a power that was an order of magnitude larger than that for the electron microscope, and stability that was 1 to 2 orders of magnitude higher, as well as figuring out how to obtain the pure iron for the magnet material, and how to polish the mirror finishes and measure them. For this reason we enlisted the help of people involved in joint research with Shuzo Hattori (who was an assistant to Professor Kantaro Senda of Kanazawa University at that time), and received a lot of guidance from these experts.

Unit No. 1 was called the JNM-1 model, and was completed in August 1956, with a resonance frequency of 32 MHz. The magnet used in this instrument was an electromagnet with a bore of 150 mm; and the pole pieces, poles and yoke were all made from pure iron (see Fig. 2).

In an effort to produce instruments with an even higher resonance frequency, the development of larger magnets with a bore of 300 mm was started in July 1956, even before the completion of Unit 1. In 1957 the 40 MHz JNM-3 model was developed, followed by the 60 MHz JNM-3-60 model in 1962. The weight of these magnets was enormous, about 2.8 tons.

Continuous wave (CW) NMR: At that time, the usual method was to sweep the magnet field or the frequency to obtain a spectrum, which was printed onto a drum recorder for observation. It

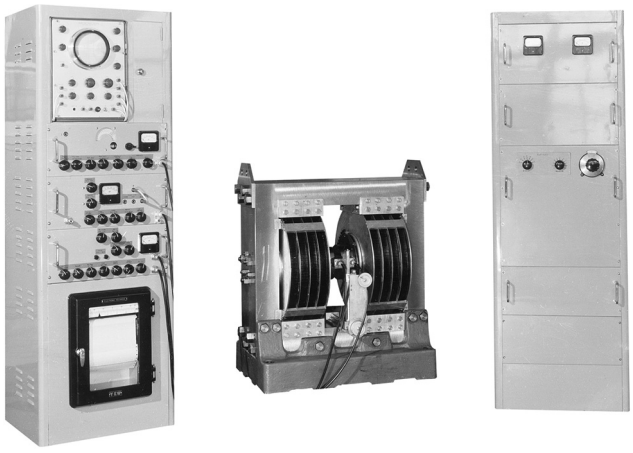

Fig. 2. JNM-1: First NMR instrument.

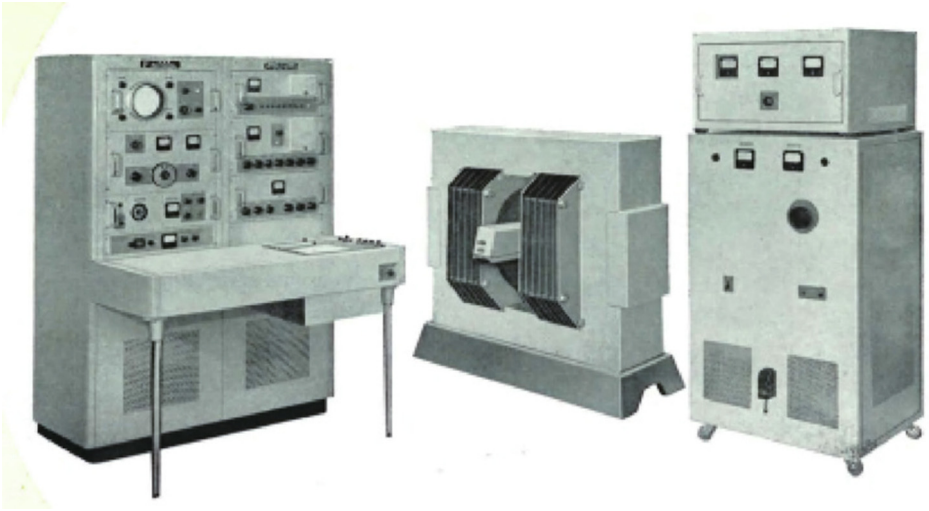

Fig. 3. JNM-4H100: The power supply chassis is large because vacuum tubes were used for the excitation power supply.

was not uncommon to be waiting for an expected signal to appear, but see only noise (see Figs. 3 and 4).

3. Changes in NMR technology

3.1. History of NMR equipment

1956 to 1970
Stability improvements:

Spectrometer	Changing from an autodyne detection method to a superheterodyne method using crystal oscillators enabled stabilization of the high frequency waves. The autodyne method has a relatively simple circuit structure, but the frequency stability is low. Since crystal oscillators are used for the superheterodyne, stability can be obtained for exceptionally high frequencies, and the sensitivity (signal-to-noise (S/N) ratio) is also improved. (applicable instruments: 3H-60 and later) Excitation power supply Stability was improved and the amount of heat generated was greatly reduced by switching from vacuum tubes to power transistors. Vacuum tube power supply: Vacuum tubes were used in the excitation power supply for the magnets of the JNM-3H-60 and 4H-100 in 1962 and 1964, so huge amounts of heat were generated, enough to boil water in a kettle placed on top of the power supply. The excitation power supply had to be installed in a separate room from the magnet, and dedicated air conditioning equipment was required. From 1968, with the switch to transistors, the instruments became smaller in size and required less power. (applicable instruments: C-60HL and later)

Magnetic field stabilization with super stabilizers:

At the start of development, the stability of the excitation power supply was about 10^{-6} at best, but NMR requires a stability of 10^{-8} to 10^{-9}. Super stabilizers were developed to address this problem, making it possible to achieve instantaneous stability of 10^{-9} and long-term stability of 10^{-8}. The early super stabilizers were mechanical mechanisms called galvanometers, which tended to malfunction when subjected to vibration, but later, super stabilizers using semiconductors were developed (applicable instruments: 3H-40 and later).

NMR lock:	The NMR lock is a stabilization circuit developed to achieve a long-term stability of 10^{-9}. An NMR signal is used, and the changes in the magnetic field are fed-back to the excitation power supply to obtain the long-term stability. There are internal and external lock methods for the NMR lock. For the external lock method the signal from a lock sample (usually, doped water) that is placed separately from the measured sample is used. For the internal method, the TMS signal or signal from a deuterated solvent mixed into the measured sample is used. Both methods were used with the electromagnets, but only the internal lock method is used with the superconducting magnets due to the physical limitations (applicable instruments: 3H-60 and later).
Uniformity improvement:	Magnetic field uniformity was improved with current shimming. The homogeneity of the magnetic field depends on the characteristics of the pole pieces attached to the tip of the magnet. Efforts were made to improve the precision of the surfaces by polishing, and to mechanize the surface finishing using lapping machines; but, there is a limit to mechanical precision improvements. Therefore, a current shimming technology was developed to generate an additional magnetic field to perform correction. (applicable instruments: 3H-40 and later)

Fig. 4. JNM-C60HL: A smaller footprint. Transistors are used for the excitation power supply, and the spectrometer, magnet and power supply can be integrated into a single unit.

Introduction of sample spinning:

In order to average out the non-uniformity of the magnetic field for a sample, spinner technologies were developed to spin samples placed inside tubes at high rotation speeds. This made it possible to acquire higher resolution spectra (applicable instruments: 3H-40 and later)

Stronger magnetic fields:

Magnets were developed to create even stronger magnetic fields: 32 MHz, 40 MHz, 60 MHz, 90 MHz and 100 MHz. The highest magnetic field with the electromagnet was the 100 MHz (2.4 Tesla) field.

1971 onward

Transition from CW to FT NMR, and progress in computer performance, technology and software.

Shift from CW (Continuous Wave) to FT (Fourier transform) NMR:

The completion of the JRA-1 integrators made an integration method possible, allowing NMR sensitivity to be improved. With this kind of method, sensitivity can be significantly increased, by a factor of 4 by repeating the integration 16 times, and by a factor of 5 with 25 repetitions. However, when observing ^{13}C nuclei, the relative sensitivity is low, making it necessary to greatly increase the number of integrations. Since one repetition took about 10 min, in actual practice, it was only possible to perform a few hundred integrations at most, so there was a limit on the sensitivity improvement that could be obtained. In comparison, with a pulse Fourier method (hereafter FT method), an instantaneous pulse is added, and the entire frequency range of the signal distribution is resonated. By applying a Fourier transform to the waveform of the response signals, the resonance frequencies and the signal intensities can be determined. In this case, the acquisition of a signal can be completed in a few seconds, allowing the number of integrations (repetitions) to be increased significantly.

This resulted in the transition to the era of FT NMR (applicable instruments: PFT-100, FX-60 and later).

It was decided to transfer the development of FT NMR to the United States, where nuclear magnetic resonance equipment technology was progressing, and a research lab (New Jersey Lab) was established at the same time that a new business office was opened in Cranford, New Jersey, with researchers sent from Japan. At this time, close collaborative development was conducted between the research group in New Jersey and JEOL headquarters, with the cooperation of Dr. Thomas C. Farrar. For the FX series spectrometers, the use of microprocessors and advanced integrated components, and the modularization of structural components by function contributed greatly to improvements in the performance and shortening of the development times. Thus, the JNM-FX60 model FT-NMR based on the Texas Instruments 980 computer was completed in April 1974. For this instrument, the modularization of each unit was considered during the design stage. In addition, for the operation, a ground-breaking technology was used, making it possible to perform operations, from the setting of measurement conditions to the analysis of the spectra, simply by aiming a light pen at the Braun tube to select the required items. Furthermore, the design was made more compact by integrating the spectrometer and computer into a single unit (see Fig. 5).

Probe development:

From ^{1}H observation to ^{13}C observation (other nuclei)

With the CW instruments, observations were almost always of the ^{1}H nuclei, so a single-tune system was adequate for the observation system. With FT NMR, however, it became possible to observe the ^{13}C nuclei, making it necessary to have a function for observing the ^{13}C nuclei while irradiating ^{1}H. A function to monitor deuterium nuclei for the NMR lock was also required, and the electronic circuitry of the probes became more complicated. In 1974 the C/H Dual probe was developed, which enabled measurement of both the ^{13}C and ^{1}H nuclei with a one-touch operation, without replacing the probe, and while maintaining the NMR lock. (applicable instruments: FX-60, X-100)

Meanwhile, a demand emerged for sample tubes of sizes other than the 5 mm diameter type, such as a 1.7 mm diameter for small sample volumes and a 10 mm diameter for measurements of polymers. In order to change the diameter of the sample, it was also necessary to replace the probe itself, requiring a cumbersome exchange procedure.

In 1978 the OMNI Probe was developed featuring replaceable probe modules for C/H observation and for multi-nuclear measurements. It also had changeable inserts to accommodate the 1.7 mm, 5 mm and 10 mm sample tubes. This was an epoch-making probe, able to handle any type of measurement without the need to replace the probe (applicable instrument: FX-90Q) (see Figs. 6–9).)

OMNI Probe

From electromagnets to superconducting magnets:

The strength of the magnetic field used for NMR was limited to 100 MHz (2.4 Tesla) while the electromagnets are used, and superconducting magnets were required in order to obtain stronger magnetic fields. JEOL had been working on the development of superconducting magnets since 1962, but the work was temporarily suspended in in 1974 without achieving a magnet that had the magnetic field uniformity and stability needed for NMR. In 1977, however, the British company Oxford Instruments successfully developed a superconducting magnet with stable performance, so JEOL resumed the work to develop an NMR instrument with a superconducting magnet, and the FX-200, with a ^{1}H resonance frequency of 200 MHz from a high magnetic field of 4.7 Tesla, was completed in 1979. This superconducting magnet consumed very little liquid helium, just 0.46 L per day, and had lower maintenance costs than 100 MHz electromagnets, so it was very attractive from a running-cost perspective. As a result, not only the users who required the high performance of 200 MHz, but also other users selected the FX200.

From this time onward, the progress has been a shift to higher magnetic fields (applicable instruments: FX-200 and later) (see Fig. 10).

NMR imaging:

JEOL began work on an NMR imaging apparatus for small animals in 1985, and released the 270WB SCM in 1987. Subsequently,

Fig. 5. JNM-FX-60: A proprietary light pen control was used based on a Texas Instruments 980 computer. Since it was possible to perform operations by touching commands on the screen with the light pen, easy and quick operation was achieved.

Fig. 6. JNM-FX90Q: Equipped with a light-pen type data system, the proprietary OMNI probe, and a power-saving 90 MHz magnet.

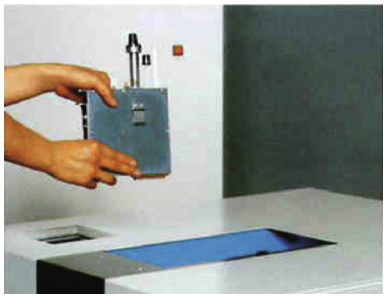

Fig. 7. Probe module: Types for multi-nuclear use and for C/H dual use. The module could be replaced without touching the probe.

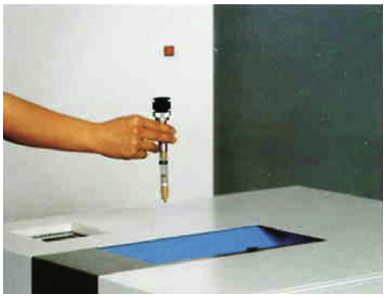

Fig. 8. Inserts: Various size inserts available, 1.7 mm, 5 mm and 10 mm. Replaced according to the diameter of the tube containing the sample to be measured.

there was further development of the surface coils used for the surface observation of small animals. At that time, the maximum resolution achieved was several tens of microns.

Solid state NMR:

Starting in 1974, work on the development of sold state NMR probes was conducted, and the FX-60Q was released in 1977. At that time, a pencil-type rotor was used, and it was necessary to lightly hold down the head of the rotor with a bamboo skewer until the rotation became stable. You had to hold it in place with the skewer for a few minutes until the spinning was stable at speeds of several kHz. This was possible at the time because the magnets were electromagnets and the upper part of the probe was free. I remember receiving a request from a food manufacturer to measure some flour, and that the flour had become bread after the measurement.

Solid state NMR is a battle with the sample rotation; the issue is how fast and how stably the rotation can be performed. With the switch to superconducting magnets, the bamboo skewers could

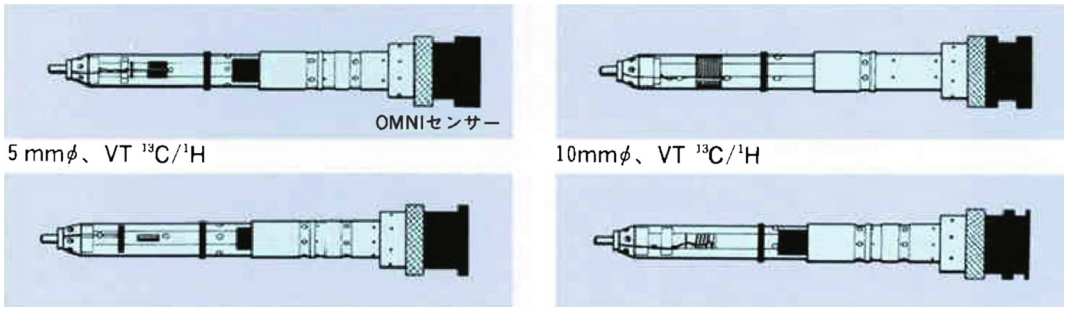

Fig. 9. Inserts: A selection of 4 types of inserts; 10 mm C/H, 5 mm C/H, 5 mm tunable and 3 mm C/H.

Fig. 10. JNM-FX200: The FX-100 spectrometer was expanded to 200 MHz.

no longer be used, so we worked on the development of probes including analysis of the spinning mechanism using aerodynamics. First, a probe for 6 mm sample tubes was released, followed by the development of a 4 mm diameter version. With even higher speeds, there was further development of 1 mm diameter and 0.75 mm diameter probes (applicable instruments: FX-60Q and later).

Fully automated spectrometer Auto tune probe:

With the practical utilization of superconducting magnets the NMR market expanded into a wide range of fields, creating a demand for enhanced operability. The GX-400, completed in 1981, was the world's first fully automatic spectrometer, with no control knobs on the spectrometer, and the capability to perform all operations for setting conditions from the data system (computer terminal). Since conditions like the shim settings and gain settings could be recorded by the data system, it became easy to make measurements using the same conditions as past measurements, enabling even novice users to operate the instrument easily (see Fig. 11).

In 1985 the Auto Tune probe was developed, providing automatic tuning of the probe. Since the tuning for ^{1}H, ^{19}F and multiple

Fig. 11. JNM-GX400: Fully automated spectrometer. The manually-operated knobs were eliminated, and it became possible to perform all operations from the computer.

Fig. 12. Auto tune probe: Observation of ^{1}H, ^{19}F and ^{31}P through ^{15}N can be fully automated. The tuning and matching of both the high frequency and low frequency sides, as well as the operation of the 5 knobs for switching the nuclei can be set fully automatically with instructions from the computer.

nuclei is performed automatically with this probe, by using it with a fully automated spectrometer, it became possible to perform measurements for various nuclei on the same sample, with the switching of the nuclei performed automatically (applicable instruments: GX400 and later) (see Fig. 12).

3.2. Development of application fields

From 1-dimensional NMR to 2D and Multi-dimensional NMR (pulse program development)

In the era of CW, only one-dimensional measurement of ^{1}H observation was possible; but, with the advent of FT NMR, new applications using pulse sequences were developed. The appearance of 2D NMR really caused a sensation. With the development of 2D NMR it was demonstrated that NMR could be used for structural analysis, which made a large contribution to the subsequent growth of the market. On the equipment side, it became necessary to develop pulsers to handle the various new demands. The pulsers had to be capable of controlling the pulses at high speed and with good accuracy, and able to control even long pulse sequences. The development of new spectrometers was propelled forward. The ALPHA series that was announced in 1991 were instruments with the performance and functions to fulfill these demands. The ECA series equipped with a Multi pulser was released in 2002 as devices to respond to various needs (see Fig. 13).

4. Development of ESR

JEOL developed the JES-1 model ESR apparatus in 1957. It was comparatively easy to develop ESR devices because the required uniformity and stability of the magnetic field is not as high as that needed for NMR, and the spectrometers used already had sufficient sensitivity in the application range. In addition, microwave communication was progressing rapidly at that time, so the required microwave components were available, and it was possible to accomplish the goal by combining parts.

The JES-1 had a magnetic pole diameter of 150 mm, and used X-band frequencies. A klystron was used to generate the microwaves, and the main issue at that time was reducing the noise in order to raise the sensitivity of the ESR, in other words, increasing the detection frequency (see Fig. 14).

The improvement from the initial low detection frequency up to 100 kHz was achieved in 1960 with the completion of the JES-3B. As a result, the sensitivity was increased to 2×10^{11} spin/Gauss, an improvement by a factor of 10 (see Fig. 15).

Initially, a type of vacuum tube called a klystron was used to generate the microwaves for ESR. There are some issues with using klystrons, such as the service life and the fact that the devices require a lot of space. So, it was decided to use Gunn diodes instead of the klystrons as the microwave transmitters. The advantages of the Gunn diodes are lower noise, longer service life, stability and safety. JEOL initially obtained Gunn diodes from a major Japanese electrical manufacturer. However, the manufacturer announced that they would discontinue production because of yield and profitability issues. Nevertheless, in light of the advantages of the Gunn diodes mentioned above, JEOL had to continue to use them, so it

Fig. 13. JNM-ECA600: Equipped with a multi pulser, compatible with both liquid and solid state NMR.

Fig. 14. JES-1 developed in 1957.

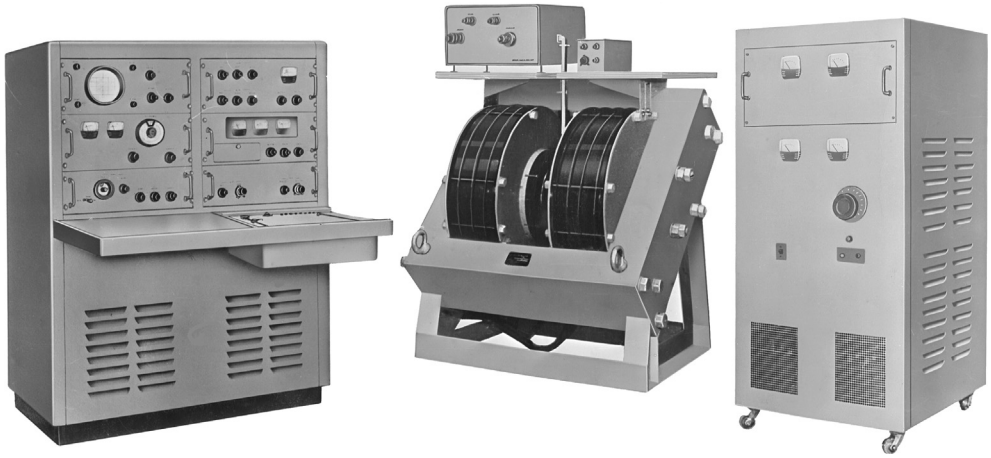

Fig. 15. The higher sensitivity JES-3B.

was decided to produce them in-house. Technical consultation was obtained from the manufacturer, and JEOL management made the decision to commit an unprecedented investment into the ESR project, and the production facilities were prepared. With the support of many stakeholders, the in-house production of Gunn diodes was successfully established, making it possible to continue to deliver low-noise, high-sensitivity ESR instruments.

Digitalization of the Instruments

The JES-RE series released in 1987 was equipped with a UNIX workstation for data processing and instrument control, as well as an MPU for digital control for the spectrometer, enabling digital data recording and communication with an external CPU.

For the software development, in addition to the advances in instrument control accompanying the progress in computer technology, there were also improvements to create a system that was easy for users to handle, including the development of graphic user interfaces (GUI) and operation units (see Fig. 16).

Starting with the JES-TE series that was launched in 1993, the operation knobs on the microwave unit were eliminated, and an auto-tuning function was incorporated. Touch panels were adopted for the spectrometer control in addition to a joystick that could be used to control the measurement conditions with an analog feel, further improving the operability for the users

For the JES-FA series released in 1999 Windows® PCs were used for the host computer, and the spectrometer became a system module. The operation panel that had previously been situated on top of the spectrometer was incorporated into the GUI of the host computer. The XY recorder that had been part of the spectrometer for many years was also eliminated, and all processes, including measurement condition setting, data acquisition, data processing and recording, became digital (see Fig. 17 and Table 2).

Expansion of Application Fields

① Measurement of physical properties:

The measurement temperature is of primary importance for the study of physical properties with ESR. Many devices have been developed since the start of ESR, and the supported measurement temperature range extends from absolute temperatures of 2.5 K to 470 K. In recent years, insertable, variable temperature devices

have been developed, allowing the temperature to be freely varied from room temperature up to 673 K. These have made it possible to evaluate the thermal decomposition of polymers.

② Time-resolved ESR:

Yamazaki and Pitle combined 2 types of solutions and rapidly introduced them into the resonator, obtaining the ESR signal intensity as a function of time, thereby establishing the first time-resolved ESR. (1961) Later, this method became widely used as a radical generation method using Fenton's reagent, and many unstable radicals were successfully observed (time resolution 10^{-5} s.) More recently, short-life signals with a time resolution of 10^{-7} s have been directly observed using high speed recorders, etc. by making use of the extreme spin polarity and accompanying large energy absorption and release that occurs when a molecule that has been excited by a pulsed laser passes through a triplet state.

③ Spin trapping-related software

In living organisms and during biological reactions, some "unstable radicals", like O_2^-, $^{\cdot}HO_2$, and OH, were considered to oxidize biological molecules and cells. However, it was difficult to detect these species directly due to their short-life time. In 1971, a method known as spin trapping was devised, by which short-lived unstable radicals can be detected as an adduct of spin-trapping reagent.

In FA series(1999), JEOL has supplied software related to spin-trapping technology.

(1) Scavenging Activity measurement program

It is useful for evaluating the antioxidant activity of foods, medicines, etc.

ESR signal intensity of O_2^- is observed by applying SOD (Super Oxide Dismutase). By changing SOD concentration, calibration

Fig. 16. JES-RE equipped with a UNIX workstation.

Fig. 17. JES-FA equipped with a Windows® PC, featuring microwave auto tuning and automation of the spectrometer.

Table 2
ESR History.

1957	JES-1	X-band, Crystron OSC, Rectangular cavity, Magic T bridge
1960	JES-3B	X, K,Q Band, 100KHz modulation, Cylindrical cavity,
1963	JES-P10	Table type spectrometer
	JDR-NEX1	Double ENDOR
1965	JES-3 BSX	Low impedance magnet
1967	JES-ME series	1X, 2X, 3X, All solid state spectrometer Hole element control power supply
1972	JES-PE series	1X, 2X, 3X, Table type spectrometer
1974	JES-EDX2	Double ENDOR
1976	JES-FE series	1X, 2X, 3X, Gun diode micro wave OSC,
1983	JES-EDX3	Triple ENDOR
1987	JES-RE series	1X, 2X, 3X,
1991	JES-FR80	Free radical monitor
1993	JES-TE series	Full auto-tune ESR TE100, TE200, TE300,
1995	JES-FR30	Free radical monitor
1999	JES-FA series	FA100, FA200, FA300, Full computer control
2005	JES-MQ series	Pulse ESR MQ100, MQ200, MQ300,
2015	JES-X3 series	X310, X320, X330

curve for SOD solution is obtained. This program makes a calibration curve and then antioxidant activity of unknown sample is determined automatically.

(2) Beer-flavor stability evaluation program.

It is known that beer-flavor deterioration is mainly caused by the OH radical. By measuring ESR signal of OH radical in beer mixed with spin-trapping reagent at slightly higher temperature, OH radical generation is accelerated. The program determines the "lag-time" which is related to beer-flavor stability. This evaluation makes it possible to predict the flavor stability of beer promptly.

5. Conclusion

The development of NMR/ESR has been remarkable. It is no exaggeration to say that this development has been a fusion of other technologies, rather than the advancement of one technology. In particular, the contribution from the development of superconducting magnets and computer technology is immeasurable. The electrical circuits have also changed dramatically, from vacuum tubes to transistors, ICs (Integrated circuits) and LSI (large-scale integrated circuit). NMR has been established as an integration of these technologies, achieving higher performance and higher functionality, with smaller device size and lower costs. The advancement of the application fields must also be acknowledged. The areas of application in the CW era were limited, specialized fields. With the appearance of FT and SCM the fields of application have been expanding without limit. Simply improving the function and performance of an instrument does not expand the areas of use. To open new fields, researchers with a passion for NMR are required.

The reason that the applications for NMR have expanded so widely is entirely due to the contributions of many talented researchers, including Jean Jeener, who discovered 2-dimensional methods, and Richard R. Ernst who developed them, P. Lauterbur, who discovered NMR imaging, Kurt Wuthrich, who established the use in the field of protein research, and A.d. Bax who has actively developed a variety of pulse sequences. Of course, we cannot ignore the contribution of the Journal of Magnetic Resonance (JMR) in disseminating the work and achievements of these researchers and others throughout the world. Those involved in the development of NMR can obtain the latest state-of-the-art information from JMR, to use as a foundation for advancing the development of the instruments.

I feel fortunate to have been able to see the dramatic progress of NMR firsthand, and am grateful to JMR for this opportunity to present this account.