Biographical Sketch

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Early NMR Experiences and Experiments

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EARLY SCIENTIFIC INTERESTS OF THE AUTHOR

I have been told that at a very early age, before I learned to walk, I showed interest in lights and plugs. It somehow must have been born in me, but not directly inherited, as my father was a banker and my mother a nurse. As I grew into my boyhood I collected batteries, lights, motors, buzzers, and the like, and was fond of hooking them together. In my early teens an uncle taught me a lot about radio. During my high school years I experimented with radio and got both a commercial radio license and a radio ham license (W6API) which I have kept up to this day. In high school I took physics and chemistry which I greatly enjoyed. My teacher in these two subjects, Mr. Gilbert Ewan, was a graduate of Stanford University, and he encouraged me to go there. I lived at home for my first two years of college, attending Reedley Junior College (now Reedley College).

ON TO STANFORD

In 1948 I transferred to Stanford as a junior. I majored in physics with minors in electrical engineering and math, receiving a B.S. degree in 1950. I continued on at Stanford for a master's degree and finally a Ph.D. For my thesis I worked on nuclear magnetic resonance (NMR) under Professor Felix Bloch, who in 1952 shared the Nobel Prize with Edward Purcell of Harvard for their discoveries. The work that Bloch did for the prize was done before I came to Stanford.

Those were exciting times. When I started my thesis work, Jim Arnold was already in the process of building a permanent magnet for a new NMR spectrometer that (hopefully) would have very high magnetic field uniformity and time stability. This would enable him (and me) to study very small shifts and splitting that he and others had recently detected in various chemical compounds.[1] Using my earlier experience with radio, I built the rf transmitter and receiver for the experiments. When the magnet and electronics were finished, we found the magnetic field dropped off faster than anticipated. To compensate for this drop-off, Jim built a set of current shims that consisted of a spiral pancake of wire on each pole face, with many taps so the current in each section could be independently regulated. The linear transverse gradients were controlled by slightly changing the tilt of the pole pieces by adjusting a set of differential screws. It was often a tedious job to adjust the field homogeneity, because the controls were not independent. In addition, small temperature changes in the room caused the magnetic field to drift, so we became very adept at raising and lowering the windows and turning a small heater on and off.

Professor Bloch suggested[2] that if we could completely stir the sample rapidly within the sample tube, the effect of the magnetic field variations over the sample volume could be essentially eliminated. After many unsuccessful attempts to achieve complete mixing, we settled upon spinning the sample, which caused averaging over concentric circles centered on the axis of rotation. This partial averaging was a great improvement as it made the job of magnet shimming much easier.[3]

My thesis work dealt with taking the NMR spectra of various chemical compounds, and then analyzing spectra to derive the chemical shifts and spin coupling constants. Quantum mechanics was used to do the analysis, which I found fascinating. The title of my Ph.D. thesis was 'Nuclear Magnetic Resonance Spectra of Some Hydrocarbons'. Several years later, after publishing a paper with the same title,[4] a chemist friend told me that the molecules that I studied and analyzed were not hydrocarbons!

In the summer of 1954, Professor Bloch received an offer to become Director General of the newly formed European Centre for Nuclear Research (CERN). It was then temporarily headquartered in Switzerland at the University of Geneva. Bloch asked me to write my thesis on the work I had been doing. Because of the time pressure, I wrote it and had it accepted in approximately two weeks.

WORKING AT CERN

Professor Bloch thought it would be good to get some research work started at CERN. Up to that time the main activity had been planning and developing the site. He proposed that Jim Arnold and I go with him to CERN, take along some of our equipment, and do some experiments. We happily agreed.

We spent an interesting year in Geneva. We did some work,[5] too, but not a lot, and did some skiing on the weekends. That was a very pleasurable year, and I met some other fascinating physicists. Professor Anatole Abragam, who was at Saclay at that time, came periodically to visit CERN. We went out to concerts and other places with him. There's a story he reported in his book, *Time Reversal, An Autobiography*, that I've told often, and now he's told it on himself.

There was to be a meeting of the Faraday Society[6] in Cambridge, England, and Jim and I decided to report about our work at Stanford. I was going to give the talk, and Abragam told me, 'These are only 10-min talks, but if you have someone in the audience ask questions, then you have some extra time while answering the questions'. So we went through all of my material and picked out a slide that needed more elaboration, and he agreed to ask a question about it. In due time, we went off to the meeting and I gave my talk, after which he asked the agreed-upon question. Then the embarrassing moment came. In response to his question, I said, 'I'm sorry, I didn't have time to show that slide'. I don't know if he's ever forgiven me for that. He said later that he knew the material so well that he wasn't listening to what I said.

Originally, Bloch had planned to stay at CERN for two years, so Jim and I would have been there two years also, but after one year, Bloch had had enough of it. It was more administration than he liked. He decided to go back to Stanford. Then I had to decide just what I wanted to do. In 1951, I had worked at Westinghouse Research Center in Pittsburgh during the summer quarter. In the summer of 1952, I worked at Varian Associates in San Carlos, at the original site where the company started. I had job offers from both companies, as well as an offer from Anatole Abragam to work at the French Atomic Energy Commission at Saclay. I was pleased that Professor Abragam had apparently forgiven me, and I think I would have gone to Saclay except the draft board contacted me and suggested that I come back to the States. Being a native Californian with the hope of keeping my roots in California and the chance to continue work in magnetic resonance led me to choose Varian.

VARIAN ASSOCIATES AND THE BLOCH–HANSEN PATENT

Before continuing with my story, let me step back and give some background of how Varian was founded and got into NMR. I give here only a bare outline; a rather complete version of the story can be found in the book *The Inventor and the Pilot* by Dorothy Varian.[7] Russell Varian (called Russ by his friends) is perhaps best known for his invention of the klystron tube, however he also made many important contributions to the field of NMR. His acquaintance with NMR started in mid-1946 when he returned to Stanford from Sperry on Long Island, New York, where he and several Stanford people had worked to perfect the klystron and incorporate it into the early radar systems. The discovery of NMR had taken place less than a year earlier at Stanford under Felix Bloch,[8] and at Harvard under Edward Purcell.[9] Russ immediately conceived the idea that NMR could have important applications as a method of chemical analysis. The only published NMR signal at that time was that of water, which is reproduced in Figure 1. On the basis of this spectrum and others like it, and from what was known about NMR at that time, it seems remarkable that Russ Varian believed it could become a useful tool for chemical analysis. At this time the chemical shift and the spin–spin couplings between nuclei were yet to be discovered. Russ told Felix Bloch and Bill Hansen about his ideas of chemical analysis and urged them to apply for a patent. Bloch felt the technique would be of interest only to a few academic physicists who might want to measure magnetic fields or magnetic properties of nuclei. Since Bloch showed little interest in applying for a patent, Russ offered to prepare a patent application and handle its filing in return for an exclusive license for himself and his brother, Sigurd, with the understanding that the license could be transferred to his company when it was established. They agreed, and Russ wrote a good part of the patent application with help from Bloch, Hansen, and his patent attorney, Paul Hunter. Russ incorporated the idea of chemical analysis in the claims and titled the patent *Method and Means for Chemical Analysis by Nuclear Induction*. The patent was filed in December 1946 and was issued in July 1951.[10]

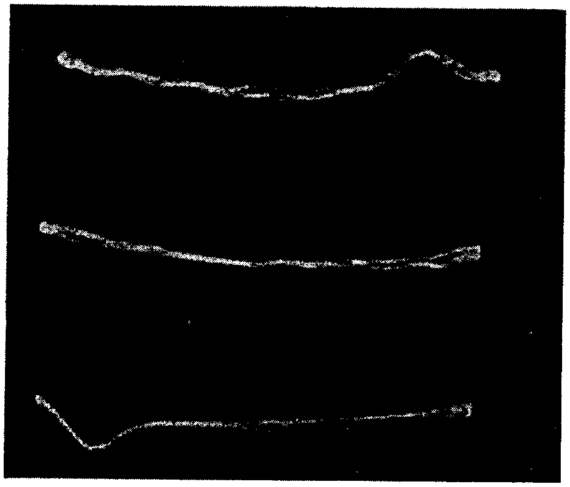

Figure 1 First NMR signals, reported by Bloch, Hansen, and Packard. (From Ref. 8c)

Tellegen, who was at Philips Research Laboratory in Eindhoven, Holland, developed the mathematical concept of the gyrator. He described it as a new electric network element that violated the reciprocity relation but was consistent with the laws of physics. He published this work in 1948 and 1949.[11] Les Hogan, who was at Bell Labs, developed a practical gyrator using ferromagnetic materials, which depends upon the gyromagnetic properties of electrons. He applied for a patent in 1950, which was issued in 1951 and immediately put under security orders. When the order was lifted, Hogan immediately published his material in the *Bell Labs Technical Journal*.[12] In this paper, Hogan pointed out that the nuclear resonance phenomena observed by Bloch also satisfied the gyrator relationship.

Marvin Chodorow, a professor at Stanford, received a copy of the *Bell Labs Technical Journal* and realized that since the phenomena described by Hogan and Bloch were the same, there was a deficiency in the Bloch–Hansen patent application. By this time, the original Bloch–Hansen patent had been issued, so it was necessary to file for a reissued patent. The wording of the original patent was changed to include resonance of electrons as well as nuclei by inserting the words 'portions of atoms', where previously the words 'nuclei of atoms' had been used. New claims were also added that broadly covered the gyrator concept. The Bloch–Hansen patent was finally reissued in 1955.[13]

Varian Associates was incorporated in the state of California in April 1948. The name 'Varian' was used because it was the well-known name of the inventor of the klystron tube, and

'Associates' because the founders wanted to convey the idea that this was going to be an association of equals. The purpose of the company, as stated in the charter, was to conduct research in the fields of physical science of every kind or nature, including heat, sound, light, X-rays, charged particles, ionizing radiation, properties of solids, liquids and gases, chemistry, and to measure the gyromagnetic ratio of nuclei of atoms, and to use the gyromagnetic properties of atoms to measure magnetic fields or for other purposes. The Articles of Incorporation described a number of fields in which the company became a leader including NMR, linear accelerators, optical spectrometers, and microwave tubes.

RUSS VARIAN AND HIS MAGNETOMETER

After I arrived at Varian Associates in September 1955, I became involved with magnetometers. This got me deferred from military service because the magnetometers had military applications, which included searching for land mines and hunting submarines. I worked on what is called a 'free precession magnetometer' that Russ Varian had invented.[14] Russ had conceived the idea in 1948, less than three years after NMR had been discovered. The idea of free precession formed an important part of what later became Fourier transform (FT) NMR. The concept of his magnetometer is quite simple. Protons in a bottle of water are polarized by sending a strong electrical current through a coil that surrounds the bottle, producing a strong magnetic field in the water sample. The coil is oriented so the strong magnetic field is approximately perpendicular to the Earth's magnetic field. After a few seconds the protons in the water become polarized, and a majority point in a direction of the strong magnetic field, i.e. along the axis of the coil, which is perpendicular to the Earth's magnetic field. Then the polarizing field is quickly turned off, and the protons are left in this position. They immediately start to precess about the Earth's magnetic field, and in doing so they induce a current in the coil which has a frequency that is proportional to the strength of the Earth's magnetic field. The coil is quickly switched to the input of a sensitive amplifier and a frequency meter. The measure of that frequency gives a very precise value for the Earth's magnetic field.

It's a simple device, but you have to be careful about several things. One of these is the current turn-off circuit. If you turn off the polarizing magnetic field too slowly, the proton nuclei will follow the changes in direction of the magnetic field, slowly swinging back until they point parallel to the Earth's field, and then they won't precess. If you turn off the current too rapidly, before dissipating the energy stored in the coil, a transient oscillatory magnetic field is produced and the protons become disoriented and do not remain perpendicular to the Earth's field. I developed a circuit that would turn off the field quickly and remove the energy that is stored in the coil without disrupting the orientation of the protons. I was also involved in developing coil configurations that would reduce or eliminate external interference arising from low frequency electromagnetic fields.[15]

In order to test the magnetometer at various values of the external field I built a set of coils to simulate the field changes that might occur naturally or occur in other parts of the world. The set, shown in Figure 2, consisted of four coils arranged so that the first uncorrected gradient was of 8th order.

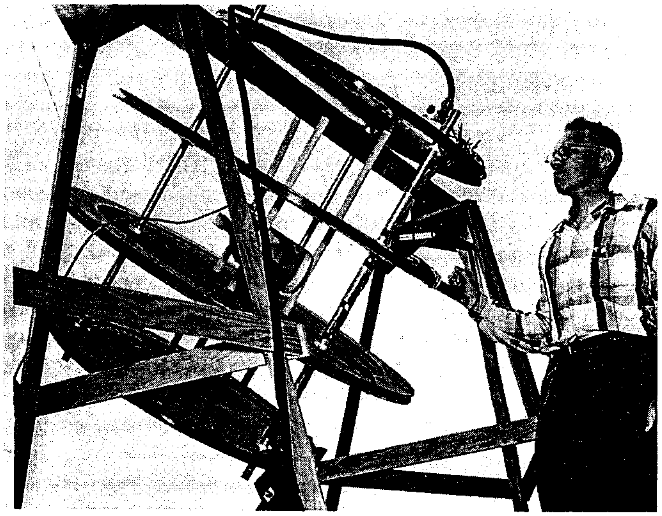

Figure 2 Young Anderson with magnetic field biasing coils used to change the magnetic field at the bottle of water sensor of a free precession magnetometer

A portable free precession magnetometer was developed and sold commercially. One application that generated a lot of publicity, but not much profit, was using the magnetometer to locate skiers buried in an avalanche. The skier would wear a small magnet obtained at the ski lift. Should the skier happen to be trapped by an avalanche, a search team with the magnetometer could quickly locate the magnet under many feet of snow and dig the person out.

Russ was a very clever guy and one of the things that I really enjoyed about the early years at Varian was the interaction with him. He would come around and talk; and he

Figure 3 Photograph of Russell Varian taken in the mid-1950s

talked to everyone, not just me. That's one of the things that's changed from the early days at Varian. There are lots of stories about Russ. One I remember is about the time Russ had a visitor from India. Russ was bringing the visitor through the front door, and Pete, the janitor, was sweeping up there. Pete said, 'Hello, Russ'. And Russ said, 'Good morning, Pete', as they walked by. The Indian visitor was astonished that the janitor would address the president of the company by his first name.

Russ was absent-minded, and another story about him was from the early days in San Carlos. He had recently moved into a new house. One day, forgetting that he had moved, he walked into his old house and surprised the people who were living there.

HIGH-RESOLUTION NMR EXPERIMENTS

Soon after starting my full time job at Varian, I also became involved in improving the performance of the NMR spectrometers to make them more useful for chemical analysis. Martin Packard was the R&&D manager, and Ralph Kane the group manager. The group was called Special Products, later called the Instrument Division, and currently called Nuclear Magnetic Resonance Instruments. At that time there was little structure and quite a bit of freedom. Jim Shoolery ran an NMR chemical applications lab, and he had an endless thirst for improvements of all kinds. We also got suggestions and feedback from customers visiting the applications laboratory and attending the NMR workshops. We were aware of where improvements could be made and that these improvements would lead to more applications. It wasn't a blind 'Let's try something and see if it goes'. We had a good idea of the importance of certain areas and where to put the emphasis. The emphasis was on higher magnetic fields, greater sensitivity, better resolution, field/frequency stability and double resonance.

I put a lot of effort on designing current shims to improve the resolution. Because of the rather long relaxation times found in liquids, it became obvious to us that we could improve the resolution if we could make the magnetic field more uniform. In order to make the shims independent, Ed Jaynes[16] had suggested winding them on the boundary of a sphere in a way that would make the shims correspond to the spherical harmonic mathematical expansion. This could be done easily for the proton free precession magnetometer where there was plenty of open space around the sample. However, in high-resolution spectrometers the sample was confined to a narrow region between two pole caps. After some thought, I designed and built a shim coil set that preserved the same mathematical relationship but would fit flat against the pole caps.[17] This was an extension and improvement of the coil set that Jim Arnold and I used at Stanford several years earlier.

Another area that required attention was magnetic field inhomogeneities due to the finite magnetic susceptibility of the rf probe coils. Up to that time copper wire had been used to wind the probe coils. Although copper has a small magnetic susceptibility, because of its closeness to the NMR sample it can introduce high order magnetic field gradients, which are difficult or impossible to compensate for by the use of current shims. We couldn't find a suitable material with zero susceptibility so we used two closely spaced materials, one with positive susceptibility, the other negative, to yield a combination that behaved like a material with zero or near-zero susceptibility.[18]

Taming the spectrometer to sweep smoothly through a spectrum was another project that took on some importance. It

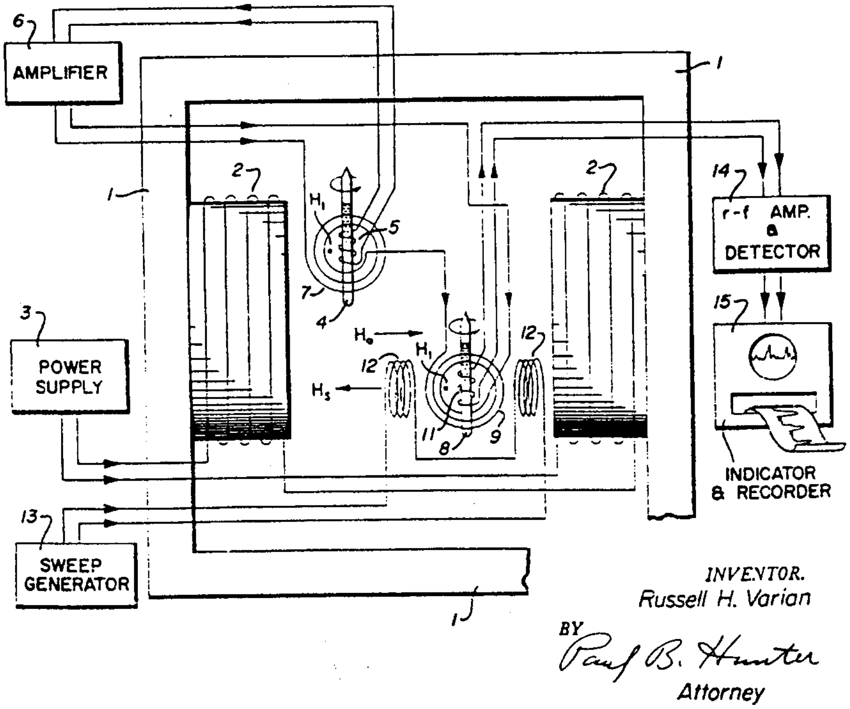

Figure 4 Drawing showing a method to stabilize the field/frequency relationship in an NMR spectrometer. (From Russell Varian, *US Pat. 3 109 732;* Ref. 19)

turned out Jim Shoolery wasn't interested in opening and closing windows, turning on and off heaters, or adjusting knobs to control the changing random drifts that were particularly troublesome when sweeping slowly through the very narrow lines of a high-resolution spectrum. A number of ideas were proposed and evaluated before a suitable solution was found. In 1956 a flux stabilizer, called a 'Superstabilizer', was introduced which removed the rapid random fluctuations of the magnetic field strength. Russ Varian came up with the concept that led to the ultimate solution to the stability problem.[19] His idea, shown in Figure 4, was to use one NMR line as a control to stabilize the field/frequency relationship of a sample group. He proposed using a control line as part of a feedback loop in an oscillator so its frequency would be determined by the resonance condition of that line. This frequency could then be used to stimulate the resonance of the sample group. Since the two samples were separated in space, a small field-sweep coil could be used to sweep through the resonance of the sample group. A number of related schemes were developed for achieving field/frequency stability that utilized a stabilizing control line either in the same sample or in a different sample.[20] In the late 1950s an accessory was offered to provide the field/frequency stabilization system to the high-resolution NMR spectrometers. One variation on Russ's NMR oscillator that I had developed, called the sideband oscillator,[21] was used in the Varian A-60 spectrometer. This was Varian's first analytical NMR spectrometer. It incorporated the use of precalibrated recorder chart paper and an integrator as standard features. The use of high-frequency field modulation also provides baseline stability which is particularly important when integrating NMR spectra.[21]

By going to higher values of magnetic field strength one gains both sensitivity and dispersion. During his graduate work at Stanford, Harry Weaver designed and built a 12-in. H-shaped electromagnet. His design formed the basis of the iron magnets that Varian sold and later incorporated into the early Varian NMR spectrometers. The first Varian high-resolution NMR spectrometers operated at a frequency of 30 MHz (approximately 0.7 T) and were designed for proton spectroscopy. Much effort was directed toward achieving higher magnetic field strengths using various pole cap materials, tapering the caps in various ways, narrowing the gap, and improving the current shims. By 1955 we were operating at 40 MHz. Then a project called SMOFF was started, which stood for Sixty Megacycles Or Fifty Five. Fortunately we met the 60 MHz goal in 1958. By the time we reached 100 MHz in 1962 we realized we were near the end of the line with iron magnets because of saturation of the iron.

After receiving his Ph.D. at Stanford, Harry Weaver spent two years at the University of Zürich and then in 1954 joined Varian in Palo Alto. Here he developed a high-resolution superconducting magnet system using a niobium–titanium alloy.[22] The result was the Varian HR-200, the HR-220, and later the HR-300 high-resolution NMR spectrometers. To achieve still higher fields, a niobium–tin alloy is used in the central core of the magnet. Using magnets purchased from Oxford Instruments, Varian has produced NMR spectrometers 400, 500, 600, and now 750 MHz (17.6 T). Figure 5 is a graph showing the highest spectrometer frequency plotted versus the year of introduction. It is interesting to note the slope of the curve is quite steep during the iron magnet period (1953–1962), somewhat flatter for the niobium–titanium alloy period (1964–1972) and still flatter for the more difficult niobium–tin alloys currently used. I might speculate that in future years we will see 1000 MHz and above, perhaps using the new high transition temperature superconducting materials (but still operating near liquid helium temperatures).

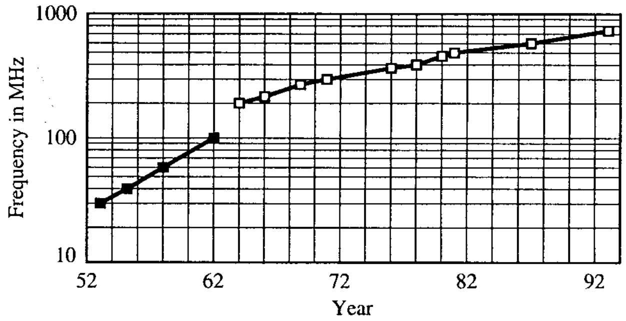

Figure 5 Plot of the maximum NMR spectrometer frequency versus year. The line segment at the left represents data for spectrometers with iron magnets; the right segment is for spectrometers with superconducting magnets

Double resonance studies provided a way to get more information than a single sweep spectrum.[23] Spin decoupling experiments demonstrated the usefulness for simplifying spectra. When Ray Freeman arrived at Varian in 1961, he was anxious to extend some of the techniques for determining relative signs of spin coupling constants that he and Whiffen had started.[24] We worked out the double resonance patterns expected for a number of different spin configurations.[25] One of the ideas we explored was that of indirect detection of naturally abundant ^{13}C nuclei by modulation techniques[26] or the small splitting on proton lines as a weak rf frequency was swept through the carbon spectrum.[27] These techniques provided the sensitivity of the proton resonance while detecting the position of the ^{13}C peaks. We also did the early experiments using multiple quantum transitions to help in high-resolution NMR spectra determinations.[28]

I also worked with Larry Piette, who was the Jim Shoolery of EPR, and Jim Hyde, who was my counterpart in EPR. Jim worked on EPR instrumentation, and Larry worked on the chemistry applications. Forrest Nelson was an electrical engineer who contributed to many NMR and EPR ideas. Richard Ernst joined the group in 1963 and Howard Hill in 1968. The strong interaction among the various members of the group as well as interactions with the applications laboratory people provided a very stimulating atmosphere. It was a good environment for exploring ideas that could improve NMR and EPR spectroscopy, and make them more useful to the scientific community.

FOURIER TRANSFORM NMR

Perhaps the most important development that I participated in was that of Fourier Transform NMR or FT NMR. It was this development that speeded up NMR data collection by a factor of 1000 or more. This is another area in which the initial suggestions came from Russ Varian. He proposed[29] using a wide band set of frequencies to increase the sensitivity of

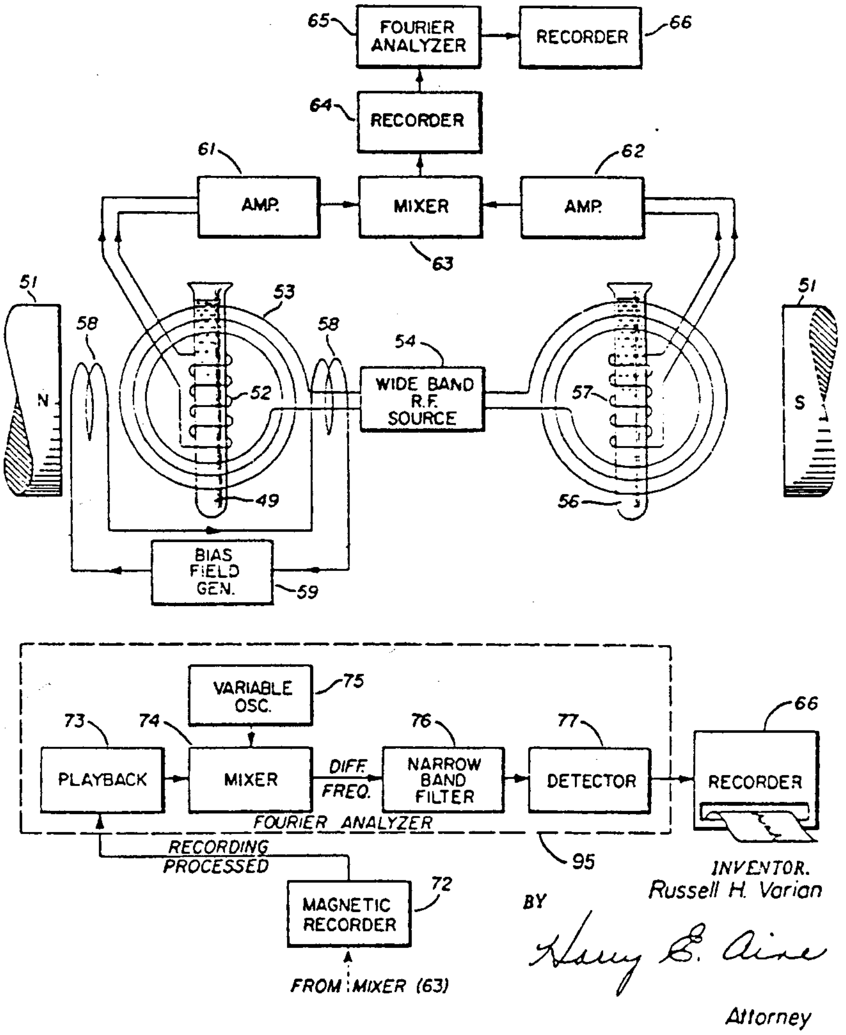

Figure 6 Drawing showing the concept of wide band excitation and a Fourier transform detection system to increase the sensitivity of a high-resolution NMR spectrometer. (From Russell Varian, *US Pat. 3 287 629;* Ref. 29)

NMR spectrometers. His method was to excite all of the lines in the NMR spectrum with a wide band noise source (see Figure 6). The resulting signals would then be heterodyned down to the audiofrequency range and recorded on magnetic tape. After the recording was completed, an endless tape would be made by pasting the end of the tape to the beginning. The endless tape would then be played back many times, each time mixing it with a different frequency. The mixer output would then be fed through a narrow band filter and recorded. Basically, it was a crude Fourier analyzer. Different mixing frequencies would select different signal frequencies and different parts of the NMR spectrum. The output of the detector represented the amplitude of a particular frequency component. This was a non-real-time system; however, the spectrometer could be getting new data while the analysis was being carried out on the old data.

One of the ideas I had was to generate each frequency by a separate oscillator, rather than use a noise source to produce a wide band of frequencies. By using separate oscillators, the individual frequencies would be coherent so that the same oscillator could be used to phase-detect each frequency. I proposed a rather simple way to generate and detect all of the frequencies simultaneously with an optical chopper wheel, called a 'Wheel of Fortune' by some and a 'Prayer Wheel' by the skeptics (Figure 7). It was a plastic cylinder about 6 in. diameter and 8 in. high, which was slowly rotated by an electric motor. The wheel contained about 20 cylindrical segments, each with a slightly different diameter. On each segment was placed a strip of a Ronchi grating (a photographic film of light and dark bands) with about 40 bands per inch. A light was placed inside the cylinder. A lens placed outside the cylinder would direct the light passing through each cylindrical segment onto a common photoelectric detector. As the wheel turned, each cylindrical segment would chop the light at a slightly different frequency, so the output of the photoelectric detector would contain all of these frequencies. This signal would then be mixed with a suitable offset frequency and transmitted to the probe to stimulate any NMR resonance signals.

This same wheel was used to separate the received NMR signals. The received NMR signals would be brought back into the audio range by mixing them with the same offset frequency. The resulting audiofrequency would then be applied to a second light source within the wheel, but on the opposite

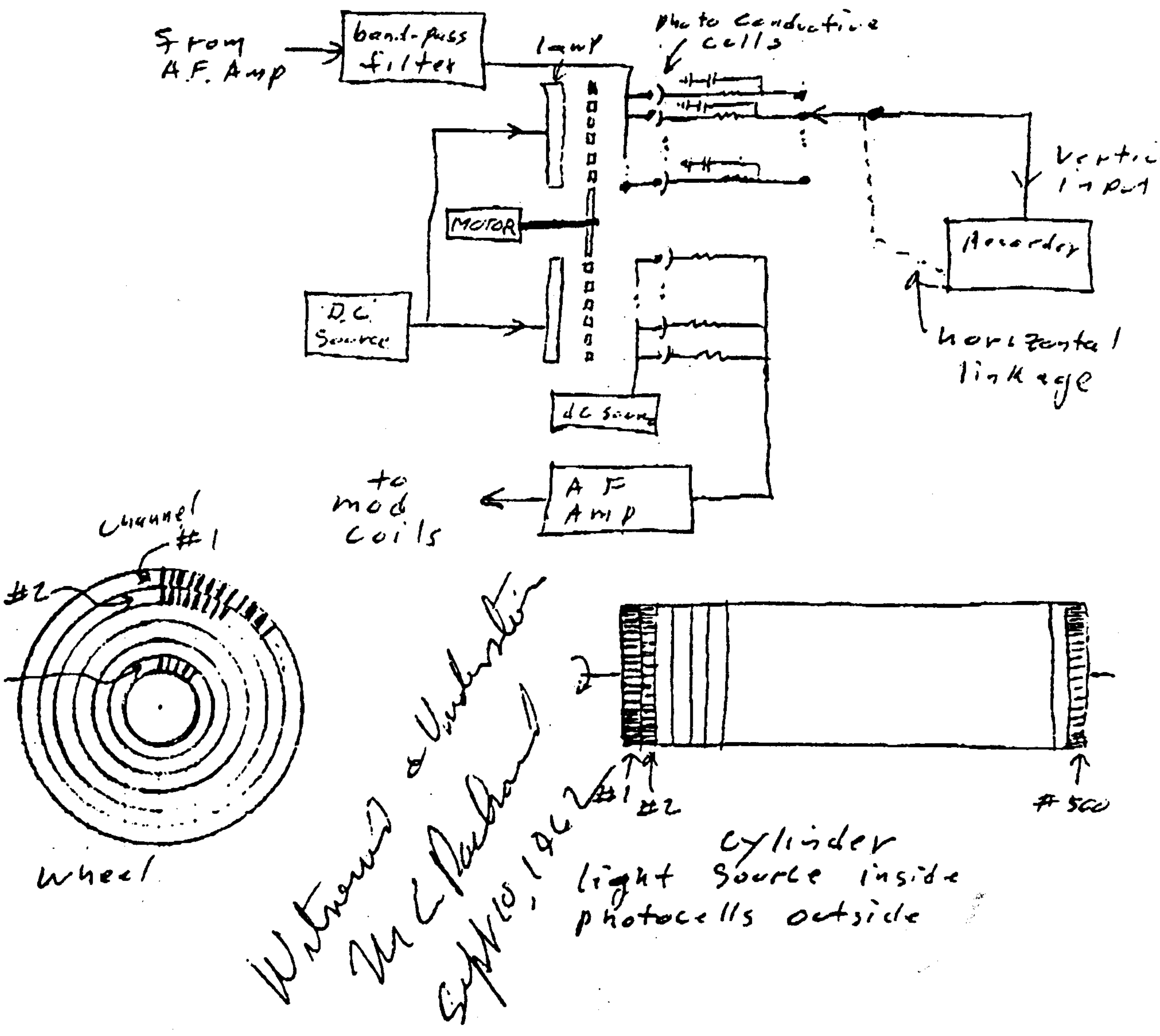

Figure 7 Excerpt from Anderson's notebook outlining the concept of the 'Prayer Wheel'

side. This time the light would be demodulated by the series of light and dark bands on the wheel. After the light had passed through each segment, it would be collected on a separate photoelectric detector. The output of each photoelectric detector would then be fed to separate integrators, and the output of each integrator would correspond to one frequency component of the NMR spectrum. This system would operate in real time, with no delay for processing the signals.

Before this system was finished, a better idea came along of using pulses and computers instead of the wheel. Eventually, the chopper wheel was donated to the Smithsonian Institution as an example of one step in the evolution of an idea[30] (Figure 8).

The new idea was even closer to the original Fourier transform idea of Russ Varian. The wide band of frequencies is generated by a series of pulses applied to the transmitter frequency. The resulting frequencies, which are all coherent, are applied to the nuclei in the magnetic field to stimulate responses from the entire NMR spectrum. The stimulated resonances are brought into the audiofrequency range by mixing them with the original rf frequency. The audio responses would then be digitized and stored by a computer of average transients (CAT) that was then commonly used to time-average NMR data (Figure 9). Richard Ernst built the apparatus and our first experiment gave us good data. However, using the technology of the day, we had to punch out the data on paper tape, convert the tape data to IBM cards, and take the cards to the Service Bureau Corporation on the other side of Palo Alto. Several days later, after waiting for payroll and factory inventory processing to be completed, the computer performed the Fourier transform step and plotted out the spectrum.[31]

As soon as possible, we ordered a minicomputer. By today's standards it was slow, and the 4000 bytes of memory trivially small; however, it enabled us to transform the data and plot it in a few minutes. With the advent of larger and faster computers and with the development of the Fast Fourier Transform (FFT) techniques by Cooley and Tukey, the transform

Figure 8 Anderson saying good-bye to the 'Prayer Wheel' as it departs for the Smithsonian

has been speeded up considerably. Today even large multidimensional transforms can be taken in seconds. Fourier transform changed the whole way of life in NMR. Varian offered an FT accessory for the HR-100 in 1968. Soon FT NMR almost completely replaced the former method of slowly scanning through the spectrum. From contributors throughout the world a whole new set of techniques have been developed to enhance further the capability of FT NMR.

THEN AND NOW

It is remarkable how far NMR has advanced during its 50 years of history. Much of the early progress can be traced to Russell Varian, from his early belief that NMR would be important to chemistry, his writing the original NMR patent, obtaining a licence under the patent, his insistence that his new company, Varian Associates, develop and commercialize NMR magnetometers and spectrometers, and because of the important technical contributions he made to the technique. He would be pleased to see how far NMR has developed in the intervening years since his death in July 1959. It has been exciting for me to play a small role in furthering the development of NMR instrumentation and to extend its usefulness.

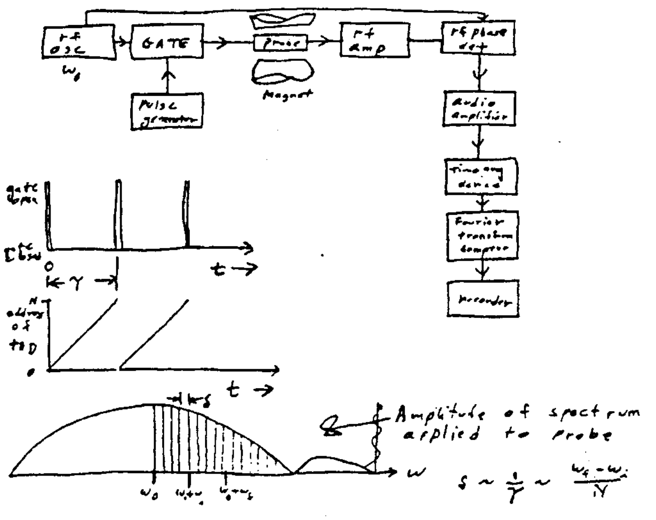

Figure 9 Excerpt from a page in Anderson's notebook outlining the idea of the FT NMR spectrometer

In 1972 I was named Director of the Varian Systems and Techniques Laboratory and became involved in other research activities. My initial activity in this new laboratory was the development of ultrasound equipment for real time medical imaging of the human heart—but that's another story.

Improvements of NMR instruments continued, building upon the earlier work. In 1974 Richard Ernst, now back at the Federal Institute of Technology (ETH) in Zürich, followed a proposal of Jeener[32] to demonstrate a new two-dimensional (2D) technique.[33] A second frequency dimension was introduced and a second FT used to extract additional NMR data. In 1975, Ernst proposed an FT method of acquiring and reconstructing MRI data[34] that is analogous to the 2D spectroscopy method. For these two achievements and our earlier work with FT NMR he was awarded the 1991 Nobel Prize in Chemistry.

Today FT NMR is playing an indispensable role in medicine with MRI instruments and a crucial role in spectroscopy as a tool for chemists and biologists. All signs point to continued development leading to a still brighter future.

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Biographical Sketch

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Structures and Electronic States of Polymers as Studied by High-Resolution NMR Spectroscopy Combined with Quantum Chemistry

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Since Gutowsky et al.[1] observed the 18 MHz ^1H high-resolution NMR spectrum of uncured Heva rubber (polyisoprene) in CS_2 in 1957, high-resolution NMR spectroscopy has developed to become the most powerful method available for characterizing the structures and dynamics of synthetic polymers in the solution and solid states. Nishioka et al.[2] and Bovey et al.[3] separately determined the stereochemical structure of poly(methyl methacrylate) prepared by radical polymerization and anionic polymerization by means of high-resolution ^1H NMR spectroscopy. These studies have provided great influences in the research fields of structure and stereospecific polymerization in polymer science.[4] In addition, Schaefer et al.[5] have recently successfully measured the high-resolution solid state ^{13}C CP MAS (cross polarization/magic angle spinning) NMR spectra of polymers in the solid state. This leads to the elucidation of structure and dynamics of polymers in the solid state.

Nevertheless, in order to provide a deeper insight into molecular structures and electronic structures of polymers, more sophisticated approaches might be developed in high-resolution NMR spectroscopy. The NMR chemical shift should provide detailed information about the structure and electronic state of polymers in the solution state and the solid state if high-resolution NMR spectroscopy is combined with quantum chemistry.[6,7] The chemical shifts of the nuclei in polymers depend on their magnetic environment which depends on the stereochemical configuration and higher-order structure such as conformation and crystal structure of the polymer chains.

My co-workers and I have developed a methodology for obtaining stereochemical configuration and higher-order structure, and the electronic states of polymers both in the solution[6,8–13] and solid state[7,14–23] through a combination of the observation and calculation of NMR chemical shifts, and have applied this to various polymer systems. Theoretical calculations of NMR chemical shifts for polymer systems have been done mainly by two approaches. One is that model compounds such as the dimer, trimer, etc., as local structures of polymer chains, are used in the calculation by combining quantum chemistry and statistical mechanics.[6,8–13] In particular, this approach has been applied to polymer systems in the solution state. However, in solid polymer systems it sometimes has to be recognized that the results of quantum chemical calculations on model compounds are not readily transferable to polymers because of differences in electronic