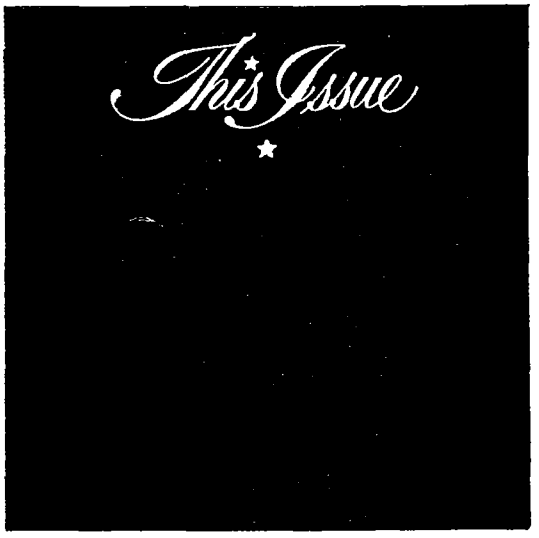
Volume 52, Number 1

Book

Lubrication

A Technical Publication Devoted to the Selection and Use of Lubricants



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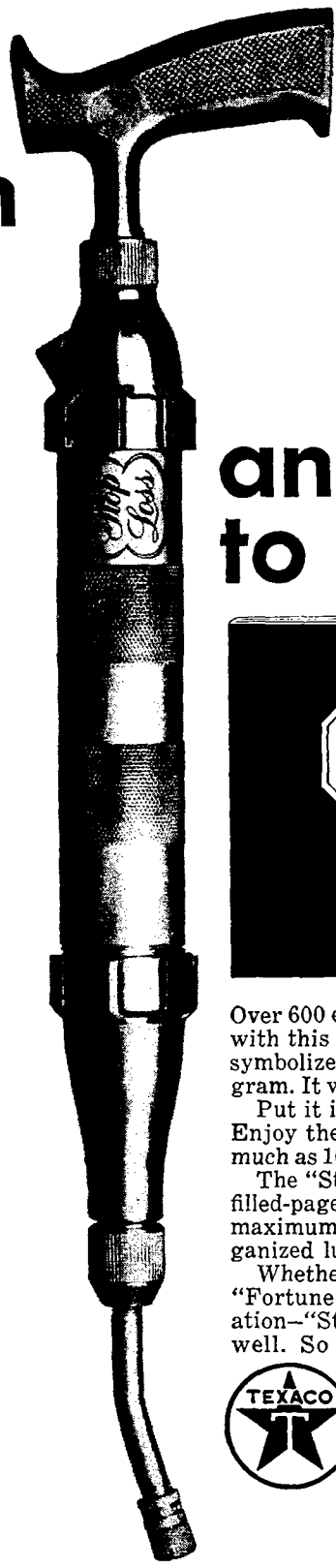

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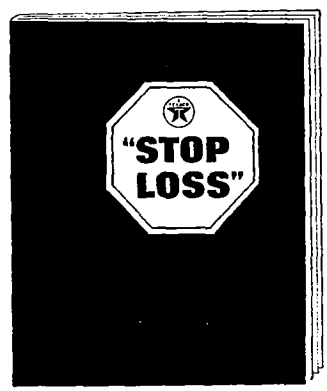

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ANALYTICAL ADVANCES

VIRTUALLY every branch of analytical chemistry discussed in previous issues of this publication[1,2,3] is influenced by new instruments, devices and techniques. Technical advances in this area have resulted in more rapid, accurate and complete answers to the ever present questions: "What is it?" and "How much?" This accelerated progress was inevitable, resulting from industrial demands for faster, more efficient processing, for better quality control, and increased emphasis on pure and applied research. It is indeed a major challenge to those responsible for industrial analysis and testing to keep abreast of these advances and to make the proper selection of instrumentation, techniques and methods in order to enhance the reliability of their work and results. This article will describe some of these advances and illustrate their application to the analysis of petroleum and related products.

Instrumental methods of analysis have been practiced in the petroleum and other industries for many years. However, with the development of automated and direct readout equipment, many basic instruments have evolved into faster, more sensitive, more specialized and more complex devices. Two major examples of this continued development are emission and infrared spectroscopy. Direct reading emission spectrometers, which are adaptations of the conventional optical spectrograph are custom built for a specific application and record results directly on dials or strip chart recorders. Infrared analysis utilizes basic principles known to scientists for over 150 years, but has been continually refined, resulting in improved accuracy and resolution, extended wavelength coverage, and many automated features as well. While various forms of emission and infrared spectroscopy have been used in analytical laboratories for years, other relatively new, more recently developed techniques have also become valuable analytical tools. Some of these include (1) nuclear magnetic resonance, (2) gas chromatography, the first account of which was published towards the end of 1952,[4] (3) activation analysis, a by-product of the nuclear age and (4) atomic absorption spectroscopy, which was first suggested as an analytical tool in 1955.[5]

In common with all instrumental methods of analysis, the methods and techniques discussed in this article depend upon measuring a key physical property or characteristic of the sample, which, in turn, can be related to its chemical composition. Since analytical instrumentation does depend upon this principle, it logically follows that each instrument must be standardized or calibrated with material of known composition before it can be used on a routine basis. Not infrequently, the availability of reliable standards is a limiting factor in instrumental analysis.

EMISSION AND INFRARED SPECTROSCOPY

Emission and infrared spectroscopy are undoubtedly two of the most important areas of analytical instrumentation. Separately or in combination, they

[1] In this issue superior figures refer to items in its Bibliography of corresponding number.

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can handle an almost unlimited variety of applications. A few examples of where these techniques are used in the petroleum industry are: (1) analysis of samples for identification; (2) analysis of intermediates and finished products for product quality control; (3) product development studies; (4) following the effect of service on products; and (5) investigation of complaints, particularly where product quality or performance may be questioned. This list is by no means inclusive of all of the possible applications of these two techniques.

A comprehensive discussion of these techniques and applications is obviously beyond the scope of this publication. However, the almost universal use of even the more sophisticated instruments illustrates the acceptance of modern instrumentation by modern industry. For a more detailed discussion, the reader is referred to texts on these subjects[6,7] and the more recent applications which are covered in the Annual Reviews of Analytical Chemistry.

Emission Spectroscopy

Recent interest in emission spectroscopy has been directed primarily toward automated direct-reading spectrometers such as the one shown in Figure 1. These instruments depend upon sensitive photomultiplier tubes and associated electronic equipment available today for the detection and reproducible measurement of very faint spectral energy. The direct-reading spectrometer has proven a stable, rugged instrument ideal for many applications. It is particularly valuable where many analyses of a repetitive nature are required, such as in the primary metals industries.



Figure 1 — A direct-reading emission spectrometer.

The essential components of a typical direct-reading spectrometer are shown schematically in Figure 2. The reader will recognize from this drawing that the direct-reading spectrometer is actually an adaptation of the optical grating spectrograph. The essential difference is that the camera portion of the conventional spectrograph has been replaced with a carefully arranged system of exit slits, photomultiplier tubes, condensers, amplifiers and recorders which automatically perform the various tedious and time-consuming steps which must be done manually with optical spectrographs. While the typical direct-reading spectrometer is programmed to determine up to sixteen elements simultaneously, larger and more sophisticated models which will determine up to sixty elements are available. The main advantage of direct-reading spectrometers is their speed; once they are properly calibrated, results are available only minutes after the sample has been received in the spectrographic laboratory. Their value in high volume, routine work is well recognized.

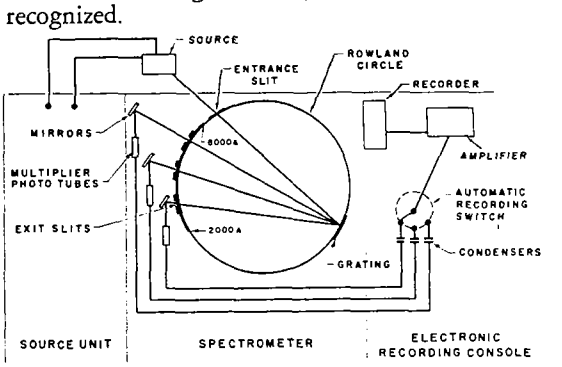

Figure 2 — A schematic diagram of a direct reading emission spectrometer.

One area of particular interest to both the users and suppliers of lubricants is the oil analysis method of monitoring impurities and wear metals as an important part of preventive maintenance programs. Many operators of diesel engines, such as railroads, truckers, and power plants, as well as oil company laboratories, use emission spectroscopy to check the condition of used crankcase oils. Although many of the elements of interest are present in the parts per million range, direct reading spectrometers are useful in used oil analysis for speed and convenience; many of these instruments can handle samples of this nature without preliminary preparation or treatment.

The speed of these instruments is particularly important in initiating corrective action when required. For example, the Bureau of Naval Weapons[8] has investigated this method for monitoring aircraft engines and other aircraft mechanisms. It was concluded from these studies that: (1) if difficulty develops in the oil-lubricated section of a jet engine and remains undetected, the chances are that single engine aircraft will fail in flight; and (2) at least half the total cost of one of these aircraft is saved each time a discrepant engine is found. Since each of these aircraft costs several millions of dollars, the value of the spectrograph in protecting this investment is readily evident. Although perhaps less dramatic, the same principle applies to many other pieces of mechanical equipment.

Infrared Spectroscopy

Versatility is the one word which best describes

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infrared instrumentation. A wide range of instruments is commercially available today, from relatively simple, easy to operate spectrophotometers costing less than $5,000 to complex high resolution spectrophotometers available at prices in excess of $20,000. Figure 3 shows an example of a relatively inexpensive table model, while Figure 4 illustrates a grating instrument covering the wavelength region from 2.5 to 50 microns. The selection of a particular instrument depends to a considerable extent upon individual requirements and preferences.



Figure 3 — A relatively inexpensive table model infrared spectrophotometer.

Accessories which enable investigators to handle almost every conceivable sample form—solids, liquids, gases, and even microscopic quantities are available for most instruments. These techniques have permitted the spectroscopist in every field of analysis to take an increasingly closer look at even the most detailed and complex molecular structure.

As an example of the new accessories, the reflectance technique provides a simple, convenient and versatile means of examining samples which previously were difficult or impossible to adapt to standard infrared procedures. Infrared energy, as shown schematically in Figure 5, strikes the crystal-sample interface at an angle greater than the critical angle. This energy is reflected from the interface and measured. Little loss of the original energy occurs except at wavelengths where the refractive index of the sample increases or decreases. Since these wavelengths correspond closely to the absorption bands of conventional infrared spectra, absorption data can be used to yield similar information about the composition of the sample. Surface films, polymers, viscous liquids and many other difficult samples have been analyzed using this approach.

Another particularly significant development is the use of infrared for routine examination of used gas engine oils. The combustion process in natural gas engines frequently promotes the fixation of nitrogen by combining nitrogen and oxygen from

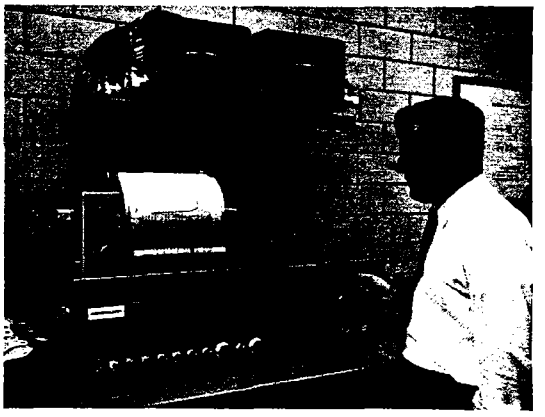

Figure 4 — A grating infrared spectrophotometer having a range of 2.5 to 50 microns.

the combustion air. The reaction of these fixed nitrogen compounds with lubricating oil forms acidic materials and other undesirable products which ultimately become oil insoluble. These materials are major factors in forming engine deposits, thereby limiting useful oil life. Measurement of these materials as they accumulate in used oils provides information which may be used to establish optimum engine operating conditions and oil drain periods. While oil oxidation and thickening may be factors in any type, size or model of gas engine, nitrogen fixation tends to be most prevalent in naturally aspirated four-cycle gas engines. Fortunately, however, infrared analysis can be easily extended to determine oxidation and water contamination as well as nitrogen fixation in used gas engine oils, as described in the following discussion.

A technique known as differential infrared analysis (DIR) is particularly useful when applied to used gas engine oils. In this technique, a sample of unused oil is placed in the reference cell of a double beam infrared spectrophotometer and the used oil in a matched sample cell. Thus, the absorbance due to the oil itself is compensated, and the net absorbance is due to differences in chemical composition between the used and unused oils which have occurred as a result of service. A typical differential infrared spectrum of a used gas engine oil is shown in Figure 6.

The possible presence of water is indicated by

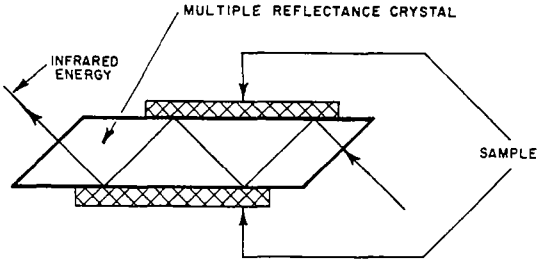

Figure 5 — A schematic diagram of the reflectance technique in infrared spectroscopy.

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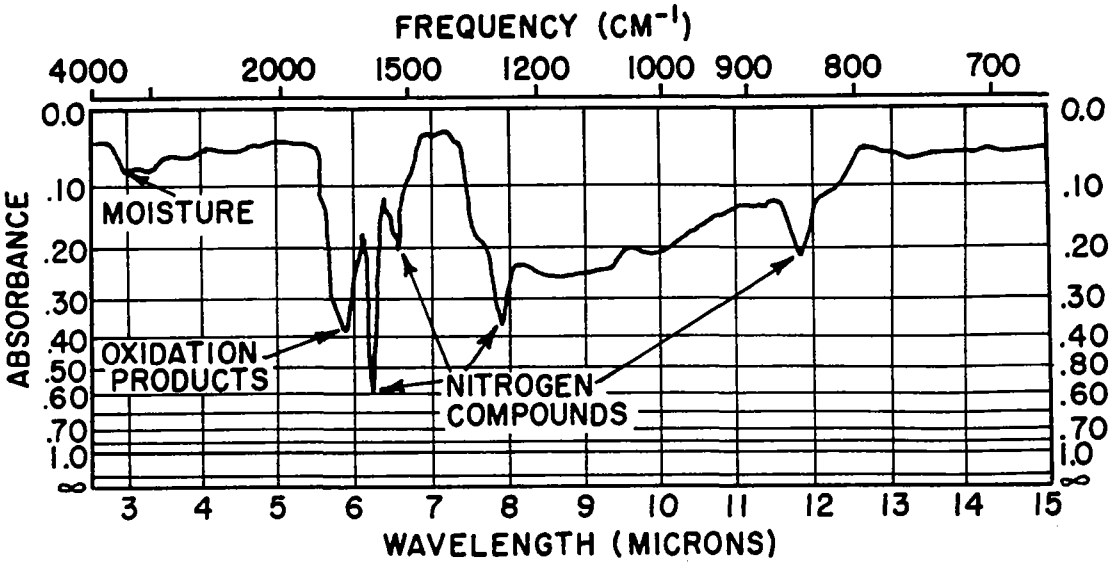

Figure 6 — A typical differential infrared spectrum of a used gas engine oil.

the absorbance in the 2.9 micron region. Carbonyl compounds (oxidation products) are shown by the downward "peak" in the 5.8-5.9 micron region. Organic nitrates and nitro compounds represent the types of nitrogen compounds which are formed most frequently in oils by nitrogen fixation. The peaks at 6.2, 7.9 and 11.8 microns in Figure 6 are due to the presence of organic nitrates, while the peak at 6.5 microns is attributed to nitro compounds.

The differential infrared technique has been used to evaluate gas engine oils in many field tests, including all types of gas engines. By correlating differential infrared data with engine inspections and conventional chemical tests, safe condemning limits for oil and filter changes have been established. While these may vary to some extent depending upon the type of oil in service, experience has shown that DIR data are as reliable as conventional chemical analyses. In addition to its advantages of speed and convenience, infrared analysis is the only reliable means of detecting early stages of abnormal nitrogen fixation in a particular engine.

Knowing the characteristic differential infrared patterns of used oils from engines of various designs, as well as operating characteristics of individual engines, this technique frequently provides valuable information concerning engine operating conditions. For instance, it is often possible to detect one or more of the following conditions by examination of used oils:

1. Hot spots, either on pistons or cylinder walls,
2. High crankcase bulk oil temperatures, possibly due to a faulty cooling system,
3. Improper air/fuel ratio,
4. Improper spark timing,
5. High rates of combustion blow-by,
6. Faulty operation of crankcase ventilating system, and
7. Engine overload.

Obviously, corrective action on any of these items could result in substantial savings, either from extended oil life or a reduction in unscheduled engine maintenance.

NEW METHODS AND TECHNIQUES

Although not used to any extent in industrial analytical laboratories only ten years ago, the remaining four techniques to be considered have since been used to solve many thousands of analytical problems. These new approaches selected for discussion include the relatively inexpensive and less complex gas chromatography and atomic absorption techniques as well as the more elaborate and costly nuclear magnetic resonance and activation analysis methods. These four techniques are merely examples of areas of expanding interest to the analyst, as many other novel approaches are now being applied in analytical laboratories throughout the world.

As with emission and infrared analysis, a complete discussion of each of these new techniques is obviously beyond the scope of this article. Rather, a brief outline of the basic principles and main areas of application will be presented, and for additional information on specific features, the reader is referred to corresponding items in the Bibliography.

Nuclear Magnetic Resonance

Nuclear Magnetic Resonance (NMR) was first discovered in 1946[9,10] and its practical applications recognized by 1952, when Felix Bloch and E. M. Purcell, the co-discoverers, received the Nobel Prize Award in Physics. NMR is primarily con-

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cerned with energy level transitions of atomic nuclei in a magnetic field. These transitions are expressed by different magnetic quantum numbers and are analogous to electronic and vibrational-rotational energy changes in other forms of spectroscopy. NMR spectroscopy involves the region of the electromagnetic spectrum just beyond the far infrared, sometimes referred to as the microwave region. The nucleus is not studied per se, but is used as a minute probe to reveal the molecular structure which surrounds it.

An NMR spectrometer consists basically of a magnet, radio-frequency (rf) transmitter or oscillator, and a suitable rf receiver, as illustrated schematically in Figure 7. By the simultaneous application of a strong direct-current magnetic field and a radio frequency field to a sample, at values related to the nuclear magnetic moments of angular momentum, a detectable "resonance" effect can be induced.

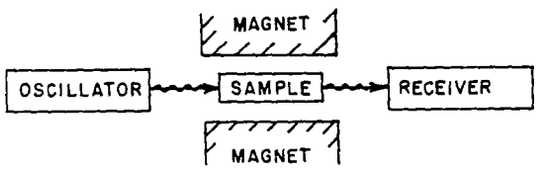

Figure 7 — A nuclear magnetic resonance (NMR)) spectrometer shown schematically.

Because nuclear magnetic resonance produces relatively weak effects, sensitive instruments such as the one shown in Figure 8 are needed for its detection. The development of these instruments to their present useful state has depended to a considerable degree upon understanding and correlation of problems in many related fields of science and technology. For example, magnets for use in NMR instruments are limited by uniformity of field requirements. However, a cryogenic magnet for a pulsed NMR spectrometer was recently delivered to Rice University; the magnet, rated at 25 kilogauss, has a field uniformity better than 1 in 10^6 and its weight is only 200 pounds, compared to the 6 tons for a comparable conventional unit.[11] Also, because of weak signals in NMR, signal-to-noise ratio in signal amplification is often a problem. A practical means of improving the sensitivity is to use a multichannel pulse-height analyzer—essentially a small computer which can store and remember several hundred traces.[12]

Two basic types of nuclear magnetic resonance spectroscopy are wide-line and high resolution NMR. Wide-line NMR is concerned with the broad resonance character of a particular nucleus in many of its interactions with its surroundings. High resolution NMR detects the slight shifts and fine structural details that represent the differing intra-molecular environments for a given nucleus. Figure 9 presents high resolution NMR spectra of three or-



Figure 8 — A high resolution NMR spectrometer in use.

ganic compounds and shows typical resonance bands. Commercial instruments for wide-line and high resolution as well as dual purpose instruments are available.

The most useful application of NMR is the determination of the molecular structure of organic compounds. NMR is used primarily in conjunction with other analytical methods such as gas chromatography, mass spectrometry and infrared analysis. Its principal advantages include speed and the certainty with which it can be used to identify certain functional groups under a wide variety of conditions without requiring precise calibration with the exact compounds being studied. It has proved to be especially valuable in petroleum research laboratories.[13,14]

Activation Analysis

Activation analysis is one of several analytical techniques which yield specific elemental analyses. Accordingly, it is not concerned as to how the elements are combined chemically.

In contrast to other instrumental methods, such as emission and x-ray spectroscopy and flame photometry, in which detection of an element depends upon excitation of the electrons in the atom, the activation method seeks out the core of the atom, — the nucleus. This technique involves the creation and detection of radioactive elements. The process of activation analysis actually begins by irradiating the sample by bombarding it with one of many species which will interact with the nucleus to form a radioactive element artificially. Specifically, such species include charged particles, high energy gamma rays, X-rays, and neutrons. As a result of the bombardment, the stable element nuclei are either converted into radioisotopes of the same element or, as frequently happens, transmuted into isotopes of different elements. It is then possible to detect

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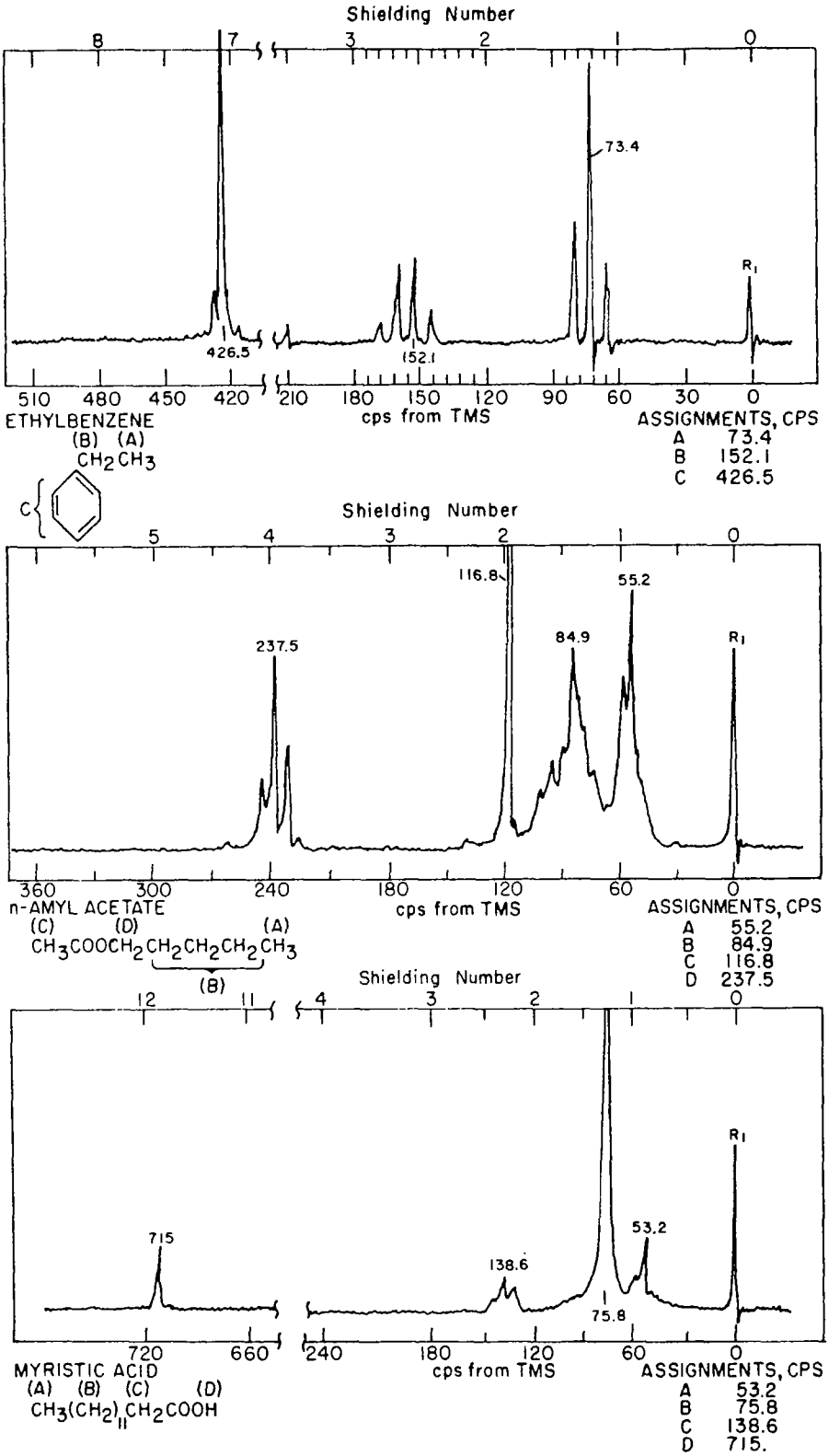

Figure 9 — High resolution NMR spectra of three organic compounds. Note typical resonance band assignments.

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these radionuclides (radioisotopes) by the radiations they emit, either at the instant of their formation or during their subsequent characteristic radioactive decay. The radiation most easily detected in either case is the gamma ray—the "prompt gamma" at the instant of formation and the "delayed gamma" during radioactive decay. Although it is not the only radioactive emission in activation analysis, the gamma ray is most frequently "counted" by detectors such as the sodium iodide scintillator. The spectrum of gamma ray energies identifies the element, while the "count" serves as an index of concentration of the irradiated element. In practice, the specific activity of an unknown sample is compared to that of a standard sample irradiated under the same conditions.

For a detailed explanation of atomic structure, radioactive decay, and transmutation processes, the reader may wish to consult additional references on these subjects.[15,16]

Recalling the various forms of bombarding species mentioned previously, it is easy to visualize that many different radioactive products could result because of differing conditions of radiation. It would also follow that the analytical approaches would necessarily be quite varied. Such is the case; one 1963 reviewer[17] places the number of references to activation analysis at more than two thousand. The 1964 review by G. W. Leddicotte[18] alone refers to more than 235 papers on activation analysis. As a consequence of the accumulated experience in this field, three textbooks in English[19,20,21] and one in French[22] have been published. The first of these references describes activation analysis methods for 85 of the 104 presently known elements.

Three types of activation are:

(1) Charged Particle Activation, which requires high-energy accelerators for the bombardment of the sample with protons, electrons, deuterons, helium ions or even heavier ions. This type of activation is limited to the specimen surface because nuclear repulsion forces prevent the particles from penetrating deeply into the sample. One major disadvantage is that high beam currents may cause excess heating which distorts the sample. Nevertheless, charged particle methods are frequently used to characterize the elements at surfaces, particularly of metals. As a typical example, helium-3 bombardments are used in the analysis of light elements such as beryllium, carbon, oxygen, nitrogen and fluorine.

(2) Photoactivation, using accelerator-produced high energy gamma rays and X-rays (Bremsstrahlung), is also useful in certain activations. The energy requirements for gamma photoactivation of the lighter elements are usually high (around 15 Mev), therefore the utilization of this approach is limited to the most powerful accelerators. Some of the heavier elements respond to less energetic (1 Mev) Bremsstrahlung produced by electron accelerators, but the sensitivities are less favorable than those of neutron activation.[23]

(3) Neutron Activation, which enjoys the widest use in the field of activation analysis. The neutron has the essential mass of the hydrogen atom and bears no charge; it can, therefore, easily penetrate matter and be "captured" by nuclei to form radioactive elements. A recent comprehensive review[24] describes how neutrons interact with most of the stable nuclei to produce one or more radionuclides. Certain elements, such as carbon and hydrogen, do not respond in this manner and hence are not readily adaptable to this method of analysis.

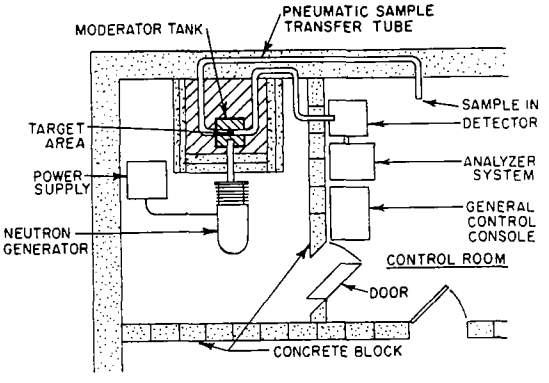

Figure 10 — A schematic diagram of a neutron generator typical of those used in industrial facilities.

Since neutron activation is the most popular type of activation analysis, the balance of this discussion will be devoted to it. Figure 10 shows a schematic diagram of a neutron generator typical of those used in industrial facilities.

Analysis by neutron activation is not necessarily the universal solution to all problems of elemental analysis. In fact, in many routine situations it cannot compete with other instrumental methods. However, in certain specialized situations it is the only method which is applicable in sensitivity or in speed.

It is interesting to review the reasons for the increasing use of neutron activation analysis. The basic reason is the growth in all of the technologies involved with nuclear science. Without the dramatic progress in physics, chemistry, electronics and related fields since the dawn of the atomic era, the potentials of neutron activation would have remained unknown. Now, however, the following characteristics may be listed:

1. Neutron activation is sensitive for trace element analysis; many determinations are in the parts-per-billion or parts-per-million range.
2. Neutron activation analysis lends itself to rapid, automated instrumental techniques.
3. The technique is non-destructive in that a relatively small number of radionuclei are actually created.

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TABLE I

SOURCES OF NEUTRONS FOR ACTIVATION ANALYSIS

Neutron Source	Mechanism of Neutron Production	Neutron Flux ($n/cm^2/sec$)	Number of Elements Activated	Remarks	Approximate Cost
Nuclear Reactors	Fission of uranium or plutonium.	10^{11} - 10^{13} 10^{17} (pulsed)	72 elements as 150 radionuclides	65 elements detected in ppm or ppb range. Automatic analysis of several hundred samples daily.	$250,000
Van De Graaff Accelerators	Deuteron bombardment of beryllium target.	10^{8} - 10^{9}	35 - 40[30]	Long-lived target suited to long irradiations.	$160,000
Electron Linear Accelerators	Bremsstrahlung radiation on gold target produces high energy photons which strike beryllium target.	10^{8} - 10^{9}	35 - 40	Also suited to long irradiations.	$140,000
Cockroft-Walton Neutron Generators	Deuteron bombardment of tritium occluded in titanium produces 14-Mev neutrons (which may be moderated).	10^{8} - 10^{9}	57[25]	48 elements activated by one research group.[31] Thirty elements boast of short-lived activities with attractive detectabilities. These accelerators require less restrictive safeguards and installations.	$ 20,000 to 30,000

4. The method is frequently interference-free.

The sensitivity for a given analysis is a function of the number of neutrons available for activation, i.e. the neutron "flux." Table I indicates that nuclear reactors have the highest fluxes and therefore activate the greatest number of elements. They are also the most expensive type of equipment to install.

The energy of the neutrons from either nuclear reactors or accelerators is usually reduced to thermal values by water moderation; these "slow" neutrons produce most of the useful reactions. In certain cases, however, only high energy neutrons (e.g. 14-Mev) initiate the desired radionuclides[18,25]; accelerators meet this particular requirement better than reactors.

Following are a few examples of where neutron activation analysis has been applied successfully or where it has interesting possibilities:

1. In basic medical research, to determine trace elements in blood, bone and tissue.
2. In police work and criminal investigations, such as cases of arsenic poisoning or proof of the presence of traces of gunpowder. To investigate sources of hair, paint and other items of physical evidence. Coding and subsequent identification of drugs and narcotics.
3. To check the composition of semiconductors in the electronics industry.
4. In oil refining and processing, to determine trace quantities of vanadium, arsenic, nickel, copper, chromium and sodium in feedstocks.[26]
5. For the determination of trace quantities of oxygen in hydrocarbons, steel, beryllium and alkali metals in a variety of industries.[27] A typical sequence for the determination of oxygen by neutron activation analysis is outlined in Table II. Many of these steps can be traced in Figure 10.
6. In labelling and other tracer work which is probably the most familiar application of neutron activation. The actual and potential applications of this are almost limitless. Radioactive piston rings used in studying engine wear are one of many examples.

While the cost of neutron activation analysis will necessarily limit its general application, it is nevertheless helpful to know if this method is attractive for a desired analysis. Reference tables[25] and handbooks[28] are useful in listing the necessary parameters. Reviews[18] which relate the experiences of others are also helpful.

Without actually showing the exact equation which defines activation produced by neutrons, it is nevertheless interesting to review the significance of a few of its items. One is "cross section," the experimentally-determined index of sensitivity to activation by neutrons of a given energy. "Half-life" is another term, an everyday expression which determines the limits for the irradiation time and the subsequent counting time. Knowing these parameters in addition to the available neutron flux and the detector efficiency, the minimum detectable amount of the element of interest can be easily calculated.

In addition to being relatively expensive, neutron activation analysis is also complicated. For example, knowing the theoretical detectability of a particular element is not enough; the analyst must also consider the sample matrix for possible interferences with his accuracy. Direct interferences sometimes occur, i.e., elements other than that being analyzed may produce the same radionuclide that is used as the basis of detection. For example, fluorine interferes in the fast-neutron activation determination of oxygen. In other instances, elements of high atomic number may "shield" the desired element from being activated by the neutrons, or they may absorb the weaker gamma rays emanating from the activated element.

A further limitation may result from counting similarities. For instance, two or more radio elements may have approximately the same gamma ray energies at a critical time in the detection of one of them. Radio-chemical separations very often resolve this difficulty. Since nearly half of the papers

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TABLE II

SEQUENCE OF ACTIVATION ANALYSIS — DETERMINATION OF OXYGEN

Step No.	Operation	Equipment and Function	Remarks
1	Prepare sample.	Sample is weighed into polyethylene vial of low oxygen content.	The C and H atoms of polyethylene are not activated.
2	Transmit sample to neutron flux.	Sample is moved by pneumatic pressure or by vacuum.	
3	Trip timing device.	Mechanical or photoelectric sensor detects sample and limits the activation time.	Identical activation time for sample and standard is preferred.
4	Submit sample to timed (30 sec) irradiation	Van de Graaff accelerator or neutron generator bombards tritium target with deuterons producing high energy neutrons according to the reaction: $D_1^2 + T_1^3 \longrightarrow$ alpha particle + neutron. The neutrons activate oxygen-16: $n + O_8^{16} \longrightarrow N_7^{16} +$ proton. The nitrogen-16 decays with a half life of 7.3s	
5	Terminate irradiation and return sample.	Timer operates the pneumatic system to remove the activated sample.	The timer also alerts the counter to begin counting after a preset delay.
6	Count for a preset time.	Multi-channel pulse height analyzer counts the gamma rays (6-7 Mev) from the N-16 decay.	A NaI crystal containing thallium detects the gamma rays. The photons of light thus produced are translated into electrical pulses by a photomultiplier tube. The gamma ray energy governs the voltage of each electrical pulse. The electrical pulses (counts) are sorted and stored in a computer memory for later access.
7	Call for the counts.	Multi-channel analyzer produces "read-out". Information shown channel-by channel or as sum of channels of interest.	The analyzer is usually equipped to show this information visually on a cathode ray tube.
8	Calculate oxygen concentration.	Relate samples to counts obtained from standard oxygen sample.	

referred to by Leddicotte[18] require radiochemical separations, a continued need for a combination of instrumental and conventional technique is obvious.

Prime attention must also be given to standardization of the irradiation conditions. Since the neutron activation method is a comparative one, it requires the best possible measurement of the actual neutron dose which interacts with the sample.[29] The total neutron dose or neutron flux measurement is very critical in the utilization of neutron generators whose targets deteriorate steadily with use.

Gas Chromatography

During the short time since the discovery of gas chromatography (GC) as a practical analytical technique in 1952 by James and Martin,[4] it has become one of the most widely used methods. The phenomenal growth of GC is due to its great versatility, simplicity of operation, and relatively low cost. Its special forte is its ability to give quick, sharp separations of the components in a wide variety of samples. With it, many separations that are impractical or impossible by other techniques are easily obtainable. Two typical laboratory instruments are shown in Figure 11.

Basically, gas chromatography is a process of physically separating the components of a sample as they are carried over a stationary phase by a mobile (gas) phase. GC is practiced predominantly in two forms—gas-solid chromatography (GSC) and gas-liquid chromatography (GLC). In GSC, the stationary phase is a finely divided absorbent such as silica gel, alumina, or molecular sieves. GSC is generally limited in application to the analysis of fixed gases. The other form, GLC, is more versatile and thus more widely used. In GLC, the stationary phase consists of a thin layer of a non-volatile liquid, such as silicone oil, distributed on a finely divided solid support such as crushed firebrick, or on the inner wall of a capillary tube.

A gas chromatograph is a relatively simple instrument consisting essentially of a sample inlet system, an inert carrier gas (mobile phase), a chromatographic column (containing the stationary phase), a detector, and a recorder. A schematic flow diagram of a gas chromatographic instrument is shown in Figure 12.

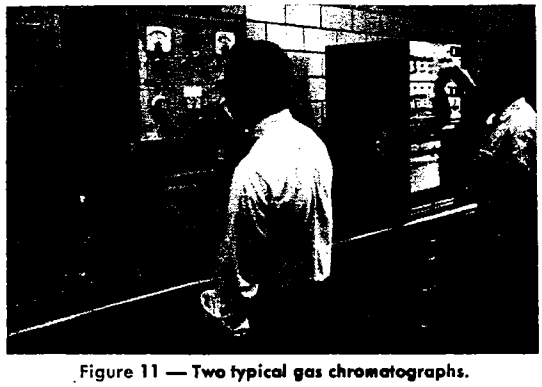

Figure 11 — Two typical gas chromatographs.

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