The analytical chemist from the days of the medieval alchemist down to the present time, has used solubility as the basis for his work. Within the past few years, the chemist has turned to other properties of matter by means of which he can distinguish between molecular and atomic species. He has done this not in the hope of finding a means of displacing solubility, but rather in the realization that the precipitate and the analytical balance will not meet all the needs of the present day.

The most recent property of matter to be utilized by the chemist is momentum. Momentum is defined as mass times velocity, and heretofore has been considered a purely physical property of matter. An instrument designed for separating molecules because of differences in their momenta has been called the mass spectrometer or the mass spectrograph, depending on whether an electrical or a photographic means of recording the various molecular masses is used. The frequent requests that the Bureau receives for information about these instruments and the principles involved in their use has made it seem worthwhile to prepare this Letter Circular on the subject.

The principle of operation in the mass spectrometer is entirely different from that used in conventional chemistry. The various molecular masses are actually separated by deflection in a magnetic field. The magnet and not the conventional test tube is the chief tool of the mass spectrometer chemist.

Molecules at rest do not have about them magnetic fields of any appreciable magnitude. Molecules which have been given an electric charge, however, will generate a magnetic field when put in motion. It is this field that is used in the mass spectrometer.

Four steps are involved in the operation. The first is to give a positive charge to the molecules that are to be separated. A positive charge of one unit of electricity can be given molecules in a number of ways. The most commonly used is to bombard the vapor to be analysed with a stream of electrons having about 50 volts of energy. In this bombardment an electron is knocked
off the molecule converting it into an ion having a single positive charge.

The second step in the operation is to give all positive ions exactly the same amount of energy. This is done by accelerating the ions through an electric field. Voltages from 500 to 5000 are often used. The velocity acquired by the ions in these electric fields is very high, often approaching one tenth that of light.

The third step is to separate the various ions by a magnetic field placed at right angles to the direction of motion of the ions. The fast moving ions generate about themselves a magnetic field which causes the ion to move at right angles to the field in an arc whose radius is proportional to the momentum of the ion. The radius of deflection for any given mass can be controlled by adjusting either the accelerating voltage or the strength of the magnetic field.

The fourth step is one in which all the molecules having a given radius of deflection are collected and recorded. Since each of the molecules carries a single positive charge, the relative number of the molecules of different masses is measured by allowing the ions to pass through an exit slit behind which is placed a plate connected to the grid of a sensitive vacuum tube and amplification circuit much the same as in a radio. The currents carried by the ions of each mass are exceedingly small, being of the order of a millionth of a billionth to a millionth of a millionth of an ampere. These small currents are amplified a billion times and then fed into galvanometers whose deflections are recorded on sensitive photographic paper.

The different molecular masses are brought to a focus in succession on the collecting plate by allowing the accelerating voltage or the magnetic field to change. The photographic record actually consists of a series of peaks, the height of each peak representing the relative abundance of each molecular species present.

The mass peaks observed on the record depend entirely upon the chemical nature of the material being analysed. In the case of a gas, nitrogen for instance, four peaks are observed. The principal peak occurs at mass 28; this peak is due to a molecule of nitrogen consisting of two atoms of nitrogen, the atomic weight of each being 14 times that of the hydrogen atom which is taken as unit mass. A very small peak occurs at mass 29 which is due to a molecule of nitrogen composed of one atom of mass 14 and one atom of heavy nitrogen of mass 15. In addition to the 28 and 29 peaks there are peaks
at $^{14}$ due to ordinary nitrogen atom and at $^{15}$ due to the heavy nitrogen atom. Oxygen, atomic weight 16, has its principal molecular peak at mass 32 with a very small peak at 34 due to heavy oxygen isotope; the atom peaks occur at 16 for the normal atom and 18 for the heavy isotope. A gas containing a mixture of oxygen and nitrogen is analysed very easily. Peaks at positions 28 and 32 indicate the presence of nitrogen and oxygen; the calibrated heights of the peaks show the amount. The analyses of hydrocarbon mixtures is illustrated by a typical example. All hydrocarbons are broken down upon bombardment by 50-volt electrons into every possible disintegration fragment. For instance, normal butane and isobutane, which are made up of 4 carbon atoms and 10 hydrogen atoms, will break up into 25 possible fragments containing carbon 12 and hydrogen. In addition, there are small peaks due to heavy carbon 13. Normal and isobutane have peaks at exactly the same positions but the ratios of the peaks are very different. In consequence, the presence of butane is indicated by the peak positions while the amounts of the two types are indicated by the peak ratios.

The first instrument which might be termed the forerunner of the mass spectrometer was built by Sir J. J. Thomson in 1912. The name mass spectrograph was first used in about 1920. Since 1920 a number of instruments have been built in various laboratories engaged in fundamental research. Prior to 1943 all of the instruments were used primarily in isotope investigations. No attempt was made to use the instrument in quantitative analytical chemistry.

About this time, Herbert Hoover, Jr., and Dr. H. W. Washburn observed that the various fragments into which hydrocarbon molecules were disintegrated upon bombardment by high speed electrons always occurred in the same ratio to each other for a given compound and also that the ratio was never the same between two different compounds.

This discovery by Hoover and Washburn made it possible to detect molecular species not only because of differences in their masses but because of differences in the way in which they dissociated. The possibility of using the mass spectrometer as a means for performing chemical analyses was thus opened up to them. Fortunately this new technique which can be applied to the analyses of complex mixtures of hydrocarbons was developed just in time to be of use to the synthetic rubber program.
What does a mass spectrometer look like? This depends on who has built the instrument. Most of the instruments have been constructed in research laboratories by the scientists themselves; in consequence, there is no set standard of appearance. The National Bureau of Standards has three instruments in operation. Two are laboratory built while the third was manufactured by the Consolidated Engineering Corporation. While the actual design is different for each, all three have large magnets weighing from 1000 lbs. to one ton. The analysing chamber where the molecules are separated is between the pole pieces of the magnet. The control panel looks something like the control board in a small radio broadcasting station with many dials and meters. A large number of vacuum tubes somewhat like those in a radio are required, the number varying from 40 to 58 in the three instruments at Standards.

The operation of the instrument is not particularly difficult. It is largely a matter of seeing that certain conditions, as shown by meter readings, are properly maintained. In fact, it is not unlike operating a radio. On a clear night a good radio will bring in some station on every broadcast frequency. If one set the radio at one end of the dial and then had a motor to slowly turn the dial to the opposite end, a series of stations would be picked up in order of their frequencies. It is just so in the mass spectrometer except that a series of molecular masses are picked up. Instead of being detected audibly, the masses are read on a visual meter and recorded on photographic or tracing paper. Any clever person with some knowledge of electricity, organic chemistry, and a little mathematics can learn to operate a mass spectrometer.

Problems that can be solved by the mass spectrometer can be grouped into two general classes: (1) Isotope analyses and (2) Chemical analyses. Prior to 1944, mass spectrometric research was confined almost exclusively to isotopic analyses. The remarkable strides made recently in gas and hydrocarbon analyses have pushed this type of work to the front. It should be mentioned, however, that mass spectrometers used in determinations of isotopes are relatively simple instruments compared to those needed for the analyses of complex hydrocarbon mixtures.

In spite of the fact that isotopes were proved to exist as early as 1912 by Sir J. J. Thomson using his early type mass spectrometer, it is only within the past ten years that they have been put to practical use. Dr. G. v. Hevesy was the first to point out that isotopes could be used as tracers or
tagged atoms in following the course of a specific compound through complicated metabolic or biological processes. This new technique was made practical by the research of Dr. H. C. Urey who developed efficient methods for the concentration of the isotopes of a number of the elements, particularly those of interest to the biologist. Both Hevesy and Urey have been awarded the Nobel Prize for their work.

Isotopes (defined as atoms having identical chemical properties but different atomic weights) are easily detected and measured in the mass spectrometer. Their application to biochemical research has made possible entirely new and much needed methods for studying the reactions that go on within the organism. There is every reason to believe that this type of research will be standard practice in biological, medical, and agricultural research.

Isotopes as interpreted by the mass spectrometer have many additional applications. An interesting example of such an application to physiology is the measurement of isotopeic compositions of potassium in various tissues of an organism. Not only is there a different ratio between the isotopes in the blood plasma and the kidney of a rat, but there is a similar difference between normal and cancerous tissue. On the small samples available for such work the most exacting chemical technique would fail to show a significant difference. With one of the instruments at the National Bureau of Standards about five analyses can be made per day. A sample the size of a pin head of any potassium-containing substances, such as clay or ash, is all that is required for an analysis.

Isotopes can also be used to determine the age of rocks and even of matter. The age of many old rocks can be computed from mass spectrometric measurements of the isotopes of lead, while measurements on the potassium-calcium, and rubidium-strontium isotope ratios make it possible to compute an upper limit for the age of matter itself.

At the present time the greatest use of the mass spectrometer is in the field of analytical chemistry. Considering the fact that this work only dates back a couple of years, the achievements cannot be considered other than phenomenal. Unfortunately, its application is so far limited to gas and hydrocarbon analysis, but this limitation is only from lack of development and is not inherent in the instrument. Analyses are made every day at the Bureau on complex gas mixtures, often containing as many as 20 compounds. While a part of these analyses could be made by conventional means, the work involved and time required would be infinitely greater.
The precision of the mass spectrometer is unusually high. No definite figure can be set for the limits of duplicability of the instrument, since some compounds can be analysed with a greater precision than can others. In general, duplicate determinations will check to within a few hundredths of one percent, although a spread of a few tenths of one percent is often encountered for certain very similar compounds. It can be stated, however, that the precision of the instrument often exceeds the ability of the operator to withdraw identical samples twice in succession.

As a consequence of the high precision of the instrument, it has been shown that the differences often reported by chemists when analysing supposedly the same material may in part be due to the extreme difficulty in obtaining duplicate samples. This problem has been particularly bothersome in the synthetic rubber program. New techniques in sampling as a result of mass spectrometric measurements may not only result in a marked improvement in the quality of synthetic rubber but will mean a big saving to the producers.

A new method for the analyses of rubbers, plastics, sizing, and organic materials of low or negligible vapor pressure has been developed at the National Bureau of Standards. Materials of this type are exceedingly difficult to analyse by conventional means. The method consists of subjecting 0.01 gram of the material in an evacuated ampoule to heat for a short period of time. A temperature of 400°C for 10 minutes has been found satisfactory for most substances. During the heating process the various materials are broken down into characteristic disintegration products which can be easily analysed in the mass spectrometer. About thirty different rubbers and plastics in addition to numerous other substances have been analysed by this technique. The method has been used to excellent advantage in the analyses of captured German rubbers and articles of clothing.

In addition to the regular samples submitted to the Bureau, special samples are often received which cannot be analysed by specified techniques. A few of these might be mentioned. Breakdown in airplane ignition cables was preceded by the formation of little blisters under the insulation. The analysis of the gas in one of these blisters showed the cause of the breakdown. The mass spectrometer is the only instrument capable of giving a complete quantitative analysis of such a tiny sample. The analysis of the sizing on a scrap of paper served to identify the source of paper. An analysis of a piece of photographic film identified the manufacturer. The advantage of the mass spectrometer in analyses of these types lies not only in its ability to analyse complex mixtures but also in the extreme smallness of the sample required.