tubes, and hence radiation reaching the outside must arise from multiple scattering processes. This consideration requires that the tubes be small.

The fluid-flow relationships involved either require relatively few large tubes or a large number of small tubes. With respect to the fluid-flow relationship, the criterion used was to make the largest individual pressure drop be that associated with the slots, since their size, as described here, is governed by other factors and not easily subject to change. As a result, many small tubes are used. The natural circulation can be improved by adding a stack to the facility, as is shown.

The over-all dimensions of such a proposed facility would be about 4 feet in diameter by 4 feet in height, with a 6-foot stack having an internal diameter of about 10 inches. The weight of such a unit would be about 13.5 tons. The inner cylindrical core (containing the rectangular slots) would be about 2 feet in diameter by 2 feet in height. Each slot would contain two cobalt strips arranged vertically, one above the other. Since 334 strips are required to constitute a megacurie, 167 slots would be required, and these would be arranged on concentric circles spaced 1½ inches apart. Each rod in a given circle would also be about 1.5 inches apart, from center to center. Since each slot is 1 inch by 0.5 inch, the thickness of lead between slots (and hence between cobalt strips) would be 1 inch in a radial direction and 0.5 inch along the circumference of the circle. The air chambers above and below the central core would be 4 inches in height, and there would be 100 1-inch tubes in the top and bottom sections to permit circulation of air.

The temperatures of interest in such a facility are those at the outer surface, in the central core, and in the individual cobalt strips. Since these temperatures are dependent on position, the values given in Table 2 refer to specific locations as follows: t_1 is the temperature of the outer surface at a point midway between top and bottom; t_2 is the temperature at the center of the core; t_3 is the temperature at the center of a cobalt strip; and t_4 is the temperature of the air in the tubes leaving the facility. The calculations that led to the results given here involved many assumptions and approximations, which are too numerous and too involved to discuss in this paper.

Bendix Time-of-Flight Mass Spectrometer

W. C. Wiley

The combination of high resolution with the speed of response and geometric simplicity of time-of-flight mass spectrometers makes possible the application of mass spectrometry to a number of analysis and research problems which heretofore have not been well suited to this technique. The development of the Bendix spectrometer began with the invention of a new ion gun (*1*) which was capable of providing very high resolving power when used in a time-of-flight mass spectrometer. Further development work was encouraged by the inherent versatility of the instrument both in its operation and in its design. Several models have now been designed and built on special order to satisfy a number of different applications. Following a description of the spectrometer's operation and a summary of its characteristics, some of these applications are discussed.

Operation

Several classes of mass spectrometers are commonly referred to as time-of-flight instruments. The Bendix spectrometer belongs to the class which probably represents the most straightforward application of time of flight to mass spectrometry and, in its simplest form, consists merely of an ion source and an ion collector situated at opposite ends of an evacuated tube, as is shown in Fig. 1.

Ions are first formed, usually by electron bombardment, between the two electrodes of the ion source. By applying a voltage pulse between these electrodes, the ion bunch can be ejected through an opening or grid in one of the electrodes. Because the ions, as a result of the accelerating field, reach a velocity that is a function of their mass to charge ratio, the original bunch of ions separates as it passes through the field-free region between the source and the detector into several bunches, each containing ions of a specific mass to charge ratio. Hence, the light ions will reach the ion detector first, followed in succession by the heavier ions.

One of the many methods in which the Bendix spectrometer can be operated is described in more detail with the aid of Fig. 2. The first event in the creation of a single mass spectrum, many thousands of which may be formed every second, is the establishment of the electron beam in the temporarily field-free ionizing region. This beam, which usually lasts a fraction of a microsecond, is produced when electrons are drawn off a hot filament by a voltage pulse applied to the adjacent electrode. After this beam is turned off, grid 1 is pulsed to eject the resulting ion bunch into the accelerating region. The direct-current source potentials are arranged so that the ions receive their major acceleration as they pass through this area on their way to the field-free separating region or drift space.

If the ions before pulsing were at rest and all in a plane parallel to the electrodes, almost any method of ejecting them from the source would provide infinite mass resolution, regardless of the total length of the flight path. The resolving power of the instrument is, therefore, a measure of the ability of the source to deliver the ions of one mass to charge ratio to the detector in a sharp pulse, even though the ions will inevitably vary in initial position and velocity. The effect of variations in the ions' initial position can be reduced by taking advantage of the fact that those ions farther away from grid 1 fall through a larger potential during the ion-ejection period than do those nearer this grid. The trailing ions will, therefore, acquire a greater velocity and will eventually overtake those in front. A proper adjustment of the fields in the ionizing and accelerating regions, usually made by varying the height of the ion-ejecting pulse applied to grid 1, causes the "crossover point" for all ion peaks to occur as they pass through grid 3 into the ion detector. The deleterious effect of initial ion velocities on the resolution of a time-of-flight spectrometer can be reduced in two ways: (i) the final velocity of the ions can be

---

Dr. Wiley is project physicist in the Research Laboratories Division of the Bendix Aviation Corporation, Detroit, Michigan.

made large relative to their initial velocities; (ii) the time during which the ions are traveling with their final velocity can be made large compared with the total time of flight. The latter method has the effect of increasing the average velocity of the ions during their total flight time relative to their initial velocities. The high resolution produced by the Bendix spectrometer compared with other time-of-flight instruments is in large measure due to its ability to give the ions a high average velocity without using prohibitively high voltages or requiring a speed of response in the ion detector and output system beyond present electronic art.

A mathematical treatment of the focusing action of this source has appeared in a previous article (*2*). The time of flight for an ion of mass M and charge q is $T = \lambda(M/q)^{1/2}$, where λ is a function of dimensions and voltages. A representative value for the flight time of a singly charged nitrogen ion ($M = 28$ atomic mass units) is 5 microseconds, and under usual conditions the time width of the nitrogen pulse at half height is about 0.015 microsecond.

A magnetic electron multiplier is used to detect and amplify the ion bunches, or peaks. The ions pass through grid 3 into the electron multiplier, strike the first multiplying plate or dynode, and produce secondary electrons. These electrons follow cycloidal paths under the influence of the mutually perpendicular electric and magnetic fields in the multiplier. After suitable multiplication, the resulting output signal can be displayed on an oscilloscope synchronized with the ion-accelerating pulse.

Characteristics

In large measure, the inherent stability and ruggedness of the Bendix spectrometer result from the simplicity of the mechanical construction. Since the resolution depends on temporal, rather than geometric factors, no accurate alignment or stringent geometric conditions are required. The size and shape of the evacuated volume is not restricted by the presence of a magnet, so that the effects of stray fields, arising from contaminated surfaces, can be minimized. This consideration, coupled with the fact that the performance of the instrument is dependent on only a small number of electrodes, permits the physical design to be quite flexible. Thus the problem of modifying the device for specific purposes is greatly simplified.

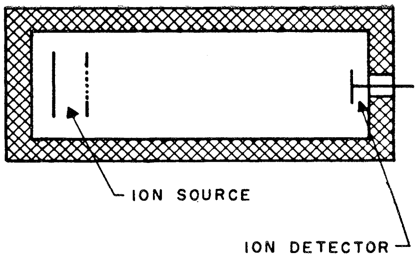

Fig. 1. Basic geometry of the Bendix spectrometer.

The resolution of the Bendix spectrometer varies with several parameters, such as flight time, flight-path length, and ion-source dimensions. As the instrument parameters are varied to improve resolution, the sensitivity drops. The best resolution achieved to date is illustrated by the oscillogram shown in Fig. 3, while the compromise between resolution and sensitivity chosen for recent models gives the "normal" resolution shown in Figs. 4 and 5. Careful oscilloscope measurements have been made of this normal resolution at many masses up through xenon. Direct measurement on higher masses have not yet been made, but extrapolation of the data taken in this lower mass range shows that mass 400 atomic mass units should contribute about 1 percent of its height to adjacent peaks and mass 600 atomic mass units has a width at half-height equal to the time separation between the centers of masses 600 and 601.

An important characteristic of this instrument is the speed with which an analysis can be made. If one takes pictures of an oscilloscope screen, it is possible to get a complete analysis recorded in a few microseconds. It should be noted that, although the mass spectrum might take 10 to 20 microseconds to be detected, the ions in this mass spectrum were all formed during a fraction of a microsecond in the ion source; and thus the spectrum represents the average composition of the sample during a period no longer than a fraction of a microsecond. As in all mass spectrometers, the sensitivity depends on the resolution. Sensitivities on the order of 1 part in a million are theoretically possible in the low mass range.

There are several ways in which the mass spectra can be recorded. The simplest is the oscilloscope display mentioned previously, which exhibits the maximum resolution of the instrument and preserves the inherent speed of analysis. Some applications, however, require greater accuracy and sensitivity than those obtainable through oscilloscope presentation. For these, the magnetic electron multiplier has been further developed to provide three separate anodes. One of these anodes is usually connected to the oscilloscope. The other two can be activated electronically (gated) so that any portion of the mass spectrum can be directed onto each of these anodes, the remainder of the spectrum going to the oscilloscope anode. The two gated anodes are usually connected to an integrating direct-current amplifier which produces a voltage proportional to the average area under that part of the mass spectrum selected. The ratio of the two voltages obtained in this way can then be obtained and recorded if desired. Ratio recording has several advantages stemming from the fact that any variable in the machine which changes the size of all peaks proportionally will have no effect on ratios. Thus, changes in the electron-beam intensity, the gas flow into the instrument, or the amplification of the multiplier do not affect the analysis and, consequently, do not require precise regulation. Applications utilizing this ratio output are described later.

A modification of this ratio-recording principle involves the use of pulse-counting techniques. Some ion peaks are so small that an average of less than 1 ion appears each cycle. The ratio of two such peaks can be taken by counting the pulses that occur during the time interval belonging to each peak and comparing the two counts periodically. The noise pulses produced by the multiplier are equivalent to an ion pulse containing about 6×10^{-6} ions, so that noise pulses do not impose a serious restriction on measuring small peaks by this method.

Applications

Probably the most obvious application is the analysis of very fast chemical reactions, especially analyses in which one is attempting to detect radicals with half-lives in the microsecond region and which must be detected before they have suffered any wall collisions. One of the instruments of this type is designed to produce a spectrum every 50 microseconds which is photographed by a high-speed camera. The ionizing region and the reaction chamber are separated by only a thin wall with a small pinhole through it,

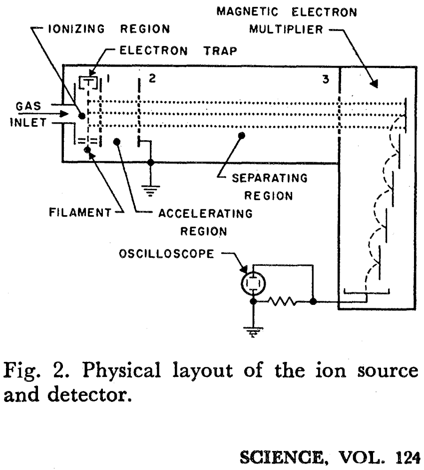

Fig. 2. Physical layout of the ion source and detector.

assuring the smallest possible path length for the radicals before ionization. The electron beam is directed to graze the inner side of this pinhole so that the gas is being ionized at the point where its pressure is the greatest.

Perhaps the biggest problem in this type of analysis is reducing the background to a sufficiently small value. Background gas in this case includes not only products from the diffusion pump and gases originating in the walls of the vessel but also any molecules that have gone through the pinhole and have rebounded against a surface at least once. Thus, it is important to keep any surfaces in front of the pinhole to a minimum, so that a particle after rebounding will have a much greater chance of being captured by the pumping system than of returning to the ionizing region. This is accomplished by using accelerating grids with very high transmission factors, providing a large evacuated volume beyond the ion source, utilizing large diffusion pumps, and preventing ions that are formed by the electron beam in a region other than that directly in front of the pinhole from ever reaching the ion collector.

A promising approach to the problem of producing chemicals more efficiently, which has been receiving attention recently, is the utilization of fast reactions nearing the speed and violence present in a ram jet engine (*3*). Some fast reactions are already utilized by the chemical industry; for instance, ethylene is made with high efficiency from propane gas by simply passing the propane through a hot tube. However, the wide application of these fast reactions is being limited by the difficulty of determining the complete chemical processes involved, especially the identity of the many intermediate products, some of which have more value than do the end-products. The ability of the Bendix spectrometer to help solve some of the formidable instrumentation problems should materially contribute to the development of this rapidly growing field.

There is another class of problems suitable for mass spectrometers which utilize only an oscilloscope as an output system but do not require the extreme speeds necessary in very fast reaction work. One of the most interesting applications is in the identification of the separated components emerging from a vapor-phase chromatographer. The common method for identifying each component is to measure the time lapse between the introduction of the mixture and the emergence of the separated component from the chromatography column as indicated by a thermal conductivity gage. If the same column has been previously calibrated with this same component under identical column temperature, carrier gas pressure, and carrier gas flow rate conditions, this emergence time can be used for identification. For general analysis applications, however, such a limitation to one set of operating conditions is a definite disadvantage, since the full resolution possible with chromatography depends on the utilization of many different column temperatures, flow rates, and especially column materials. Switching from one set of operating conditions to another not only varies the emergence times of separated compounds but, in some cases, the order of emergence as well. The mass spectrometer has been used to identify the emergent compounds, but heretofore this has required tedious collection of each component in a separate sample bottle and subsequent admission of each sample in turn to the spectrometer.

Using the Bendix spectrometer, the identification of the emerging components can be made simply by allowing a portion of the effluent gas to pass into the spectrometer. As each unknown emerges, its unique spectrum will rise and fall on the oscilloscope screen, affording positive identification in most cases. Photographs of the mass spectra can be taken if a permanent record is desired, and the relative abundance of the components can be determined by monitoring multiplier output current or utilizing a conductivity cell in the conventional manner.

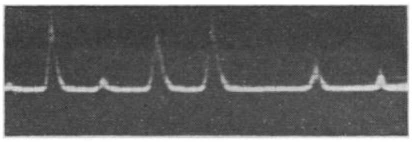

Fig. 3. Oscillogram of the mass spectrum of some xenon isotopes. The masses are, from left to right, 128, 129, 130, 131, 132, 134, and 136 amu.

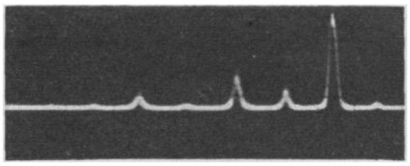

Fig. 4. Oscillogram of a section of the n-butane mass spectrum. From left to right, the masses are 39, 40, 41, 42, 43, and 44 amu.

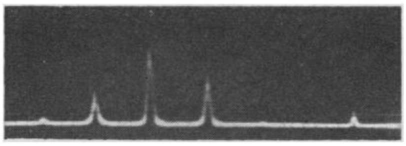

Fig. 5. Oscillogram of a portion of the spectrum produced with a mixture of air and n-butane. The masses, from left to right, are 26, 27, 28, 29, 30, and 32 amu.

Because of its inherent characteristics, the ratio system described here promises to create important applications for this instrument in the process monitoring and process control fields. The relative independence of the ratio output with source pressure, source temperature, electron-beam current, and multiplier gain leads to a relaxation of regulation and calibration requirements, and the simplicity and ruggedness of the design facilitates adaptation to industrial-plan operation. Another advantage derived from the independence of the ratio output on source pressure is the feasibility of automatic calibration by rapid sample stream switching. Consider a ratio system that switches the sample stream between a standard and an unknown or process stream many times a second and then detects the ratio difference existing between the standard and the unknown with a null detector tuned to the frequency of the sample switcher. It would be difficult in such a system to hold the source pressure constant, but this is not necessary with ratio operation, since both peaks of the ratio are affected proportionately by source pressure changes. Sample switching coupled with the null detection of a ratio greatly reduces dependence on operating variables and produces a continuously calibrated signal.

In some pilot-plant operations, the ratio output could be used to optimize more quickly the process under investigation. In those stages of the process which could be optimized by maximizing or minimizing a ratio of two peaks or two sections of the spectrum, much time could be saved by inserting the sample system of the spectrometer directly into the process stream and changing the plant-operating variables while watching the ratio. The oscilloscope spectrum could also contribute valuable information during this procedure.

Applications in the chemical laboratory also exist for the Bendix spectrometer. In many cases, the samples produced in laboratories are analyzed by a separate mass-spectrometer group, often resulting in serious delays. The simplicity and low cost of this instrument when it is equipped with only an oscilloscope output make it practical for a chemist to use it in his own laboratory as a versatile, fast-responding tool to aid him in simple analyses and the monitoring of chemical reactions. A number of accessories can be used with this instrument to increase its versatility, such as standard sample systems, independently timed oscilloscope sweeps on alternate cycles so that any two mass peaks can be brought into coincidence on the screen for direct comparison, simple pulse-counting systems that measure peaks containing less than 1 ion per spectrum which allow one to utilize the full sensitivity range of the instrument, and simple gating systems which allow conventional recording of mass spectra.

An experiment recently performed concerning the detection of metallic ions may suggest other applications for the instrument. It was desired to check the dependence of resolution on initial energies considerably higher than those usually encountered, and for this purpose a beam of metallic molecules, thermally emitted from a hot source, was allowed to pass through the ionizing region at right angles to the electron beam and parallel to the source electrodes. As was expected, the resolution was unaffected by this transverse velocity. In general the resolution and intensity obtained with metallic vapors have proved to be very similar to those that would be obtained with gases at the same molecular density. It was possible, however, to detect a shift in the direction of travel of the metallic ion beam as compared with the background ions, the metallic ions being displaced at the collector in the direction of their high initial velocities. This fact can be turned to advantage by aiming the metallic ions directly at the collector, causing the majority of the background ions to be lost to one side. With aluminum vapor, an improvement of a factor of 10 for the sensitivity of the metallic vapor as compared with the background gas was obtained in this way.

Another application in the experimental field is to measure the lifetime of different types of ions by varying the time between the shutoff of the ionizing electron beam and the beginning of the ion-acceleration pulse. With most source geometries it is possible to have a lag between ion formation and ejection from the source of about 5 to 10 microseconds.

Conclusions

Many of the applications of the Bendix Time-of-Flight Mass Spectrometer make use of the instrument's high resolution, speed of response, and simplicity. Among these are studies of fast reactions, the monitoring of chromatography columns, fast, moderately accurate chemical analyses, the optimizing of pilot-plant operations, the detection of metallic vapors, and studies of ion lifetimes.

Further experience is expected to uncover other applications to the problems of science and industry where the unique characteristics of this instrument can be of service.

References and Notes

1. U.S. patent 2,685,035.
2. W. C. Wiley and I. H. McLaren, *Rev. Sci. Instr.* **26**, 1150 (1955).
3. L. P. Lessing, *Sci. Am.* **188**, No. 5, 29 (May 1953).

News of Science

Phosphagen of Tunicates

It has been established that invertebrates and vertebrates differ with respect to their phosphagens. Thus, phosphoarginine is characteristic of invertebrates and phosphocreatine of vertebrates.

The invertebrates, however, exhibit some variability [Baldwin, *Dynamic Aspects of Biochemistry* (Cambridge Univ. Press, ed. 2, 1952)]. Although most of the five extant classes of Echinodermata possess nonprotein arginine and so follow the general invertebrate pattern, the Ophiuroidea contain creatine and the Echinoidea both arginine and creatine. A few invertebrates are devoid of both phosphoarginine and phosphocreatine but possess one or the other (gephyreans, some polychaete annelids) or both (some polychaetes) of two recently discovered phosphagens that contain neither arginine nor creatine. On the other hand, phosphocreatine is the only phosphagen present in vertebrates.

The protochordates (Hemichordata, Urochordata, Cephalochordata), although they are grouped together with the vertebrates to form a single phylum, the Chordata, are recognized as being morphologically intermediate between invertebrates and vertebrates. Their biochemical affinities, and hence their phosphagens, are therefore of considerable interest (see Baldwin, 1952). Only phosphocreatine is present in Cephalochordata (lancelets), which thus most closely resemble vertebrates, as they do in their morphology. On the other hand, the Hemichordata (sea acorns), which exhibit the greatest structural affinities with invertebrates, appropriately possess both the arginine and creatine compounds. Since 1932, the Urochordata (tunicates or sea squirts) have been regarded as quite anomalous among chordates in this respect, for the studies of both Flössner and Needham *et al.* have indicated the presence of phosphoarginine, but not of phosphocreatine, in these animals. Hence, in this respect, the tunicates have been thought to resemble the invertebrates.

Morrison, Griffiths, and Ennor have recently reported a study of two species of tunicates, *Pyura stolonifera* and *P.* sp. [*Nature,* **178,** 359 (18 Aug. 1956)] in which they found no traces of arginine, phosphoarginine, or arginine phosphokinase. However, the presence of creatine, phosphocreatine, and an enzyme possessing creatine phosphokinase activity was established. The authors note that, although it may not be permissible to conclude that tunicates as a class possess phosphocreatine, their findings on *Pyura* do relieve these animals of their anomalous position and provide biochemical support for their accepted classification among the chordates.

It would seem of interest to investigate the phosphagens of other species of tunicates, including those already studied by earlier workers. It may well be that Flössner, Needham *et al.,* and Morrison *et al.* are all correct; if so, the tunicates possess more than one type of phosphagen, which varies with the species, sometimes being phosphoarginine, as in invertebrates, sometimes phosphocreatine, as in vertebrates and lancelets, and sometimes, perhaps, both of these compounds, as in hemichordates. This would befit the accepted phylogenetic position of the Urochordata.—W. L. S., Jr..

French Atomic Power

France became the first country on the West European continent to produce electricity by atomic means on 28 Sept. On that date the atomic center at Marcoule, on the Rhone River north of Avignon, began to produce sufficient heat to make vapor, which in turn started the operation of specially constructed turbines.

The pile, the first of three that will be built at Marcoule, began operating in