During the past few years, it has become clear that there are three important problem areas in which important advances can be made with the aid of mass spectrometry. Beynon [3] has shown that substances of unknown identity may often be characterized by a single measurement of molecular weight if that measurement can be made with sufficient precision. Hood and O'Neal [7] and others have shown that much valuable information on the structure of high molecular-weight materials can be obtained if mass spectra can be extended into the region well above 1000 a.m.u. And Dempster [5], Hannay and Ahearn [6], and Craig, Errock and Waldron [4] have shown that the mass spectrometer can be used to identify impurities in solids at abundances of \(1:10^8\) and below.

All three problem areas require double-focusing mass resolving systems, although for different reasons. The first two problem areas mentioned above require mass resolution in excess of \(1:1000\), and preferably approaching \(1:10,000\). To obtain this resolution, a double-focusing mass resolving system is required even though the velocity spread of the ion beam may be comparatively low. In the third problem area, it is desirable, for the sake of nonpreferential ionization, to use a radiofrequency spark ion source, (in which the ion beam unfortunately has a very high velocity spread), so that a double-focusing mass resolving system must be used to achieve a mass resolving power of even a few hundred.

The radiofrequency spark ion source produces an ion beam with very large velocity spread. Another characteristic, which places a second requirement on the mass resolving system to be used with it, is that the ion beam from it is so unsteady that one must record the whole mass spectrum at the same time, on a photographic plate which averages the fluctuations in ion current and integrates all the individual currents simultaneously.

The two main characteristics of the radiofrequency spark ion source—the high velocity spread of the ion beam and the unsteady nature of the ion current—dictate that the Mattauch-Herzog [8] mass resolving system must

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be used with it. The question then arises whether the Mattauch-Herzog resolving system would also be suitable for use in extremely high resolution work according to the technique of Beynon, and for work at high molecular weights. If so, it would be possible to arrange for work in one area or another simply by selection of appropriate ion sources and ion detectors, using the same basic mass resolving system for all three. Such an arrangement would also permit the use of the photographic plate for qualitative work, over a broad region of the spectrum and at extremely high mass resolution, when using a gas ion source for work at high molecular weights or for work at extreme resolution in the lower molecular weight region.

The great power and versatility of a mass spectrometer system based on this approach area is easily seen.

We have done a considerable theoretical and experimental study [10] to determine the limitations of several double-focusing mass resolving systems. Our conclusion is that the Mattauch-Herzog mass resolving system, incorporating a modification due to one of us [9], is well suited to use in all three problem areas.

**THE MASS RESOLVING SYSTEM**

The basic geometry is shown in Fig. 1. It has the classical arrangement of a 31.8° electric sector followed by 90° magnetic deflection. The system has been modified by introducing a curved boundary at the edge of the magnetic sector, which nullifies both of the second-order velocity-dependent aberrations simultaneously at one point on the focal plane, thus effecting a considerable improvement in resolving power at that point and some improvement throughout most of the focal plane. The mean radius of the electric sector is approximately 64 cm and the radius of curvature of the ion beam in the magnetic field may range from approximately 5 to 30 cm, giving a ratio of about 37:1 between the maximum and the minimum ion masses.
that can be covered in a single exposure. The path length of the ion beam varies from 113 cm to 153 cm, depending on the mass of the ion.

In the classical Mattauch-Herzog mass resolving system, there is no focusing in the direction parallel to the magnetic field. We have provided a three-element unipotential electrostatic lens between the object slit and the electric sector to provide such focusing. This lens improves the sensitivity of the system by about 5:1. With the gas ion source and a Knudsen cell, where ions may have substantial transverse velocities due to the high initial energies in the Knudsen cell, this lens serves to make the system conserve ions which would otherwise be lost.

A Herzog shunt at the boundary of the magnetic field has been provided so that the detailed shape of the fringing field would be known accurately. The electric deflector plates are made of vacuum annealed Armco iron in order to obtain magnetic shielding in the electric sector, and magnetic shielding has been installed between the electric sector and the Herzog shunt. These precautions have resulted in a marked narrowing of the lines which have their origin in metastable or charge-exchange processes occurring between the electric sector and the magnetic field. We will show an example of potential interferences which are avoided by such careful control of the magnetic fringing fields (Fig. 7).

The vacuum system is divided into three sections, each independently pumped through its own liquid nitrogen trap and mercury diffusion pump. Each section can be isolated from the other two, and from its pumping system, by means of valves. Thus it is possible to change samples in the ion source, or to change photographic plates, in five minutes or less, and to pump down the ion source or the photographic plate holder in approximately twenty minutes. If the speed of changing samples and of changing photographic plates were the principal limitation on the work-handling capacity of the instrument, it would be possible easily to run more than a dozen samples per eight-hour day. However, other factors, such as the availability of personnel to prepare and clean the samples and to analyze the photographic plates, usually limit the number of samples that can be run, intelligently and with profit, to a fraction of this figure.

The voltage supply for the electric sector, and the current supply for the magnet, operate from a common voltage reference which is stable to better than $1 \times 10^{-5}$. Thus the electric deflecting voltage and the magnetic field are both stable to approximately 15 parts per million over long periods of time. The principle features in the design of these supplies are described elsewhere [1, 2] and need not be discussed here. The maximum magnetic field of 12,500 Gauss is sufficient to contain ions of mass approximately 450 a.m.u. at the full accelerating voltage of 15,000 V. For work at higher masses, the ion accelerating voltage may be reduced to 7.5, 3.75, or 1.875 kV.
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Fig. 2.—Top view of mass spectrometer with radio frequency spark ion source.

In using the gas ion source, where it is possible to produce a mass spectrum by moving the ion beams past a fixed slit, scanning is accomplished by varying the magnetic field by means of a slowly and smoothly changing reference potentiometer which is driven, through a gearbox, by an electric motor. Scanning speed is selected by choosing one or another of several fixed gear reduction ratios. In this way, the scanning speeds are very accurately reproducible, and the mass scale on the record is reproduced accurately from one spectrum to the next. A mass range of approximately 25:1 can be accomplished in a single scan.

The photographic plate ion detector

Fig. 2 shows the instrument arranged for use with the radiofrequency spark ion source. In this mode of operation, the ions are detected by a photographic plate placed on the focal plane. The plate can be moved between one exposure and the next (or, if desired, during an exposure), through a total distance of 3.35 cm. Ordinarily, the system is arranged to produce spectral lines approximately 2 mm long, with a clear space of approximately $\frac{1}{2}$ mm between successive spectra, thirteen distinct spectra being produced on a single plate. It is a comparatively simple matter to modify the system, if desired, to produce much shorter lines, and consequently many more spectra per plate. In fact, it may be very useful in the study of transient
phenomena to shorten the lines to a few tenths of a millimeter and to trans­
port the plate continuously during an exposure, thus providing a contin­
uous series of high-resolution mass spectra during the entire duration of the
phenomenon under study.

THE RADIOFREQUENCY SPARK ION SOURCE

The geometrical arrangement of the electrodes in the radiofrequency spark
ion source is based on an earlier arrangement by Hannay and Ahearn. Radiofrequency power, at a frequency of about one megacycle and at
voltages up to 100 kilovolts, is provided by a pulsed oscillator—power
amplifier arrangement capable of providing instantaneous power output
as high as twelve to fifteen kilowatts. The pulse repetition rate is adjustable
from one pulse per second to 10,000 pulses per second, at a pulse duration
adjustable from about five microseconds to about forty microseconds.

Optimum operating conditions will depend on the nature of the sample.
It usually seems preferable to run with pulse length and repetition rate
adjusted to avoid appreciable heating of the sample, so as to avoid distilling
volatile impurities out of the sample at a disproportionate rate. Thus the maximum ion current which can be obtained with a given sample will depend on its melting and boiling points, its thermal conductivity, and other factors. With care, low-melting alloys such as Pb-Sn solders can be analyzed with good results. A partial list of materials which have been analyzed successfully would include Be, C, Al, Si, Fe, Cu, GaAs, As, Se, Zn, Au, Er, Nb, InSb, W, stainless steel alloys, and various solders and brazing alloys.

The sensitivity for a given element will obviously vary with the abundance of the most abundant isotope; the detection limit is lower for essentially monoisotopic elements than for elements such as Mo in which the most abundant isotope may represent only 24 per cent of the total. We have no evidence that variations in the sensitivity, from element to element, are larger than can be explained by variations in isotope distribution and variations in sensitivity of the Q plates.

Under the vigorous sparking conditions used in analyzing metals, it appears that the analysis is essentially atomic. However, it is possible to analyze complex hydrocarbons with the radiofrequency spark under proper experimental conditions. Mr. W. L. Baun, at the Materials Laboratory, Wright Air Development Division, United States Air Force, has obtained full spectra from amino acids such as acetyl glycine by packing them in hollow graphite spectrographic electrodes which are then sparked in the usual way. The parent peak, a peak at the parent position plus 1 a.m.u., plus the usual fragment peaks, have been observed.

The electron multiplier ion detector

Fig. 3 shows one configuration for the detector assembly, in which maximum attention has been paid to versatility. In this configuration, changing from photographic plate to electrometer or electron multiplier can be done in the length of time required to change photographic plates. In fact, this configuration would make it possible in principle to use photographic plates, electrometer, and electron multiplier simultaneously, although we do not at the moment see any problems in which such elaboration would be useful.

In the arrangement of Fig. 3, changing from photographic plate to electrometer or electron multiplier detection involves removing the photographic plate and substituting for it, in the same plate holder, a metal plate into which the desired resolving slit configuration has been placed. This metal plate can also be moved vertically through a distance of 3.35 cm. Thus it is possible to arrange several different combinations of slit widths, multiple slit spacings, etc., in the slit plate, and to select the desired slit width or configuration simply by moving the slit plate vertically until the desired
configuration is in register with the magnet gap. Two ion beams having mass ratio up to about 2:1 can be measured simultaneously with any combination of electrometer and electron multiplier detector. Thus is is possible (for example) to scan two spectra, one at high resolution with an electron multiplier detector and one at lower resolution with an electrometer detector, in a single operation.

ARRANGEMENT FOR ANALYSIS OF GASES AND LIQUIDS

Fig. 4 shows an arrangement for analysis of gases and liquids with inlet system temperatures up to 350°C. The heated inlet system used in this arrangement is shown in Fig. 5. A front view of a complete instrument is shown in Fig. 6.

EXPERIMENTAL RESULTS

Fig. 7 shows a microphotometer trace of a plate produced with the radio-frequency spark ion source, using a Zircalloy sample. Resolution of the potential interferences between the $^{180}$Hf contaminant, the $^{90}$Zr$_2$ molecular ion, and the $^{90}$Zr$^{+2-1}$ charge exchange line are easily achieved with the mass resolving power available.
Fig. 6.—Front view of complete instrument.

Fig. 8 illustrates a resolved doublet at mass 52 a.m.u. showing the use of high mass resolution in resolving the potential interference between $^{52}\text{Cr}$ and $^{208}\text{Pb}^{+4}$. Detection of small amounts of Cr in Pb would be difficult or impossible without resolving power well in excess of 1:1000.

Fig. 9 is a microphotometer tracing of the mass spectrum in the neighborhood of mass 27 a.m.u., the sample being aluminum. The exposure is sufficient to permit detection of impurities at concentrations of a few parts in $10^8$. The $^{28}\text{Si}$ peak, representing approximately 3 ppm, is saturated; the $^{29}\text{Si}$ peak, having atomic abundance approximately 0.3 ppm, is above the detection threshold by approximately an order of magnitude. This plate illustrates again the importance of high mass resolution in metallurgical analysis, since hydrocarbon background peaks may be resolved from metal ions (see, for example, the doublets $^{\text{C}_2\text{H}_6-^{29}\text{Si}}$, $^{\text{C}_2\text{H}_6-^{28}\text{Mg}}$, $^{\text{C}_2-^{24}\text{Mg}}$, etc.).

The narrowness of the lines which results from high resolution permits producing a visible line on the Ilford Q2 plates which we ordinarily use with only about 3000 ions. Thus a detection limit of approximately $0.05 \times 10^{-6}$, for essentially monoisotopic species, results from a total exposure of only $10^{-8}$ coulombs. Such an exposure can be delivered in about five to ten minutes, depending on the sample. With such comparatively weak exposures,
Fig. 7. — A microphotometer tracing of a triplet at mass 180 A. M. U., illustrating the usefulness of high mass resolution in the suppression of interferences due to secondary effects. The sample is zircalloy; the magnetic radius of the members of this triplet is about 10.2". Fig. 8. — A microphotometer trace of the doublet $^{52}\text{Cr}^+ + ^{208}\text{Pb}^+$. The magnetic radius of this complex is about 5.4". The physical separation of these two lines on the plate is about 0.0039". The Cr line is somewhat broadened by over-exposure.

the spreading of the strong lines in the spectrum is minimized. Thus we are able to detect minor impurities only one a.m.u. removed from the strongest lines in the spectrum in nearly all cases, as is shown in Fig. 9.

Fig. 10 shows a portion of a plate exposed with the gas ion source. The identification of the line at mass 29 a.m.u., permitted by the high mass resolving power available, made it possible to establish definitely that the line in question is due to a recombination process. At mass 28 a triplet is
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registered showing resolution of 1:3000. At mass 28, made with a gas ion source, Fig. 11 shows a reproduction of a recorder tracing of the same triplet using electrometer ion detection.

**DISCUSSION**

In the electrical recording of mass spectra at high resolution, there are serious fundamental problems. If the mass resolution is as high as 1:5000, there may be as many as 200 to 500 distinguishable positions, between consecutive atomic mass numbers, at which a line could occur. Although most of these positions would be vacant in the usual case, the frequency pass band of the recording system must be wide enough to record a peak at *every distinguishable position* if acceptable fidelity is to be achieved. Under such conditions, the scan speed of a system is severely limited by the intrinsic statistical fluctuations in the ion beam. If, for example, one wishes a detection limit of only 1:10⁴ (approximately 10⁻¹⁴ A), then the maximum possible scan speed, in a completely noise-free recording system having a frequency pass band of 10,000 cycles, is of the order of one a.m.u. per second. Even in such an unattainably idealized system, a minute or two might be required for scanning a mass spectrum of sufficient width for exploratory purposes. Obviously, it would be very difficult to use such an approach for the study of transient events. However, the photographic plate, under the same conditions of total ion current, will produce a detectable line, at any position at which it may occur, in approximately 50 milliseconds. Major
components would be detected in a few microseconds. We suggest that there are many problems in reaction kinetics, in identification of gas chromatograph effluents, in studies of the change in composition of a vapor stream with changes in temperature, and related problems in which photographic plates will be found indispensable during the early exploratory phases of the investigation.

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