Construction and operation of a 90° Nier type single focusing mass spectrometer

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A 90° Nier type mass-spectrometer with a nominal radius of curvature of 15 cm for ion trajectory has been set up. An electromagnet capable of generating magnetic field up to 6000 oersteds is used in the instrument This is energized by a stabilized magnet current supply circuit, in which the current can be varied continuously from 10 to 115 mA Ion accelerating voltage is supplied from a highly stabilized 2000 volts supply together with a potential dividing circuit Filament emission is also controlled from a suitable stabilized circuit The sample handling system and vacuum system are described in the paper.

INTRODUCTION

A 90° sector field single focusing mass spectrometer with a nominal radius of curvature of 15 cm for the ion trajectory has been constructed and successfully operated in this laboratory (Nier 1940). The instrument has been built for studies of ionization and fragmentation of molecules by electron impact.

The principle of the first-order single-focusing, sector-field mass spectrometer is well known Since in these instruments only directional focusing is used, the magnetic field actually gives a momentum spectrum. This necessitates the use of an ion source (*e g.*, of the electron bombardment type) which produces nearly mono-energetic ions The usual mass spectrometer equation then becomes

$$M/e = 4.79 \times 10^{-5} r^2 H^2 / V$$

where M is the mass of the ion in a m u , e is the charge of the ion in units of electronic charge, r is the radius of the ion trajectory in the magnetic field, H is the magnetic field in oersted, and V is the ion-accelerating potential in volts In the present instrument r has a nominal value of 15.24 cm (6 inches) and so for singly charged ions,

$$MV = 1.11 \times 10^{-2} H^2.$$

V can be varied from 0 to 2000 volts and H from about 500 to 6000 oersteds. The usable mass range is, therefore, from 4 to 400 a.m.u , although the resolution at higher masses will necessarily be poor.

ANALYSER TUBE

The analyser tube, made of copper, was obtained as a gift from Prof. H. G. Thode of McMaster University, Hamilton, Canada, and has been described elsewhere (Graham *et al* 1947, Thode *et al* 1949). It is made from a 3/4" copper tubing of 1/32" wall thickness, bent through 90° on a 6" radius The sector portion is flattened to 3/8" to fit in the pole gap of the electromagnet The original pyrex glass enclosures at the two ends for housing the ion-chamber and collector assembly have been dispensed with. Instead, two 5" copper flanges have been silver soldered to the analyser tube just beyond the two ends of the sector, the analyser tube extending about 4" beyond these flanges on both sides The ion source along with the focusing half plates and the ion entrance slit forms one composite assembly, the protruding tubular end of which fits snugly into the analyser tube at one end. Similarly, the exit slit with secondary electron suppressor plate forming a composite assembly with a protruding tubular end fits snugly into the analyser tube at the other end. The entrance and exit slits lie in planes defined by the two free ends of the analyser tube.

The spacings and the sizes of the various electrodes and slit sizes on the source side and in the collector assembly are the same as in the original instrument of Thode. The filament is a 6-mil diameter tungsten wire in the form of a helix, spot-welded to the leads of a two-wire press seal at the end of a pyrex glass stem.

Stainless steel tubes with copper flanges can be fitted on to the flanges fixed to the analyser tube to make vacuum-tight enclosures on the source and collector sides with the help of O-rings, the other ends of the stainless steel tubes being closed by copper plates silver-soldered to them. Electrical leads are brought out by means of glass to metal seals soldered to the copper flanges attached to the analyser tube, so that the stainless steel tubes enclosing the ion chamber and the collector assembly at the opposite ends can be removed, whenever needed, without disturbing the electrical connections to the various electrodes.

Two windows are provided on the source side enclosure by drilling two 0 4" holes on the back plate of the stainless steel tube forming the casing. The purpose of this is to provide a means for seeing the ion source assembly which is necessary for proper positioning of the sample introducing tube. The openings are covered with small glass plates each of which is placed between two small copper flanges with O-rings in between. The whole arrangement is bolted on to the back plate over the holes and made vacuum tight by means of O-rings.

Some modifications have been later made in the collector assembly of the instrument to adapt it to the study of the measurements of kinetic energy of the ions produced by electron bombardment on some organic samples. In the new arrangements, we propose to maintain the analyser tube at high voltage, whereas, the source and the collector assembly will be almost at ground potential The details of these modifications will be communicated in due course.

Ions passing through the exit slit are collected on a collecting electrode and the ion current measured by means of an EKCO Vibrating Reed Electrometer.

VACUUM SYSTEM

A Metrovac 03B diffusion pump (of 30 litres per second unbaffled pumping speed) is used for pumping the vacuum chamber The pumping manifold includes a flexible copper bellows for providing small movements to the analyser tube which might be required for maximising the ion current. The fore-pump used is a rotary vacuum pump of Indian make having a nominal pumping speed of about 100 liters per sec capacity

The gauge manifold consists of a copper tube of $1\frac{1}{2}''$ internal diameter fitted with flanges on both sides On one side, it is connected to the side arm of the stainless steel casing on the source side of the spectrometer tube, while on the other side it is connected to the pumping manifold. All vacuum tight connections are made with the help of O-rings. Vacuum measuring gauges are connected through copper-glass seals to the three small tubes attached to the manifold. The pressure of the vacuum system is measured with the help of a commercial combined Pirani and Ionization Gauge circuit. The ultimate vacuum attained without the use of a cold trap is of the order of 2×10^{-5} torr or less.

An all-metal liquid air trap designed in this laboratory has been incorporated in the vacuum system The volume of the liquid air container is about 700 c c. and once fully charged it can work for about eight to ten hours. Pressures of the order of 5×10^{-6} mm of Hg have been obtained when the trap is charged with liquid air.

ELECTROMAGNET

The electromagnet is of a double-yoke type with the pole faces machined to the proper sector shape so that the ions can describe a circular arc-shaped trajectory of 15 cm nominal radius within the magnetic field, the deflection of the ions in going through the field being $90°$. The magnet is made of mild carbon steel with less than .08% of carbon and has been cast for us by a local firm. The pole pieces are held on to the yokes through tapered holes by means of a single bolt and a clamp on each side. The gap between the pole pieces is adjustable and is now set at 0.5 inch. The magnet is energized by passing current through four coils, two on each pole piece. Each coil has about 22,000 turns of 29 swg super-enamelled copper wire which are protected on two sides with 1/8″ sindanyo discs and the top and bottom being protected with glass-mica-sheets. Each layer, having exactly the same number of turns of wire, is varnished by brushing with Dow Corning silicone varnish. The total resistance of the four coils is about 10,000 ohms.

ELECTRICAL CIRCUITS

The electrical circuits used for the operation and control of the mass spectrometer are of conventional design (Graham *et al* 1947).

The coils of the electromagnet are energized by means of a highly stabilized high-voltage low-current power supply system. The current is continuously variable between 10 and 115 mA and provides a maximum magnetic field of about 6000 oersteds. The long-time stability of the magnetic field is better than 1 part in 5000. This is inferred from the reappearance of the ion peaks at a given magnetic field setting when the ion acceleration voltage is brought back to the value at which the peaks had been originally observed.

The ion acceleration voltage is supplied from a 2000 volts highly stabilized high voltage unit. Precision wire wound resistances are used and the measured stabilization ratio is of the order of 1 part in 10^4. The acceleration voltage is varied with the help of a potential dividing system, using a set of wire wound resistors of total resistance $0.5M\Omega$ which acts as a constant load to the high voltage supply. Kelvin-Varley principle is applied to select a constant part of the voltage. This again is applied to a high resistance bank so that an almost linear variation of the voltage with resistance is obtained.

The current for heating the filament is supplied from an emission control unit, which utilizes the principle of the ion gauge control circuit devised by Ridanour & Lampson (1937). The filament emission current produces a voltage drop across a resistance which is applied to the grid of an amplifier tube. Any fluctuation in this voltage drop resulting from fluctuations in the filament emission current is amplified and helps to control the plate current in a pair of tubes acting as a variable load on the secondary of the transformer supplying the filament current. The corresponding variation in the primary current keeps the filament current under control. A line voltage variation of 10 volts produces negligible changes in the emission current. This circuit also supplies the necessary voltage for electron acceleration, which is variable from 5 to 100 volts.

As mentioned earlier, the ion current is measured with an EKCO Vibrating Reed Electrometer. The smallest current which can be detected by it is of the order of 5×10^{-15}amp. Zero shift of the instrument is a frequent trouble, which can however, be minimized by blowing hot air over the input components and connecting leads.

PERFORMANCE TESTING

In order to test the performance of the instrument we have studied the following gases : argon, carbon dioxide and chlorine. The mass peaks have been scanned by keeping the magnetic field constant at a suitable value so that the ion

accelerating potentials are as high as possible. Ionization efficiency curves for the different mass peaks have also been determined. The corresponding appearance potentials are in satisfactory agreement with accepted values. Although the lowest detectable ion current by our electrometer was about 5×10^{-15}amp we have not studied in details peaks whose heights were below 1×10^{-13}amp. The peak heights of the residual gases and of fractionated hydrocarbons were considerably less than 10^{-13}amp.

The peaks of the two chlorine isotopes Cl^{35} and Cl^{37} are easily recognizable. In addition, peaks of H^1Cl^{35} and H^1Cl^{37} were observed, since HCl gas was present as contamination in the chlorine used. The heights of these peaks at the mass numbers 36 and 38 were however much reduced when care was taken to remove all traces of the HCl gas from the raw chlorine. The ratio of the peak heights of Cl^{35} and Cl^{37} is in fair agreement with the standard value.

The calculated value of the resolving power of the instrument, considering the slit widths and the radius of curvature would be 1/130. Preliminary measurements with our potential dividing system showed fair agreement with the calculated value and the peaks of consecutive mass numbers were found to be well separated (figure 1). The measured values of the resolving power were however
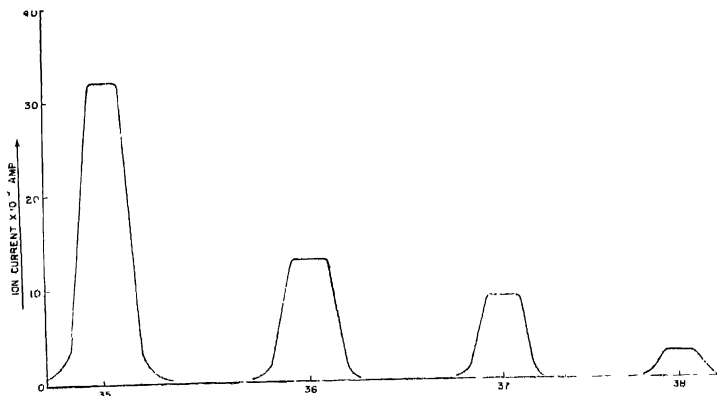

Figure 1 Mass peaks at $M/e = 35, 36, 37, 38$, using chlorine gas

not very accurate, since the assumption of linear variation of the voltage with resistance in the potential dividing system used in these measurements was not justified. A modified potential dividing system which did away with this

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difficulty was later incorporated and used for studying the variation of resolving power with pressures (Ghoshal *et al* 1971).

Table 1. Comparison of the percentage yield of fragments for n-propyl alcohol

	Values obtained with our instrument	Values obtained by earlier worker Friedel *et al* 1956
19	1.6	1 09
27	18.3	18.9
29	16 4	17.6
30	2.6	2 55
31	100	100
33	1 06	1 39
41	6.88	6 96
42	9 71	9.38
43	3 47	3 47
45	2 33	1 81
58	0 255	0 246

The instrument was also used for preliminary studies of the cracking pattern of some organic compounds
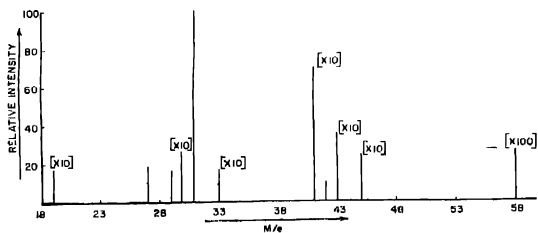

Figure 2. Mass spectrum of n-propyl alcohol

Results of a typical case (n-propyl alcohol) are shown in figure 2, and are compared with earlier work (Friedel *et al* 1956) in table 1. Except at $M/e = 19, 33$ and 45 the agreement between our measurements and earlier work is quite good.

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