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A 90° SOLID SOURCE MASS SPECTROMETER

by

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Scopes and Contents of Thesis

An investigation of several solid sources for use in isotopic analysis by means of a mass spectrometer is reported. In particular, the compound copper acetylacetonate has been successfully employed to obtain ion currents corresponding to the copper isotopes. The second portion of this thesis deals with an energy filter method of reducing scattering effects in a mass spectrometer tube.

ACKNOWLEDGEMENTS

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INTRODUCTION

The use of solid sources in mass spectrometer work is becoming increasingly important. In nuclear physics and chemistry there are many problems of isotopic separation, identification and abundance measurements which often involve the heavy elements. Of particular interest are those above uranium in the periodic table and also the elements in the fission product range. It is often very difficult, if not impossible to obtain gaseous samples of such materials and hence satisfactory methods of handling the solid materials directly are of extreme importance. With many nuclear problems arising in this laboratory, the construction of a solid source mass spectrometer seemed a necessary requisite.

There are several ways in which ions can be produced from solid samples. One of these involves the thermionic emission from a hot filament impregnated with the sample. This type of ion source has been used successfully to study the isotopes of a large number of elements. Another method is the spark source where one electrode carrying the sample is sparked against a second electrode with a large potential difference between them. Hence atoms of the sample are liberated in ionized states. A third procedure involves the use of a small furnace in which the sample can be vapourized and from which the vapours can pass into the electron beam of the source. Here they are ionized by electron impact as in the gas type source usually employed. A complete list of references on these three types of sources has been compiled by Mr. R. H. Mills[1]. The present thesis deals with the design,

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[1]Mills, R. H., M.Sc. Thesis, McMaster University, 1949

construction and operation of the third type of source.

In a satisfactory furnace source, two fundamental conditions must be fulfilled. First, there must be an accurate control of the furnace temperature to create a uniform vapour flow. Unless this is possible, the ion beam would vary in intensity, which would make isotopic abundance measurements unreliable. Secondly, the ion source must operate efficiently so that unused vapours are reduced to a minimum. This means that the vapours from the heated source must flow into the ionization chamber so as to give maximum ion formation over the slit through which they are accelerated. If the ion source is not efficient, higher vapour pressures are required to secure ion currents of satisfactory intensity. This leads to vapour condensation on the cold plates and other tube parts, which is very undesirable.

The problem of tube contamination is one of the major difficulties encountered, for it is almost impossible to completely clean the internal surfaces of the mass spectrometer tube without dismantling the apparatus. The only way to control this situation is to design the furnace source so that a minimum quantity of vapour is necessary to give ion beams of good intensity, and to shield cold parts of the tube from the vapour stream as much as possible. In the case of certain substances that vapourize at temperatures below 300° C. it is often possible to operate with the whole source end of the tube at elevated temperatures. This procedure should eliminate condensation of vapours in the source end of the tube where the pressures are the highest.

Previous work done by Mr. R. H. Mills consisted of an investigation of furnaces fashioned from nickel sleeves. These furnaces had the advantage of being simple and easy to mount. Further, a whole new assembly could be quickly installed for each new sample. The first type (Figure No.1) has the sleeve held in a vertical position. The sample is packed into the sleeve

after which the lower end is plugged. This plug contains a small notch to allow the hot vapours to escape. The vertical nickel sleeve is aligned above the top plate of the source assembly, and is heated by passing a current through the sleeve. Cuprous chloride was used as a typical solid sample, and the abundances of the copper isotopes were determined. Although the sleeve heats in the region of the sample, the plug at the bottom creates a cold spot, so that the vapours tend to condense and block the opening. When this happens, the pressure increases to a point where the sleeve explodes or the opening is suddenly cleared. In either case, the whole sample amounting to several milligrams may be lost. For this reason the sleeve type source are not very satisfactory. If this difficulty could be overcome, however, they might be extremely useful.

A second nickel sleeve source used by Mills was more permanently mounted in a closed box (Figure No.2). The sleeve contained a small hole to allow the vapour to escape, while the box was used to stabilize the temperature and to restrict the flow of the vapours, preventing them from depositing on the side walls of the mass spectrometer tube. After trial runs proved unsuccessful, an examination of the plates seemed to indicate that most of the sample sprayed out and condensed along the sides of the source slits. It is difficult to understand why ion currents were not obtained.

A companion problem to that of the furnace design is the proper choice of the compounds under study. Samples similar to cuprous chloride require temperatures in excess of 300° C. The use of such high temperatures presents several difficulties. One is the outgassing of the heated furnace which may be sufficient to raise the pressure above the operating level of the tube. Another factor is that high temperatures require large currents which in turn set up large electric fields. Such fields could upset the path of the ion

1 PRESS SEAL

2 LEAD WIRE

3 NICKEL SLEEVE

4 SAMPLE

5 PLUG

6 WIRE

FIGURE 1

1 LEAD WIRES

2 KOVAR SEALS

3 BOX

4 NICKEL SLEEVE

5 PLATE ASSEMBLY

FIGURE 2

beam. Thirdly, the construction of a furnace capable of withstanding high temperatures for a long period of time is difficult to achieve. Although nickel sleeves can be raised to high temperatures, they are in danger of losing their shape and alignment. On the other hand, a furnace with a large mass of metal requires very large electrical currents to heat it. Obviously those compounds which give appreciable vapour pressures at low temperatures are to be preferred. In this connection, compounds of the heavy elements which are volatile are always of interest.

A group of compounds which have not received much attention in mass spectrometer work and which seem to have promise are the acetylacetonates. White and Cameron[2] used magnesium acetylacetonate in a mass spectrometer and attempted to investigate the magnesium isotopes. Their results were unsatisfactory, however, in view of overlapping hydrocarbon ion currents in the range of the magnesium isotopes. Dr. K. Starke in this laboratory was preparing other acetylacetonates for different purposes and his work suggested that these compounds might be tried. With the very heavy elements such as thorium, hydrocarbon ion currents might not interfere. Table I gives a list of acetylacetonates which have been prepared, along with their vapour pressures. It will be seen that many of these compounds have appreciable vapour pressures in the temperature range from 120° to 180° C. No definite information is available as to how the compounds split through electron impact, but one possibility is that certain combinations could easily have the same masses as the element under investigation. As an example, copper acetylacetonate has the formula:

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2 White, J.R. and Cameron, A.E., Physical Review, 74, 991, (1948)

It can be seen that the breaking of certain hydrocarbon bonds might result in mass fragments close to the copper range. This compound has been investigated and the results reported in this thesis suggest that many other elements which are difficult to form as normal volatile compounds might be investigated in a mass spectrometer in the form of acetylacetonate compounds.

TABLE I

ACETYLACETONATE COMPOUNDS

Element	Compound	M.P. °C.	B.P. °C.	Characteristic
Aluminium	$Al(C_5H_7O_2)_2$	198		-decomposes at 314-5° -vapour pressure of 10 mm. at 140°
Barium	$Ba(C_5H_7O_2)_2\ 2H_2O$			
Beryllium	$Be(C_5H_7O_2)_2$	108	270	-sublimes near 100°
Cadmium	$Cd_2O(C_5H_7O_2)_2$			
Calcium	$Ca(C_5H_7O_2)_2\ 2H_2O$			
Cerium	$Ce(C_5H_7O_2)_2$	171-2		
Chromium	$Cr(C_5H_7O_2)_2$	214		-decomposes at 340° -sublimes in vacuum
Cobalt	$Co(C_5H_7O_2)_2$			-sublimes
	$Co(C_5H_7O_2)_3$	240		
Copper	$Cu(C_5H_7O_2)_2$	150		-sublimes
Cesium	$Cs(C_5H_7O_2)$			
Gallium	$Ga(C_5H_7O_2)_3$	194-5		-sublimes at 140° -vapour pressure of 10 mm.
Indium	$In(C_5H_7O_2)_3$	280		-sublimes at 140° -vapour pressure of 10 mm.
Iron	$Fe(C_5H_7O_2)_3$	184		
Lanthanum	$La(C_5H_7O_2)_3$	151	185	
Lithium	$Li(C_5H_7O_2)$			
Magnesium	$Mg(C_5H_7O_2)_2$			
Manganese	$Mn(C_5H_7O_2)_3$	172		-sublimes in vacuum at 130°.

Table I (cont'd.)

Molybdenum	$Mo(C_5H_7O_2)_2$			-sublimes at 90° -does not melt
Neodymium	$Nd(C_5H_7O_2)_3$	144-6		
Nickel	$Ni(C_5H_7O_2)_2$	228	220-35	
Platinum	$Pt(C_5H_7O_2)_2$			
Praseodymium	$Pr(C_5H_7O_2)_3$	146		
Samarium	$Sm(C_5H_7O_2)_3$	146-7		
Scandium	$Sc(C_5H_7O_2)_3$	188		-sublimes at 157° with 8-10 mm. pressure
Sodium	$Na(C_5H_7O_2)$		230	-sublimes
Strontium	$Sr(C_5H_7O_2)_2\ 2H_2O$			
Thallium	$Tl(C_5H_7O_2)$	160		
Thorium	$Th(C_5H_7O_2)_4$	171		-sublimes in vacuum
Vanadium	$V(C_5H_7O_2)_3$	185-90		
Uranium	$U(C_5H_7O_2)_4$	176		
Yttrium	$Y(C_5H_7O_2)_3$	131		
Zinc	$Zn(C_5H_7O_2)_2$	138	124	-sublimes
Zirconium	$Zr(C5H_7O_2)_4$	193-5		-sublimes -0.01 mm. pressure 82° -1.0 mm. pressure 120°

EXPERIMENTAL

INSTRUMENTATION

A 90° sector type mass spectrometer was employed, being of conventional design[3], except that a ground glass joint is used to close off the source end of the tube. This joint is sealed with silicone grease when the tube is in operation. Due to previous contamination, the mass spectrometer was completely dismantled. The metal tube was thoroughly cleaned and new glass leads were installed, along with new press seals for the source and collector leads. The source was similarily reconditioned, and the whole tube is now mounted on a standard rack. A sample line built into the mass spectrometer represents an addition over the original design. A 4 mm. lead is blown onto one of the main tube's side arms and an external leak is attached to this. The other end of the leak unit goes to the sample line proper, and this line can be closed by a stopcock. The sample line has its own oil pump and a small mercury diffusion pump. A flask of xenon is permanently tied onto this line, and a mercury toepler is incorporated to vary the pressure behind the gas leak. Four General Radio Variacs are installed on the rack itself to supply the necessary power to heat the furnace, and room was made to accomodate the d.c. amplifier so that the unit is now complete in itself, except for the recording galvanometer (a Leeds and Northrup Speedomax Recorder) and the main electronic units.

A Nier type source[4] is employed and can be removed at any time by taking

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[3]Graham, R. L., Harkness, AL., and Thode, H. G., J. Sci. Instruments, 24, 119, (1947)

[4]Nier, A. O., J. Sci. Instruments, 18, 398, (1947)

the header off the mass spectrometer tube. The top plate of this source contains a rectangular opening 10 mm. by 5 mm. into which a shallow box is fitted. The depth is such that the transverse electron beam travels immediately below the bottom of the box. A 1.0 mm. slit on the bottom plate of the box lines up with the slits in the source assembly. By using this arrangement, it is possible to mount the furnace as close as possible to the electron beam.

The collector system of the mass spectrometer is of slightly different design since it has been built to utilize the energy filter system described by Fox and Hipple[5]. A complete discussion and description of this collector system is given in the second portion of this thesis.

ION SOURCES

The three types of sources under investigation are:

i. Horizontal nickel sleeve.
ii. External furnace with heated capillary lead.
iii. Solid metal furnace box.

These furnaces are designed so that they are completely supported by, and attached to the removable header. This means that the whole furnace can be conveniently lifted out at any time without having to touch the source. Also, since the furnaces are isolated, the heating elements do not have to be floating at the high potential of the source.

In the first source (Figure No.3), the nickel sleeve is spot welded across the leads of a two wire press seal, after the sample has been packed within the sleeve. A small hole drilled intthe sleeve is lined up with the slit in the box so that vapours will pass down into the electron beam. Current passes

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[5]Fox, R. E. and Hipple, J. A., Rev. Sci. Instruments, 19, 462, (1948)

through the nickel sleeve which can thus be heated to any temperature.

The external furnace with a heated lead tube is shown in Figure No.4. The sample is placed in the tube S which is blown onto the capillary lead at B. This lead tube passes through the header H by means of a ring seal at A. The internal end of B is drawn down to a small tip and is designed to sit directly above the slit array of the source. External heating is achieved by winding tube B with nichrome wire over a layer of asbestos. The portion of B within the header has a flat strip of nichrome wound in a spiral manner from the ring seal at A to the tip T. The two wire press seal D carries the current to heat the internal element. The header is narrowed at A so that the external and internal methods of heating overlap.

Furnace number three, above, is similar to the first one except that instead of a nickel sleeve, a solid block of nichrome 5 mm. by 3.mm. by 4 mm. was used. In block A (Figure No.5) there is drilled a cavity B to hold the solid sample. After the sample is placed in B, a tight fitting cap C is clipped on. This leaves as the only path of exit for the vapours a small hole drilled through from the cavity B to the bottom of the furnace. E and F are two holes so spaced that the box can be fitted onto a two wire press seal. The furnace is heated directly by passing a current through the whole block, the maximum current being about five amperes to bring the temperature over 150° C. To facilitate the passage of the vapours from D into the region of the electron beam, the slit in box C is enlarged by drilling centrally a 1/8" hole. A thermocouple of copper-constantan is tied directly onto the side of the box, and the wires are brought out through a two wire press seal.

FIGURE 3

FIG. 4

FIGURE 6

OBSERVATIONS

The nickel sleeve of the first furnace was packed with cuprous chloride and heated slowly. The results obtained were quite unsatisfactory. Copper ions did not appear until the furnace had reached such a temperature that the sample blasted out of the small opening, depositing itself upon the source and walls. Although copper peaks were obtainable, the problem of contamination was quite serious. The one advantage of the system is the fact that a clean furnace can be quickly mounted in place for each new sample.

Several attempts were made to obtain ions with the sample heated in the external type of furnace. Howevere, there has not been sufficient time to develop satisfactory operating techniques and the results to date have been unsatisfactory.

COPPER ACETYLACETONATE COMPOUND

The small nichrome furnace source described previously was used to investigate a sample of $Cu(C_5H_7O_2)_2$. The sample was packed into the cavity and installed on the apparatus. The temperature of the furnace was raised slowly until ion currents due to the copper isotopes appeared. Temperature control was found to be very critical. In the first attempts made to secure ion currents, it was not possible to control the pressure, and ocassionally the pressure rose beyond the working level of the tube and the ion currents were blanked out. However, by using a thermocouple on the source and a galvanometer as an indicating device, it was possible by careful control of the temperature to obtain steady ion currents of good intensities. Several

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repeated runs have indicated the stability of such a source. Using electron energies of 100 volts, and an accelerating voltage of 1500 volts, the copper spectrum was recorded. A spectrogram of the copper isotopes is given in Figure No.6. The Cu^{63}/Cu^{65} ratio as calculated from an average of six spectrums was found to be 2.25 .03. This is in good agreement with the value of 2.24 given by Seaborg and Perlman[6].

A check was made to identify the hydrocarbon peaks from the acetylacetonate compound. The results are given in Table II.

TABLE II

Approximate Mass Found	Intensity	Suggested Origin of Mass
15, 16, 17, 18	Strong	C, H, O combinations; water vapour.
27	Fair	CH_3-C
56	Weak	CH-CO.CH_3

[6]Seaborg, G. T., and Perlman, I., Rev. Modern Physics, 20, 588, (1948)

FIG. 6
CU
PEAKS
ION CURRENT
61
62
63
64
65
66
MASS

DISCUSSION

The most important result of this work is the fact that the copper acetylacetonate compound was successfully analyzed in the mass spectrometer. The ratio of the copper isotopes obtained indicates that there was no interference from hydrocarbon ion currents in the higher mass ranges. This suggests further investigation of similar compounds, particularily of the heavy elements, such as thorium and uranium acetylacetonate.

The mass spectrometer techniques for analyzing acetylacetonate compounds require a very accurate control on the temperature of the furnace box, for the vapour pressures of these compounds often go beyond the operating level of the tube with very small changes in temperature. Also, it would be very wise to investigate first the properties of the various compounds on a separate vacuum system, and obtain accurate vapour pressure data.

Considering the temperature range which is used in analysing these compounds, the external furnace seems the logical type of source to employ. Further work along this line would be of interest for the source can, with this type of furnace, be modified to include metal valves to close off the mass spectrometer tube. Thus the main vacuum could by maintained while changing samples.

PART II

THE USE OF RETARDING POTENTIALS ON A MASS SPECTROMETER

INTRODUCTION

One of the major problems in mass spectrometer work has been the creation of sharply defined ion beams. Although source and field adjustments are important factors in determining peak shape, scattering in the analyzer tube may still be sufficient to give undesirable results. Such results consist of 'tails' on either side of the peak at the base line. Fox and Hipple[7] have suggestrd a means of improving this condition by using an energy filter system. This filter effectively prevents any ions which have lost energy through scattering from reaching the collector.

THEORY

Usually, mass spectrometers are designed with the whole source assembly at the high voltage level, the analyzer tube then being at ground potential. However, it is possible to have the source at ground potential (or near ground) and the analyzer tube at a negative potential, the collector still being at ground. The motion of the ions is now controlled by two factors, if we disregard the bending due to the magnetic field. One is the initial energy of acceleration in the source assembly, and depends on the potential gradient between succeeding plates. The second force is the retarding potential between the analyzer tube and the collector. If E_1 is the force of initial acceleration, and E_2 the retarding force, then E_1 must exceed E_2 for the ions to reach the collector. Let $E_1 - E_2$ E, where E measures the energy difference of the filter and represents the degree of filtering. The smaller E is made,

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[7]Fox, R. E., and Hipple, J. A., Rev. Scientific Instruments., 19, 462, (1948)

the more will scattered ions be rejected. That is, suppose an ion of initial energy E_1 loses E_1' energy in passing through the analyzer tube. Then if the ion is to be rejected, $E_1 - E_1'$ E_2 which can be rewritten as $E_1 - E_2$ E_1' which gives E E_1'. Hence if E_1' exceeds E, the ion is rejected. Therefore, E determines the maximum energy loss permissable. If E is very small, then those ions which have lost only a minute fraction of their initial energy will be stopped. There is a limit to E for practical mass spectrometer work, since the finite width of the exit slit in the source precludes some spreading of the beam. If E were zero, then only one path of ions would be accepted, which would give rise to a peak of infinitesimal width. Such would be impossible for scanning purposes.

CONSTRUCTION

It is necessary to alter the design of the collector when the energy filter system is employed. Normal collectors consist of two plates and a collector cup: the first plate contains the defining slit, and the second a repeller plate to stop secondary electrons from being ejected from the cup. This present collector assembly contains five plates. Referring to the first diagram, there is shown a general plan of the assembly. S_1, S_2, and S_3 are three plates directly fastened to the exit end of the analyzer tube, their slit widths being, respectively, 0.5 mm., 1.0 mm., and 2.0 mm. These plates are held rigidly in place by a sleeve of nichrome. A weak magnetic field is applied in the region of these slits.

Above this is another nichrome sleeve holding slit plates S_4 and S_5 of widths 3.0 mm. and 4.0 mm. The last two plates are insulated from the first three and kept at ground potential. The spacing between succeeding plates is; S_1-S_2, 4.0 mm.; S_2-S_3, 4.0 mm.; S_3-S_4, 8.0 mm.; S_4-S5, 10 mm. The upper plate

holder is fastened to the lower holder by four bolts which are well insulated by using glass sleeves and spacers. The flange on the upper holder is designed to shield the collector cup (sitting directly above S_5) from the four bolts which are at the full negative voltage of the analyzer tube. The flange is 7.0 mm. in width from the outer face of the holder, and covers the shaft and bolt assembly quite effectively.

Since the S_1 - S_3 array is tied directly to the analyzer tube, they are at the analyzer potential. Secondary electrons will be emitted from the analyzer side of the S_1 slit as the ion beam passes through. It is possible for the main magnetic field of the spectrometer to bend these electrons back through S_1 where they would be accelerated to the collector. This condition is relieved by using S_2, S_3 and a small permanent magnet in the region of the three plates. S_2 and S_3 give a short distance in which there is no potential gradient, while the magnet acting in this region, bends the electrons in such a manner that they become trapped in the two slit assembly.

Hipple points out that the rejected ions would also give rise to secondary electron emission. This is because those ions which are not permitte to reach the collector cup are drawn back towards the first slit assembly (S_1 - S_3) and strike it with their full kinetic energy. A suitable material coated on these plates will reduce the emission effect.

S_5 is also an added slit over the conventional collector assembly. Its purpose is to shield the collector from any electric field penetrating into the region of this part of the assembly from the potential on the S_1 - S_3 slits.

DISCUSSION

There are several advantages when this method of ion detection is employed. First, it means that the various plates of the source are not held at the high potential of the accelerating voltage. The insulation problem is therefore considerably reduced. The sensitivity of the mass spectrometer is increased, and one is able to make accurate measurements on a small peak which lies very close to a large peak, which otherwise would be masked entirely. Considerable work has been done by Hipple, Fox and Condon[8] using the energy filter system to study the appearance of non-integral masses in hydrocarbons which arise from metastable ions.

This collector unit was built in this laboratory to be used along with the solid source mass spectrometer, since scattering problems are increased greatly when analyzing the heavy elements. To date it has not been employed, but it is mounted on the spectrometer as a conventional collector. This means that the S_1 - S_3 slits are grounded, while slits S_4 and S_5 act as the repeller and carry a negative potential of 45 volts. Using the collector in this fashion has proven satisfactory.

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[8] Hipple, J.A., Fox, R.E., and Condon, E. U. Physical Review, 69, 347, (1946)

DETAIL OF

HOLDING ARRANGMENT

SCHEMATIC OF

COMPLETE

ASSEMBLY

LOWER PLATE HOLDER

UPPER PLATE HOLDER

Same as Lower Plate Holder

Assembly to have 10 mm. spacing between flange on lower holder and bottom flange on upper holder.

TOP VIEWS OF HOLDERS

SLIT S_1
Ø.5 mm.
34 mm.
SLIT S_2
1.0 mm.
20 mm.
SLIT S_3
2.0 mm.
24 mm.

SLIT S_4

SLIT S_5