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BHABHA ATOMIC RESEARCH CENTRE

**INDIGENOUSLY BUILT RESONANCE IONIZATION  
MASS SPECTROMETER**

by

**M.A.N. Razvi, T. Jayasekharan, K. Thankarajan,  
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Spectroscopy Division

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## **ABSTRACT**

Design, fabrication and performance testing of an indigenously built Resonance Ionization Mass Spectrometer (RIMS) is presented in this report. The instrument is totally indigenous, but for the laser components consisting of the excimer laser and tunable dye lasers. Constructional details of atomic beam source and linear time-of-flight mass spectrometer are included. Finally, commissioning and performance testing of the instrument is described. Mass resolving power of 400 and a detection limit of 100 atoms has been achieved using this RIMS set-up.

# INDIGENOUSLY BUILT RESONANCE IONIZATION MASS SPECTROMETER

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## **Introduction**

Present report describes a Resonance Ionization Mass Spectrometry (RIMS) set-up designed and fabricated entirely in the Spectroscopy Division of BARC. Technique of RIMS is of comparatively recent origin. It became popular after late 70's with the availability of reliable pulsed tunable lasers. The technique uses tunable laser radiation to resonantly excite and finally ionize a free atom or molecule; the ions thus obtained are analysed mass spectrometrically, usually employing a time-of-flight mass spectrometer (TOF-MS), which is ideally suited for pulsed laser operation. Outstanding features of the technique include its high sensitivity ( $10^{-12} - 10^{-15}$  g) and high selectivity ( $>10^{15}$ ). Because of these remarkable properties RIMS has found wide applications in many areas of pure and applied science. Its major applications are, however, in areas like ultra-trace elemental analysis, laser spectroscopy, study of clusters, characterization of macro biomolecules in biology and medicine etc.

RIMS set-up can be operated in two ways,

- a) in the time scan mode or
- b) in the wavelength-scan mode .

In the former, for every laser pulse entire mass spectrum is captured. This mode is employed in mass spectroscopy applications like isotopic analysis, characterization of biomolecules and study of clusters. In the wavelength scan mode, gated detection of the photoionization signal is carried out. The detector is 'on' only after a pre-set time delay following the trigger supplied by the laser pulse. This means that one is now looking at ions of a given specific mass only. The variation of photoionization current is studied as a function of tunable laser wavelength which gives information about energy levels. Operation in this mode is very common in laser spectroscopy applications. We have extensively used the indigenous instrument to investigate the complex spectra of Sm atom for its high lying even parity levels including Rydberg and autoionizing levels. Entire operation of the indigenous instrument in the above two modes is fully automated. Data acquisition and storing is done on PC and analysis of the data is carried out using software that has been locally developed. A photograph of the RIMS setup is shown in Fig. 1.

### **Development of Resonance Ionization Mass Spectrometer**

As discussed above RIMS basically involves the resonant photoexcitation and ionization of atoms or molecules. The atoms or molecules, thus converted into positive ions, are then extracted into a TOF-MS and are mass analysed. A RIMS spectrometer, shown schematically in Fig. 2, essentially involves three main components : a) The atomic beam source , b) The lasers for photo ionizing atoms and c) The TOF-MS for ion detection and mass analysis. This , however, is a broad picture. In reality there are a large number of sub assemblies which go into the making of the RIMS set up. These sub-assemblies are i)

interaction chamber , ii) low and high temperature atomic beam source iii) Time-of – flight mass spectrometer, iv) High vacuum pumping station, v) Excimer laser pumped continuously tunable dye lasers vi) High voltage power supplies, Ion detector, preamplifier, transient digitizer etc.

In the following section we will discuss the design and fabrication of various sub assemblies which fit into the broad outline given above.

### **The Interaction Chamber**

The interaction chamber is basically a vacuum chamber connected to a high vacuum pumping station. It has several ports to which the Time-of-flight Mass spectrometer (TOFMS) and the atomic beam sources are connected. The main body of the chamber is a cylinder (305 mm long, 215 mm dia), made of SS 304 with flanges (275 mm dia) on both the ends. It has got eight ports welded on a circular plane around the cylinder. There are two diagonally opposite ports (55 mm dia) and glass windows (see Fig. 3). A high temperature furnace is connected to a 48 mm dia port. This port can be isolated from the main chamber with the help of a flap and lever mechanism using Wilson seal technique. This helps to avoid atmospheric exposure of chamber while changing samples. After loading the samples, the port can be evacuated to low vacuum ( $10^{-3}$  mbar) through a bypass evacuation line with isolation valve and after attaining the vacuum it can be opened to the high vacuum main chamber. There are other smaller ports of 20 mm dia with glass windows for viewing the interaction region and for monitoring atomic beam source temperature with optical pyrometers. The low temperature atomic beam source is connected to one of these ports. To one of the end



flanges a TOFMS is connected. The other end flange contains five electrical 'feed throughs' and is also connected via an L-bend to the high vacuum diffusion/rotary pump system (Fig. 4). Provision is also made to connect a Penning gauge head for monitoring the chamber vacuum. All the joints in the chamber are made by argon arc welding. To obtain a high vacuum inside the chamber, extreme care is taken in the design and fabrication of the chamber, especially because there are large number of openings (29 nos. in total). Secondly, the inner and outer surface is given a very good finish. All the flanges have viton 'o' ring vacuum seals and are fastened with nuts and bolts.

#### **Low Temperature atomic beam source**

We tried several different designs and fabricated at least five low temperature atomic beam sources, improvising the successive sources from the experience gained. Finally, the present version of the atomic beam source (ABS) is arrived at and that is described here. The present source, totally indigenous, has a number of features viz. it is extremely compact, requires very low electric power, has excellent temperature control and stability along with superior quality and easy sample changing facility. The source is tested up to 1200 K. Fig.5 shows the sectional view of the low temperature atomic beam source. The source consists of a tiny stainless steel crucible (36 mm long, 415 mm dia). It is fabricated out of an SS 304 rod by drilling a hole, and in the open end threading is made to accommodate a beam collimating channel ( 36 mm long, 1 mm ID). The crucible can be removed and reinstalled easily. The sample crucible is inserted into a ceramic tube of 5.0 mm ID and is resistively heated with the help of a canthal wire helically wound closely around the ceramic tube. The ceramic tube is

covered by two larger diameters coaxial quartz tubes which serve as thermal and electrical insulators. This assembly is mounted on two water cooled flanges. These flanges also serve as electrical contacts for the heating coil, hold the assembly in exact position and also help in vacuum isolation purpose. The sample crucible rests on a chromel-alumel thermocouple supported by a double bore ceramic rod. The thermocouple rod is connected to a glass feed-through which is welded to another flange. The main assembly is permanently coupled to one of the ports of the interaction chamber and only the thermocouple assembly (which is coupled to the main assembly) is removed and the ampule slips down by gravity. The heating coil has more number of windings in the upper portion so as to keep the collimating channel at a slightly higher temperature to avoid condensation and coagulation in the channel.

### **High Temperature Atomic Beam Source**

The main problems that arise at higher temperature are the following :

- i) The choice of the material for the oven, the gaskets, orifice etc. : These materials have to endure the necessary temperature without changing their properties, but also should not react to form an alloy with the beam material.
- ii) The supply of sufficient heating power : Wire heaters made of molybdenum cannot be used beyond 2000 K because at high temperature the wire material reacts with alumina insulation. Still higher temperatures can be obtained by using thin walled molybdenum, tungsten or graphite tube heated directly by passing a large current through the tube walls. Electron bombardment heating is still another way of achieving very high temperatures.

- iii) Adequate shielding of the source is necessary to minimise heat losses and to prevent outgassing from the chamber walls.

We have followed the design of Bekov et al with a graphite tube directly heated by passing 200 – 300 Amp. ac current supplied by a low voltage (20V, 300 A) transformer. A photograph of the oven is shown in Fig.6. The graphite crucible is shaped in the form of the dumbbell, with a hole of 3 mm dia. along the length and reaching up to the middle of the crucible. the ends of the crucible are shaped to keep best contact with the body of the chamber and also to maintain the orientation. The body of the chamber enclosing the graphite crucible is made of copper to minimise resistance heating and it is also water cooled to reduce outgassing of the walls. The graphite crucible is supported on a pedestal and is coupled to the main body of the furnace assembly by helical threading. The top of the chamber has a 3 mm dia. orifice in the centre to allow the atomic beam. Above the chamber a system of three circular plate electrodes with concentric hole is coupled. The electrodes are kept at negative, ground and positive potentials respectively to suppress the thermal ion and electron background from reaching the interaction zone. The temperature of the source is controlled with a variac which controls the primary voltage of the high current isolation transformer. The power is supplied by thick copper strips to the atomic beam source. Viton gaskets are employed for vacuum sealing.

### **Time-of-Flight Mass Spectrometer**

Ions of different masses are separated in the time domain in the TOFMS, unlike spatial separation in other mass spectrometers. A TOFMS is non-magnetic and employs

electric fields (DC or pulsed) to effect the mass separation. There are various advantages of a TOFMS over other types of mass spectrometers. Some of them are :

- i) It is possible to record the entire mass spectrum in a few micro seconds
- ii) It has unlimited mass range and therefore can be used in many applications
- iii) As there are no slits in this spectrometer, the throughput is large and this results in increased sensitivity.
- iv) It is possible to display the entire or a section of the mass spectrum
- v) It is simple in construction, easy to use and quite inexpensive

However, the resolution of TOFMS is relatively poor. In this section we will briefly describe the basic principle of operation and later on discuss construction details and assembling of the indigenously built TOFMS.

### **Principle and Construction**

The mass separation of TOF analyzers results from the dependence of the flight time on the masses of ions formed at the same time and the same point within an electrostatic field. Equal kinetic energy is imparted to all the ions. Ions with different masses acquire different drift velocities in a field free drift region, and reach the detector at different times and are thus mass analyzed.

The construction of a TOF mass spectrometer is done in a modular fashion. The modular design is chosen to facilitate positioning the detector at various distances from the source, which is useful for initial set-up and while assembling. The different modules are as follows : i) The ionization and acceleration gaps, ii) The region for

accommodating ion beam deflection plates and iii) The drift tube. The entire assembly is made of stainless steel SS 304 material. Fig. 7 shows a schematic of the TOFMS.

**i) The ion extraction and acceleration electrodes**

There are three electrodes in the form of circular discs of 100 mm dia. and 5 mm thickness made of stainless steel. The first electrode, the repeller plate, is a complete solid disc, whereas the grid electrodes have circular aperture of 20 mm dia. in the centre. The discs are polished to get a 'mirror finish' smooth surface. The grids are made of circular copper rings of 20 mm O.D. and 14 mm I.D. and a brass mesh of size 60 (60 lines/inch) with a wire thickness of 0.02 mm soldered to the copper ring. The surface of the grid is polished again after soldering and fastened to the grid electrode with screws. The three electrodes are separated by three precisely machined teflon spacers of 20 mm length and 10 mm dia. and are tightened by teflon nut and bolt arrangement.

**ii) The deflection plates**

The capacitors, made of rectangular copper plates (10 mm x 20 mm) are mounted perpendicular to each other in a specially designed teflon housing. The capacitor plates are separated by 10 mm and two capacitors are mounted one after the other with a gap of 20 mm. The teflon housing is inserted into a stainless steel tube of 50 mm ID. which is coupled to the main chamber and the accelerating electrodes with the help of flanges and fastened with nut and bolts. The capacitors are used to correct the ion beam path horizontally and vertically and direct it on to the detector for optimizing the signal.

### **iii) The drift tube**

The drift tube is a hollow stainless steel tube of 50 mm ID and a total length of 900 mm. The tube is divided into two parts and is coupled to each other and to the main chamber with the help of flanges. There is a small port in one of the tube parts which is connected to another small high vacuum system ( $10^{-6}$  mbar). The pumping system also provides mechanical support to the drift tube.

### **Assembling and Preliminary Testing**

The RIMS spectrometer is assembled in the following manner. The main interaction chamber (weight 30 kg.) is supported on a steel frame with the help of brackets welded to the chamber and four big bolts and nuts. The steel frame is resting on the pumping module. The height of the chamber and its orientation can be adjusted with these bolts to an accuracy of 1 mm. The L bend SS tube is connected to the HV pump and it is then coupled to one end flange of the chamber after suitably orienting the chamber. The TOF sub-assemblies are connected at the opposite end flange of the chamber after making electrical connection with the teflon insulated coaxial cables to the feedthroughs. The drift tube is then fixed to the TOF sub-assemblies and is also connected to the HV pump. The atomic sources and quartz, glass windows are then fixed to the respective ports.

Thorough vacuum testing is done extending over a long period of time. Initially part by part, adding one component each time. The chamber is first tested for vacuum with blind flanges, then the respective components are connected and tested again. Finally,

the entire spectrometer is tested for several days and the residual pressure of  $<10^{-6}$  mbar is obtained which is the ultimate vacuum achievable with D.P./rotary pump system.

### **Photoionization of barium and Ytterbium**

To test the capabilities of TOFMS, we tried detecting atoms of barium (with atomic mass around 138 amu) and ytterbium (with atomic mass around 172 amu) using a two photon resonant, three photon ionization schemes. The mass spectra and oscillograms are shown in Fig. 8 for barium and in Fig.9 for ytterbium. All the naturally occurring seven isotopes of barium ( $^{130}\text{Ba}$ ,  $^{132}\text{Ba}$ ,  $^{134}\text{Ba}$ ,  $^{135}\text{Ba}$ ,  $^{136}\text{Ba}$ ,  $^{137}\text{Ba}$ ,  $^{138}\text{Ba}$ ) are recorded. Similarly all the eight natural isotopes of ytterbium are also recorded ( $^{168}\text{Yb}$ ,  $^{170}\text{Yb}$ ,  $^{171}\text{Yb}$ ,  $^{172}\text{Yb}$ ,  $^{173}\text{Yb}$ ,  $^{174}\text{Yb}$ ,  $^{175}\text{Yb}$ ,  $^{176}\text{Yb}$ ) with abundance as low as 0.1%. The percentage abundance is mentioned over the corresponding peaks in brackets.

### **Results and Discussion**

The main aspects in the performance testing of a Resonance Ionization Mass Spectrometer are its ability to detect ultra low concentration of atoms, its ability to separate and measure the abundance of adjacent masses and the overall efficiency of converting a neutral atom present in a sample into a perceptible photo ion current.

### **Minimum Detection Limit**

In conventional techniques, one keeps diluting the concentration of the sample and arrives at the minimum concentration that could be detected. The main limitation in these techniques (e.g. involving detection of photons) is due to the background noise and the signal to noise ratio S/N, which can not be improved beyond a certain limit. In contrast, resonance ionization technique being a highly selective process generates very

low background ions by non resonant multi-photon ionization. The use of time-of-flight mass spectrometer and gated detection not only does mass analysis, but also improves S/N ration by separating the unwanted ions of different masses. The secondary electron multiplier detector has extremely low (0.0.1 count/sec) background. The use of gated integrator improves the S/N further. With all these favourable aspects, the ultimate detection limit of 'single atom' becomes possible by this technique.

In our experiments, we reduced the number densities in the interaction volume by controlling the temperature. The temperature was brought down to reaching the detector. Number of ions  $N_{ion}$  reaching the detector is calculated from the following relation :

$$N_{ion} = \eta_{det} \cdot \delta t_{obs} \frac{V_{obs} \cdot 1}{R_{in} \cdot q} \frac{1}{g_{det} \cdot g_{preamp}}$$

Where  $\eta_{det}$ ,  $g_{det}$  is the efficiency and gain of the detector ( $\eta=1$ ,  $g_{det} = 10^7$ ),  $V_{Obs}$ ,  $\delta t_{obs}$  are the observed signal voltage and pulse duration,  $R_{in}$ ,  $g_{preamp}$  are the input impedance and gain of preamplifier and  $q$  is the charge of the ion. Assuming the transmission of the TOF grids to be hundred percent,  $N_{ion}$  is the number of ions produced in the interaction volume. This value can be compared with the calculations using number densities from the available pressure data. However, there could be an error of one or two orders of magnitude in these estimates. Bearing in mind this fact, we have taken into consideration the worst possible values for number density and interaction volume, giving a conservative estimate of the detection limit of approx. 1000 atoms in the interaction volume for the single colour scheme. To improve the detection limit further,



we employed two step resonant excitation and ionization scheme using two different lasers pumped by the same excimer laser. Rydberg states of sodium are populated via the  $3^2P_{3/2}$  intermediate state using 589.0 nm radiation and scanning the coumarin dye laser in the range 460 – 510 nm. With this ionization scheme we reached a detection limit of less than 100 atoms.

### **Resolving power of TOFMS**

The resolving power of the time-of-flight mass spectrometer is measured from the experimentally observed mass spectrum using the following relation

$$R = M/\Delta M = M \cdot (T_M - T_{M+1}) / 2\delta t$$

Where  $T_M$  is the time-of-flight for mass  $M$  and  $\delta t$  is the observed pulse width. Under optimum conditions of space focusing and at lower temperatures (which reduces the velocity spread of atoms) the resolving power  $R$  measured with potassium is about 400. However, as the temperature is increased, the observed pulse width  $\delta t$  increases and the resolution is decreased. To compensate for the spread due to velocity distribution a reflectron type of mass spectrometer is under construction.

### **Summary**

A Resonance Ionization Mass Spectrometer using indigenously built atomic beam sources and a time-of-flight mass spectrometer is set up around an excimer pumped dye laser system. The detailed performance evaluation of the spectrometer is carried out. Under optimum conditions about 1000 atoms are detected with a single colour three photon ionization scheme and this limit is further improved using a two colour scheme

of sodium to detect less than 100 atoms. All isotopes of natural samples of potassium, barium and ytterbium are clearly resolved. The resolving power  $\Delta M$  of the TOFMS is measured to be 400. Isotopic abundance ratio measurements of natural samples of the above elements show good agreement with well known published literature. The salient features of the spectrometer are summarised in Table 1.

### **Acknowledgement**

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Table 1

**Salient features of Resonance Ionization Mass Spectrometer**

**Interaction Chamber**

Dimension	:	300 mm length, 225 mm diameter
No. of ports	:	10
Order of vacuum	:	$10^{-6}$ mbar

**TOFMS**

Length of the drift tube	:	1.0 m
Gain of the detector	:	$10^7$ at 3000 V
Area of detector	:	5 mm X 5 mm
Resolving power of TOFMS:		400

**Dye Laser**

Pulse energy	:	20 mJ/pulse
Pulse duration	:	20 ns FWHM
Repetition rate	:	10 – 50 Hz

**General**

Preamplifier bandwidth	:	300 MHz
Typical run time	:	5 min
Detection limit	:	$10^5$ atoms/cc in the beam
Applicability	:	Almost all atoms and molecules

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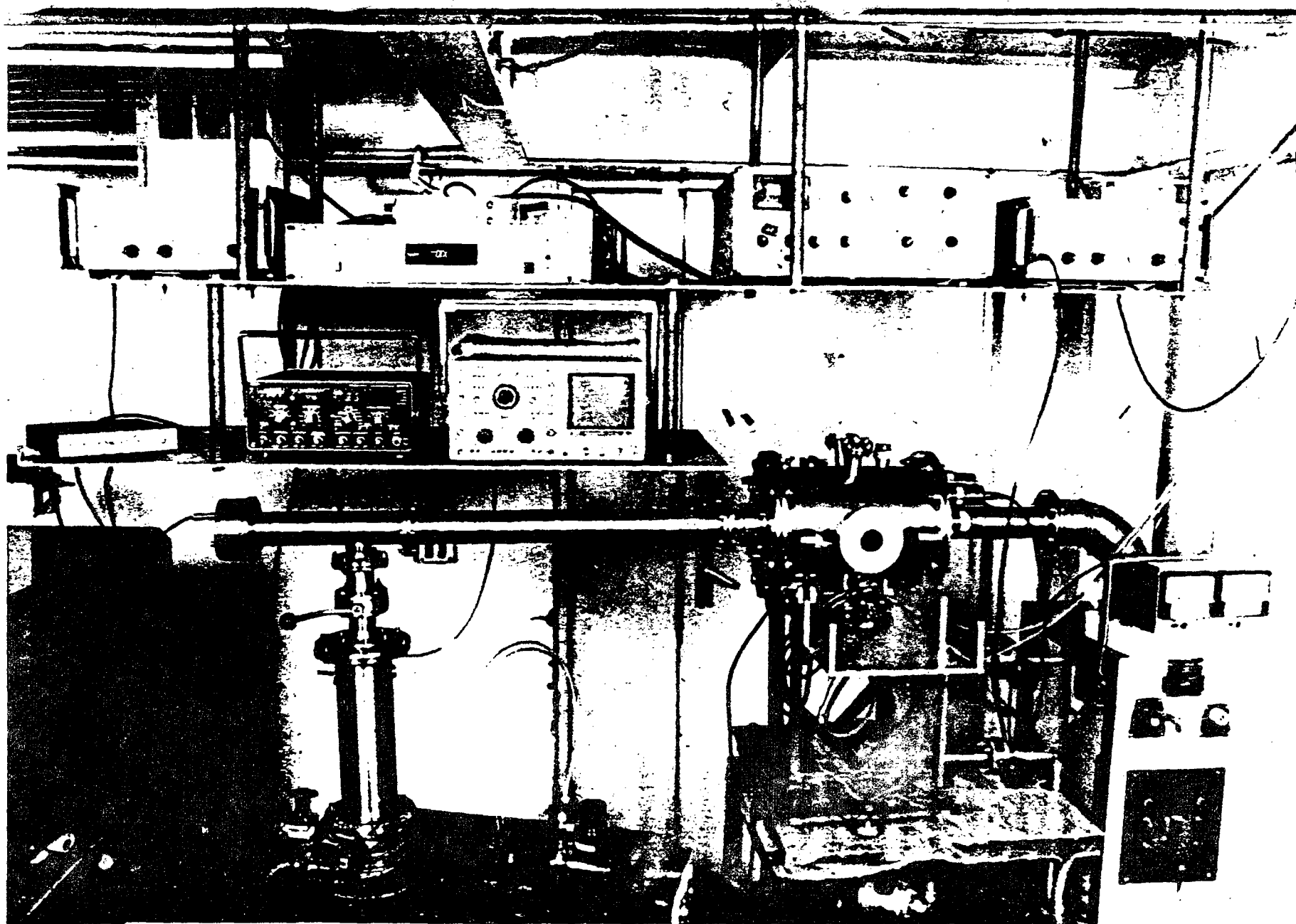


FIG.1 RESONANCE IONIZATION MASS SPECTROMETER

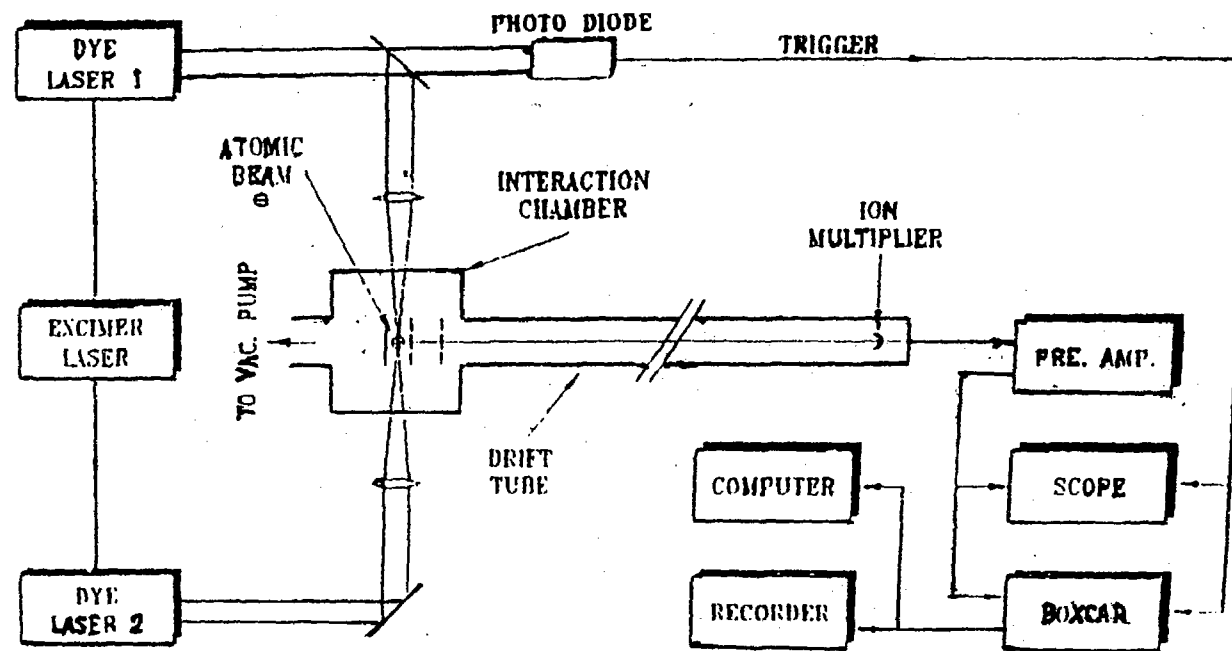


FIG. 2 SCHEMATIC OF RESONANCE IONIZATION  
TIME-OF-FLIGHT MASS SPECTROMETER

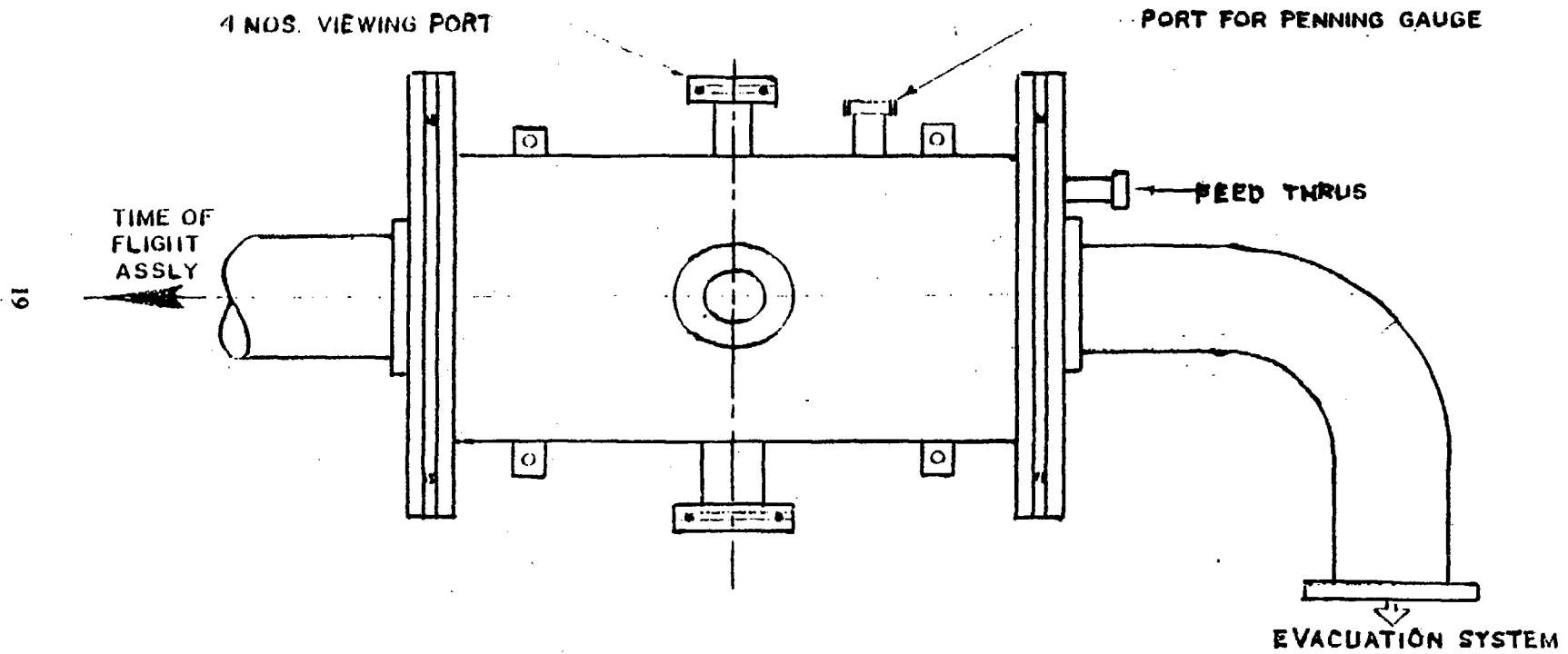


FIG. 3 INTERACTION CHAMBER

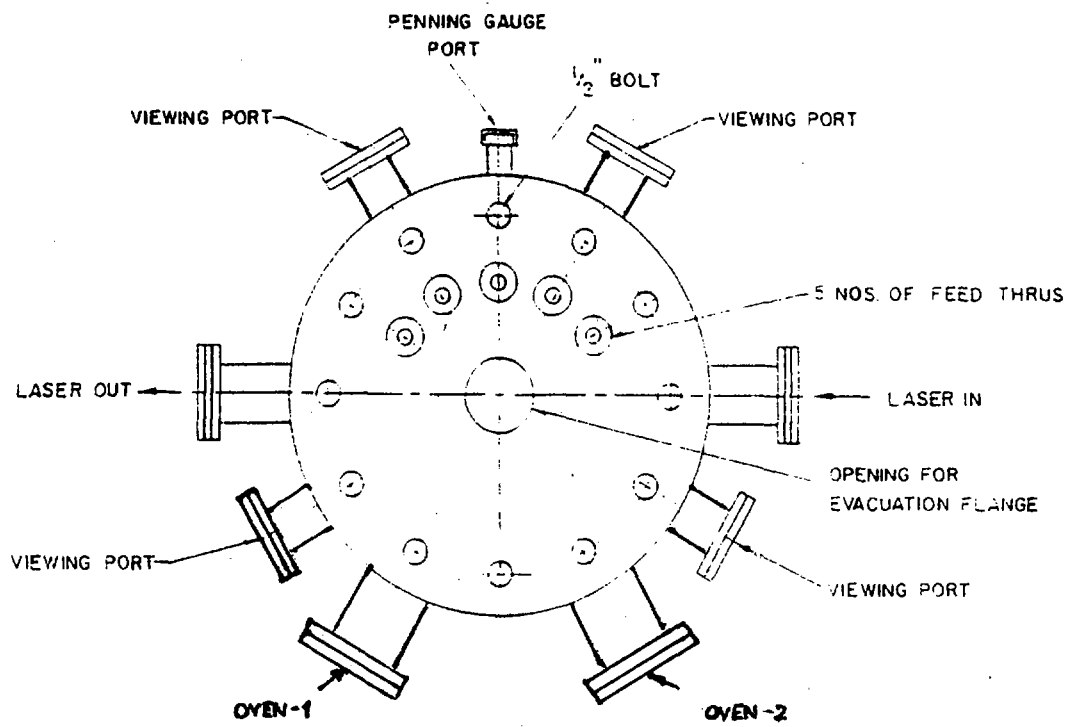


FIG. 4 END VIEW OF INTERACTION CHAMBER



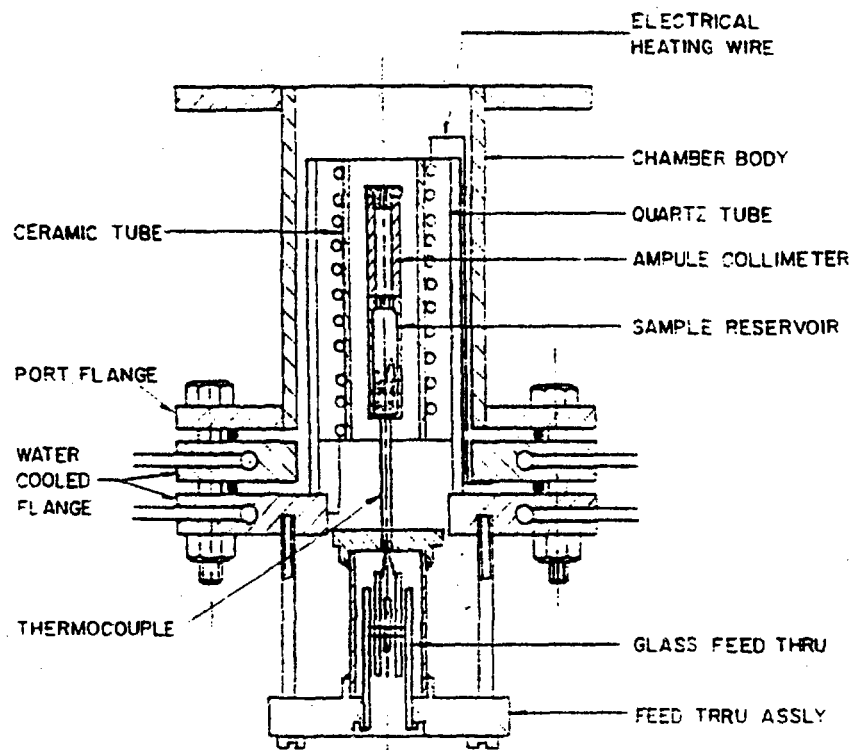


FIG. 5 LOW TEMPERATURE ATOMIC BEAM SOURCE

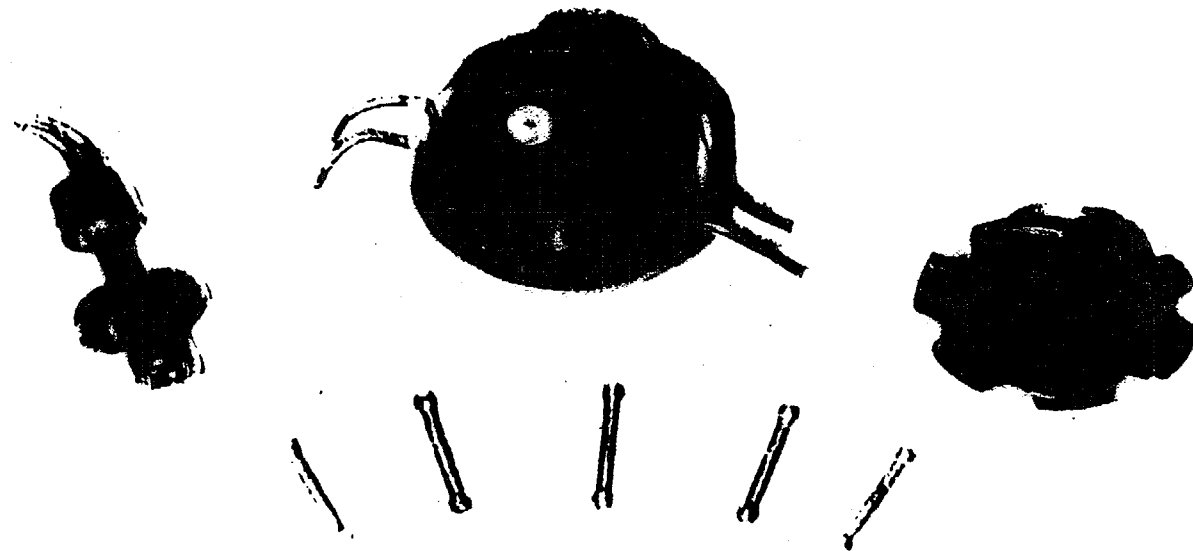


FIG. 6 PHOTOGRAPH SHOWING PARTS OF  
HIGH TEMPERATURE ATOMIC BEAM SOURCE

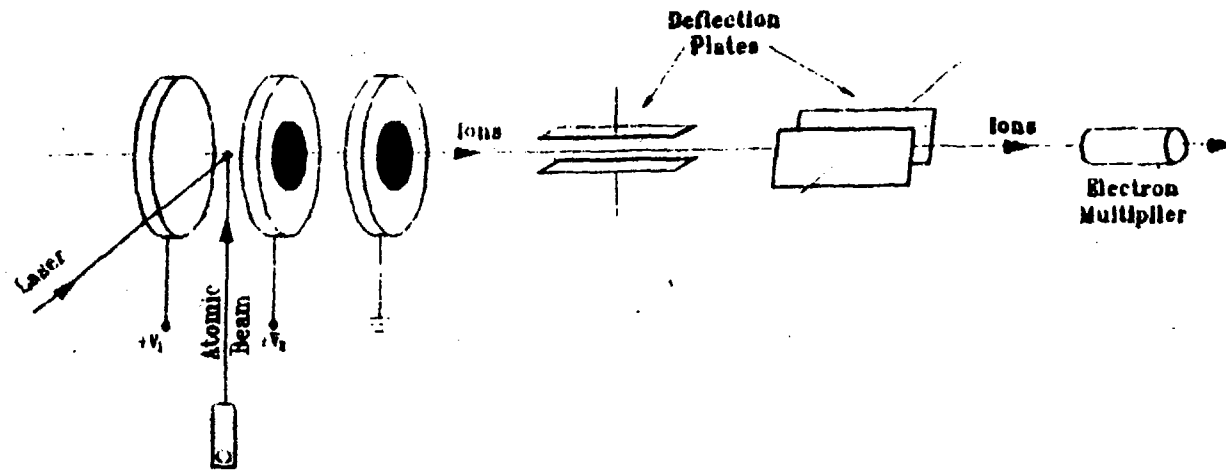


FIG. 7 SCHEMATIC OF TIME-OF-FLIGHT MASS SPECTROMETER

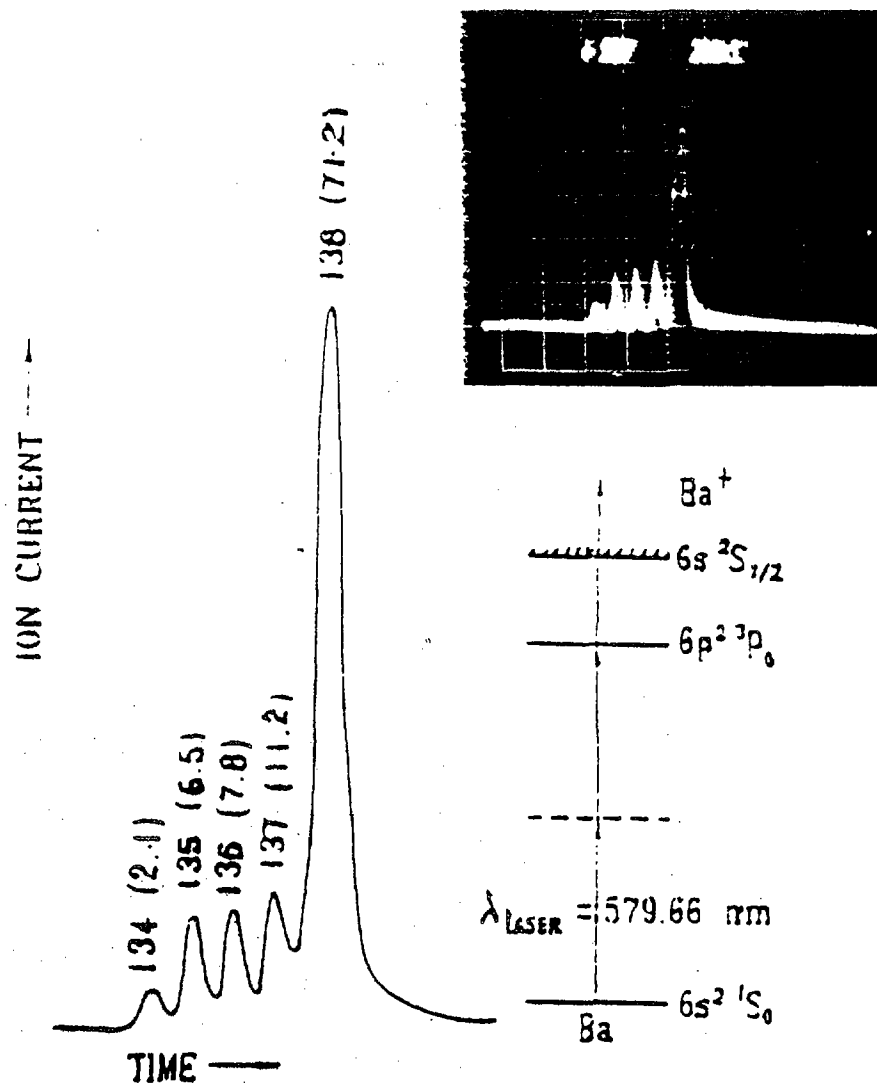


FIG. 8 PHOTOIONIZATION SCHEME AND MASS SPECTRUM OF BARIUM ISOTOPES

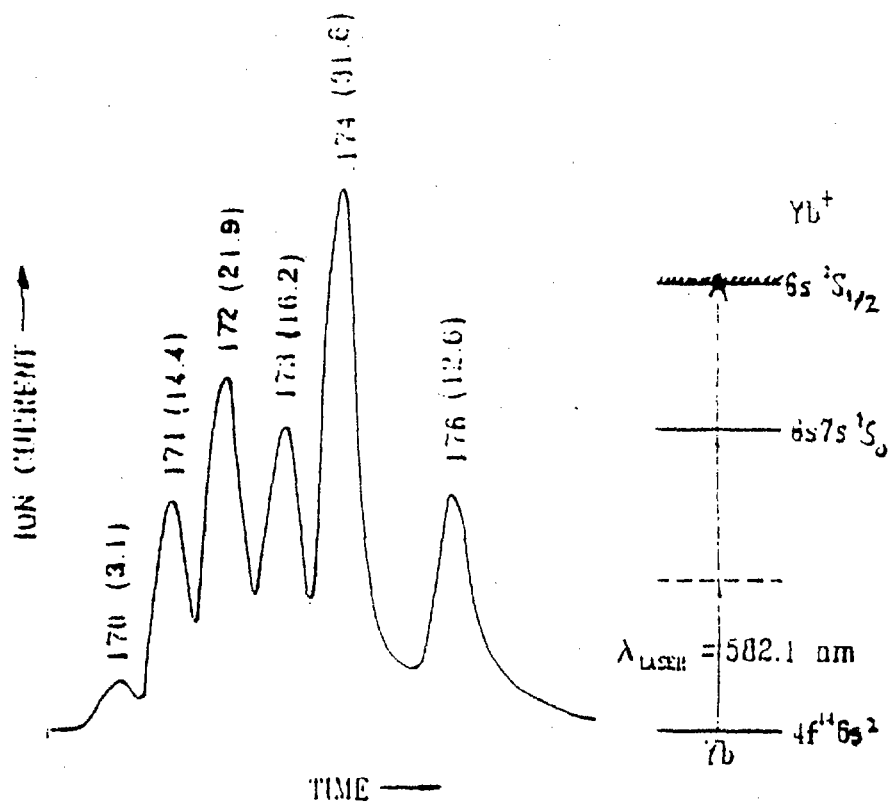
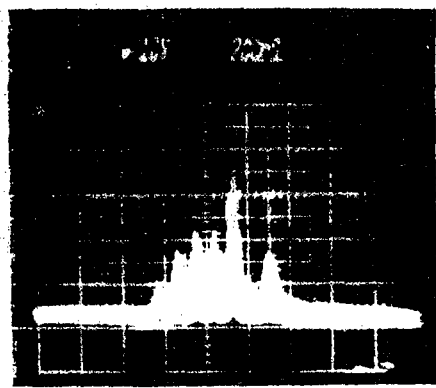
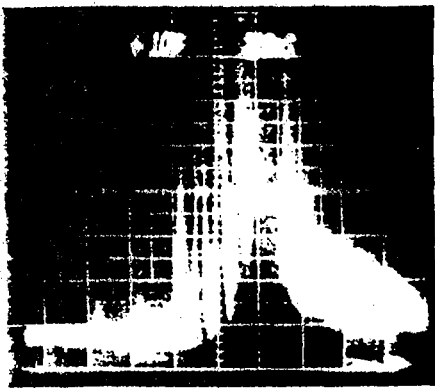


FIG. 9 PHOTOIONIZATION SCHEME AND MASS SPECTRUM

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