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TIME-OF-FLIGHT MASS SPECTROMETRY 07.00

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The future high speed gas chromatograph (GC) using short narrow bore silica capillaries (i.d. 50 - 150 µm) needs a very fast response detector which is also sensitive. The detector must also produce mass spectra for analysis of sample components injected into the capillary. The only instrument which is capable of this at present is time-of-flight mass spectrometer (TOFMS). TOFMS can produce 10.000 - 100.000 mass spectra/s, exceed the minimum mass resolution R = 500 necessary for practical work and have practically unlimited mass range.

Our aim is to develop a reflectron-type [1] TOFMS having mass resolution R = 1000, mass range up to 1000 amu (expandable) and rate of spectra 5000/s. The preliminary prototype constructed has mass resolution R ~ 750 and mass range 1000. The ions are produced by electron bombardment and are accelerated to approximately the same energy by using an electric field having a very short risetime driving them into the actual static acceleration field. After acceleration the ions travel into a field-free drift tube (0.7 m), reflect from an electrostatic mirror and travel back near to the ion source where the detector lies. As a detector we have used an ion multiplier tube.

The dispersion in mass is caused by the differences in velocities. The ions disperse during the flight into bunches composed of ions of same mass and we can observe them at the detector as a train of mass peaks. The effect of the mirror is to compensate for the variable ion energies gained in the ion source. The compensation arises because the ions having larger kinetic energies penetrate deeper into the mirror field thus having a longer distance to travel. This method increases the mass resolution at least by a factor of 10 compared to the earlier TOFMS:s with the same parameters.

The sensitivity was not measured but at a pressure p = 1.5 10E-6 Torr we were able to observe many remnant gases in the vacuum chamber. The strongest mass peaks were those of H_2O^+, N_2^+ and O_2^+. Several other unidentified peaks belonging to the diffusion pump oil fragments were observed at higher masses up to 324 amu.

ref.
[1] B.A. Mamyrin, D.V. Shmikk, Sov. Phys. - JETP 49 762(1979)

Principles of Time-of-Flight-Mass-Spectrometer (TOFMS)

TOFMS separates ions on the basis of their individual flight times through a field-free flight tube. The group of ions produced by an electron beam in the ion source is first accelerated using a 400 V potential. The lighter the ion the higher the speed it obtains and the faster it flies through the field-free tube to the secondary electron multiplier detector. Time-of-flight (T) of an ion with mass M can be expressed by the equation $T = A\sqrt{M}$, where A is a constant which depends on the instrument. Typical flight times with the instrument developed are between 2 µs and 200 µs. This means that TOFMS is at least 1000 times faster than other MS methods and can therefore be used to monitor very fast sample flows from rapid reactions or from micro capillary columns in GC.

The first instrument constructed had a direct flight tube, an ion source at one end and a detector at the other end of the system. This instrument, however, produced only a low mass resolution (60), which is a consequence of a wide energy distribution of ions with the same mass. Acceleration energy for an ion close to repeller plate is greater than the energy for an identical ion further away. The most effective improvement is an electrostatic mirror at the place of the detector in the simple flight tube.

Ions with a higher kinetic energy penetrate deeper into the electrostatic mirror before reflecting back than the ions with less kinetic energy. When flying back from the mirror the identical ions become focused to sharp bunches at the detector. The mirror focusing produced a great improvement in mass resolution (R) 1000 at 200 V acceleration).

Experimental setup of TOFMS

The TOFMS is built into two vacuum vessels evacuated by an oil diffusion pump in the first chamber down to 10E-7 mbar. The first chamber contains the ion source and ion detector (Fig. 2.) which are constructed on the same base plate whose orientation is adjustable. The electron gun (as all components in this TOFMS-prototype except the ion multiplier tube) is constructed in our laboratory and gives about 400 eV energy for the electrons.

The acceleration voltages +V1 and +V2 are 80 V and 400 V respectively giving an average ion energy of 440 eV. The distance between the ion repeller plate and the first grid is 2 mm and the acceleration field is 20 mm long. The deflection system consists of condenser plates producing homogenous fields into the region where the ion beam passes. The ion multiplier is a commercial type having minimum pulse width 10 ns and current gain 10E6. The total length of flight is 1400 mm in field-free space.

The second chamber is pumped through the the flight tube (450 mm) and contains only the electrostatic mirror system. It is constructed of grids and field homogenization rings together with a voltage divider on a frame made of SS. Its orientation is also adjustable and in practice its mirror plane is set perpendicular to the ion source symmetry axis using a laser beam. The mirror potentials +V3 and +V4 are 305 V and 450 V and the distances of the grids are 10 mm and 100 mm respectively. The pulse generator

can produce voltage pulses up to 450 V having a risetime of 10 ns. The acceleration pulse +V1 is about 5 μs long and has a repetition rate of 5 kHz. The preamplifier has a gain of 100 and BW = 100 MHz. As a spectrum display unit we have used a 100 MHz oscilloscope.

Results

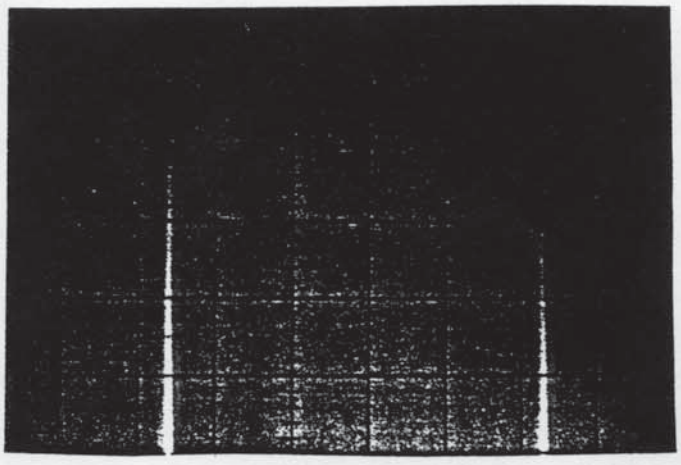
1. Medium resolution Time-of-Flight mass spectrometer was designed and constructed for the first time in Finland. The construction is based on published information on components but the complete system was developed here after long ion optical calculations. Four preliminary prototypes were constructed before achieving the present performance.

2. Results indicate that TOFMS can be constructed in a simple university workshop. Electronic parameters and components are rather critical whereas mechanics is relatively simple compared to other mass spectrometer types. It is obvious that TOFMS will be popular in the future because of continuously increasing costs of fine-mechanical engineering. Digitalization of mass spectral information for computerized data handling is more difficult than with other spectrometer types due to extremely fast (better than 10 ns) time resolution needed.

3. Mass resolution is the most important parameter for an organic mass spectrometer and was therefore our primary challenge. Resolution 1000 is our goal determined by the intended applications e.g. for micro capillary gas chromatography. This resolution was already achieved using lowered acceleration voltage (200 V).

4. Specific data.

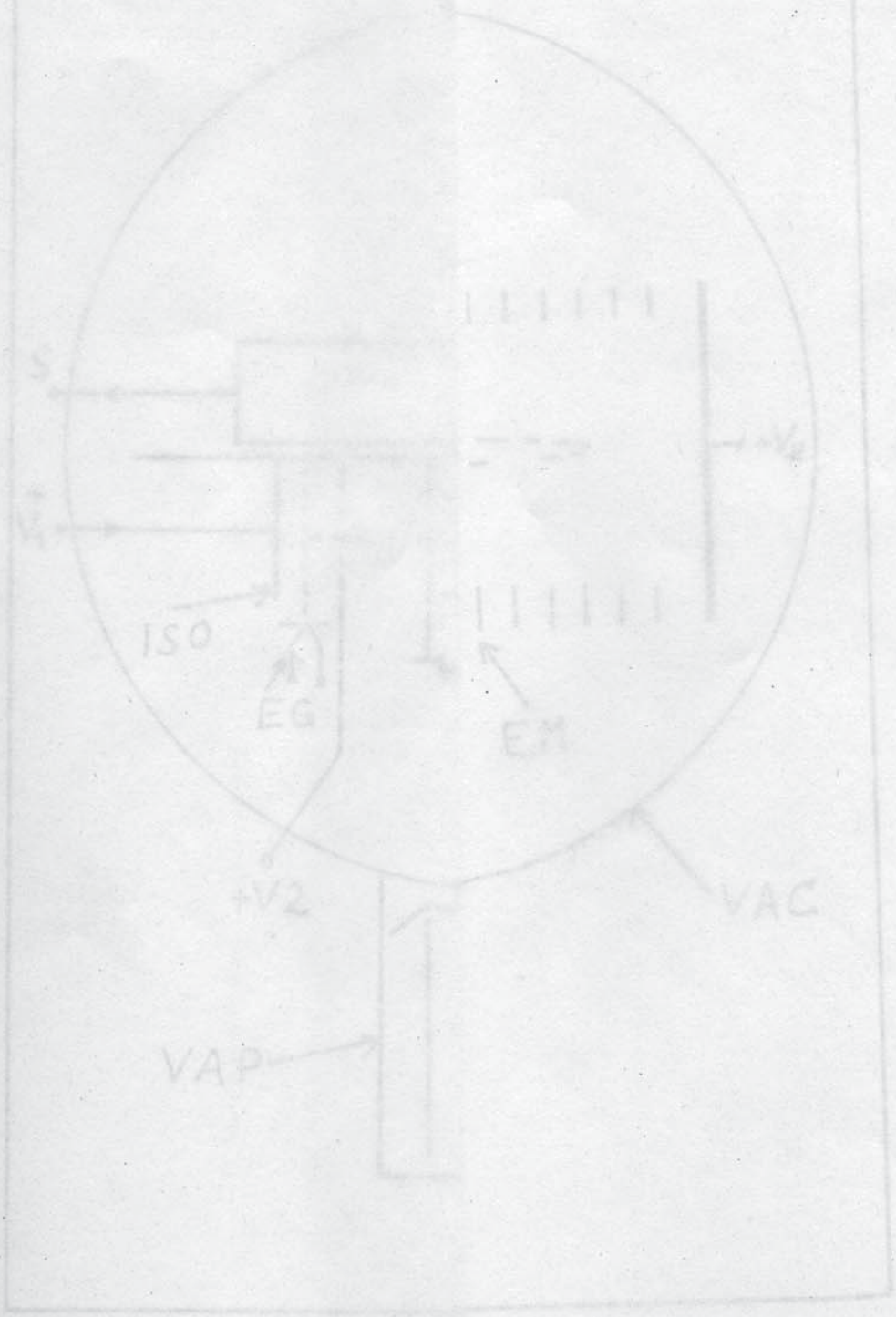
The mass resolution is an ability to separate adjacent mass peaks and in TOFMS it is defined as $R = (M\Delta T)/(\Delta M \Delta t)$. Here M is the ion mass, ΔM is the mass difference between the adjacent masses, ΔT is the time difference between mass peaks and Δt is the peak width measured at half height. Our prototype has the following values for ions (all masses in amus) M1 = 28 (N2+), M2 = 32 (O2+), $\Delta M = 4$, $\Delta T \sim$ 2500 ns, and $\Delta t \sim$ 25 ns. So we get $R \sim 750$ (Fig.3.). We expect the mass resolution to be approximately valid through all mass spectrum.



N2+ (M = 28) O2+ (M = 32)

Fig. 3. Two adjacent mass peaks belonging to N2+ and O2+ having parameters $t \sim 25$ ns and $T \sim$ 2500 ns giving $R \sim 750$. The oscilloscope scale is 500 ns/cm. Here T(O2+) = 37.75 us.

We were able to observe at a pressure of 2E-6 mbar more than 40 mass peaks up to mass 324. By lowering the acceleration potential to 200 V we obtained R ~ 1100. The acceptable mass range is up to 1000 amu and can be easily enlarged. Only the method of ionization limits the mass range by not producing heavier ions.



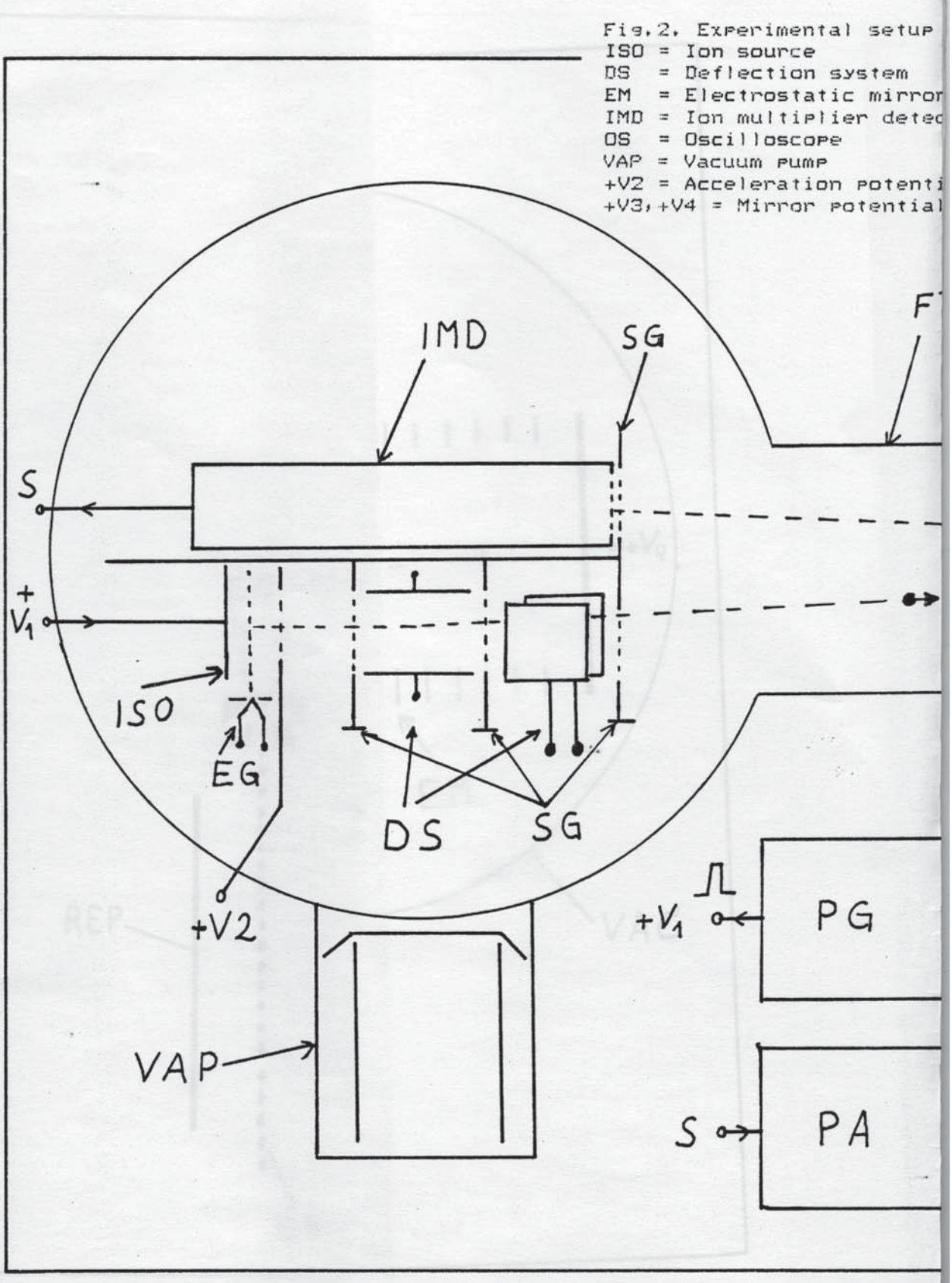
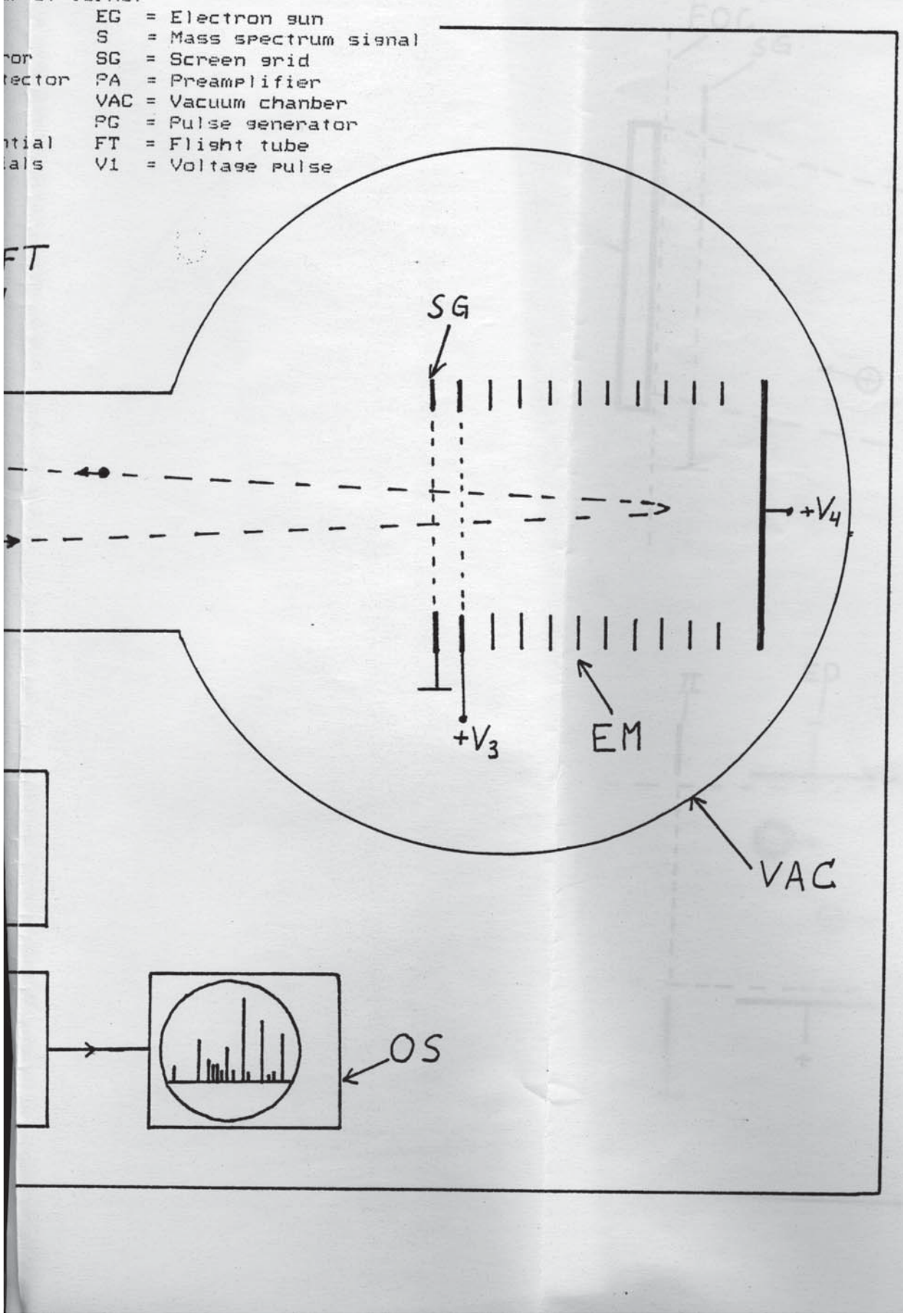
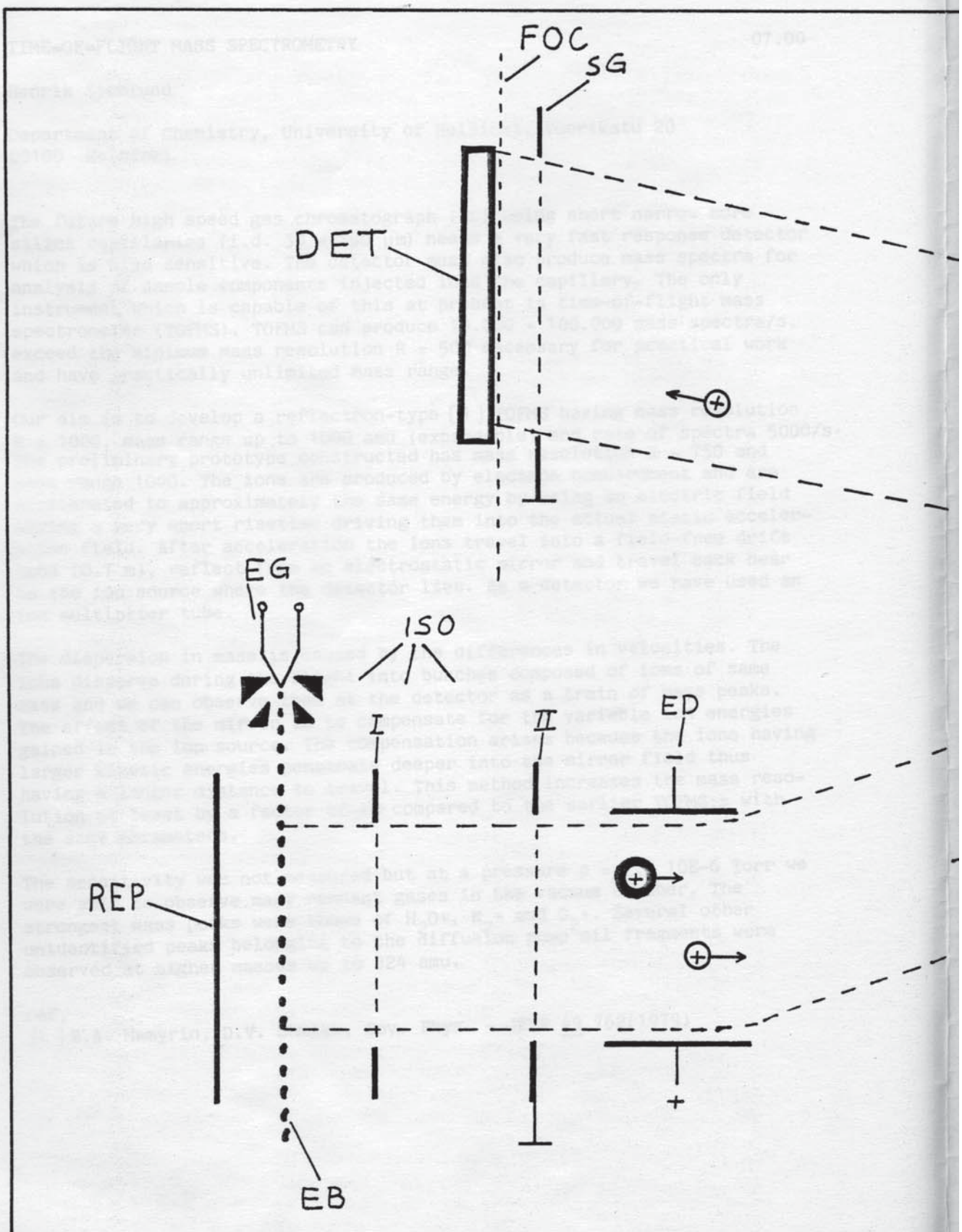


Fig.2. Experimental setup
ISO = Ion source
DS = Deflection system
EM = Electrostatic mirror
IMD = Ion multiplier detec
OS = Oscilloscope
VAP = Vacuum pump
+V2 = Acceleration potenti
+V3, +V4 = Mirror potential
IMD
SG
S
+
V1
ISO
EG
DS
SG
+V2
VAP
+V1
PG
S
PA

ıp of TOFMS.

EG = Electron gun
S = Mass spectrum signal
SG = Screen grid
PA = Preamplifier
VAC = Vacuum chanber
PG = Pulse generator
FT = Flight tube
V1 = Voltage pulse




FOC
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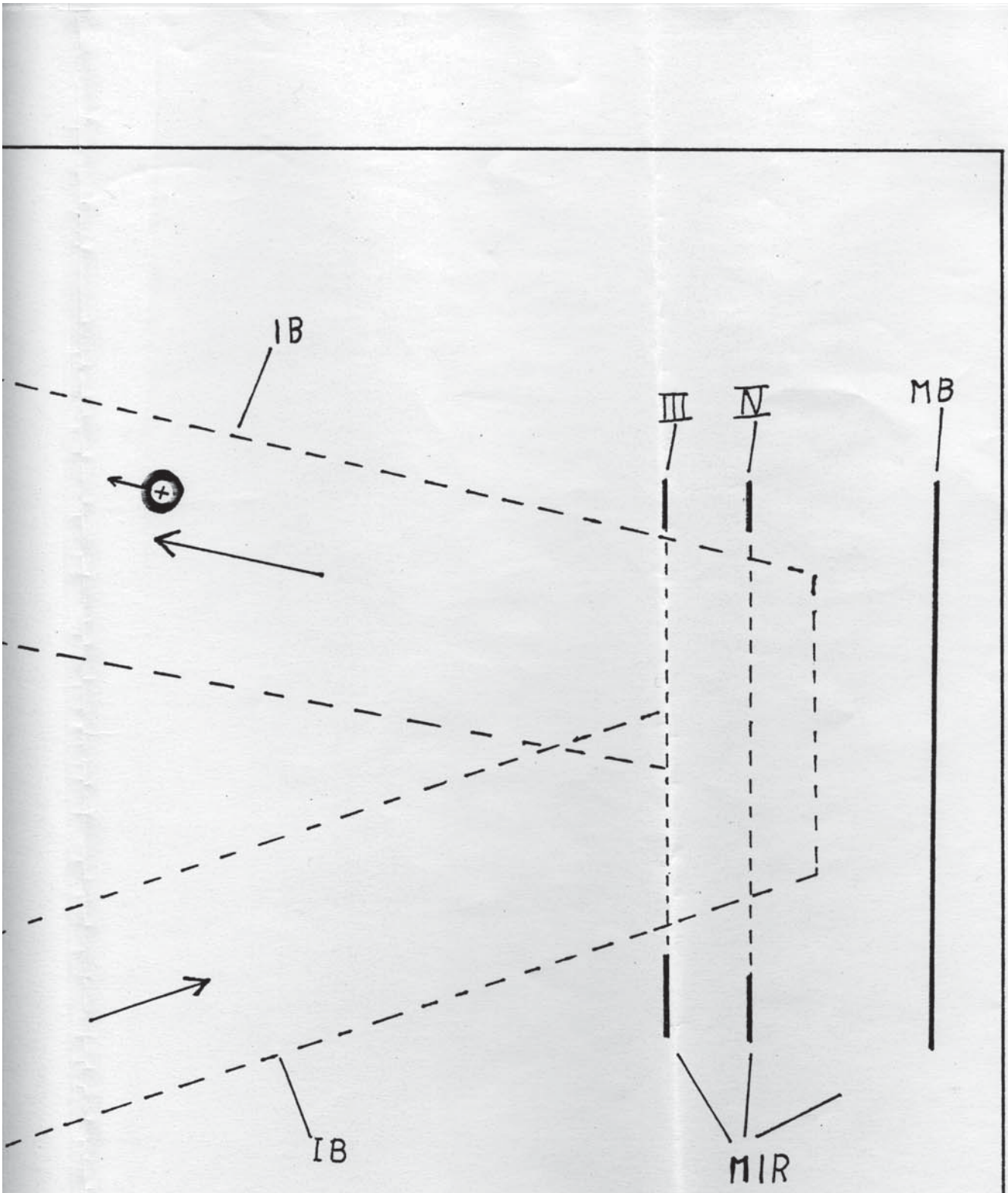

Fig.1. Principle of TOFMS.

ISO	= Ion source	MIR	= Mirror system
EG	= Electron gun	REP	= Ion repeller plate
EB	= Electron beam	I	= First grid at +V2
II	= Second grid at V = 0	IB	= Ion beam
ED	= Electrostatic deflector	MB	= Mirror backplate at +V4
III	= Third grid at V = 0	IV	= Fourth grid at +V3
DET	= Ion detector	SG	= Screen grid at V = 0
FOC	= Focusing plane		