CHAPTER 4

Experimental and Results

This chapter describes details of the process of the experiment in 2 parts. First part (I) is conceptual design of the quadrupole mass analyzer. Second part (II) is the experimental set up with the quadrupole gas analyzer.

Part I: Conceptual design of quadrupole mass analyzer

Before construction SIMS system by using quadrupole mass analyzer, the range of importance parameters such as radio frequency, d.c. voltage, and a.c. voltage must be known. These parameters can designed from the quadrupole mass analyzer principle (see Chapter 2), by the exact value of resolution and maximum mass. The SIMS system diagram is shown in Figure 4.1.

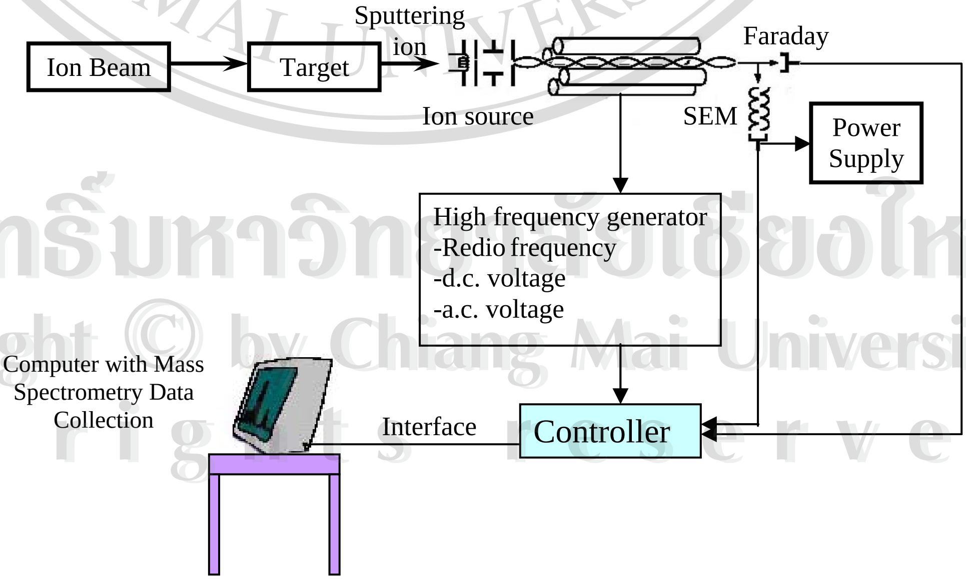


Figure 4.1 Diagram of secondary ion mass spectrometry system.

4.1 Description of Quadrupole Mass Analyzer

A quadrupole mass analyzer (series QMA 400, Balzers, Liechtenstein) consists of ion source, mass filter with rod system and ion detector (SEM and ion deflection unit with Faraday cup) as shown in Figure 4.2. Ion sources, the ionization are achieved by electron impact. Electrons are thermally emitted by a cathode and focused by electrical extraction fields so that they reach the ionization area. Mass filter, the proper material selection and very precise manufacturing methods ensure a high measure of linearity and reproducibility. For higher mass ranges as well as optimum stability and reproducibility, 8 mm in diameter and 200 mm in length molybdenum rods are used because of the superior electrical and thermal properties of the material. Secondary electron multiplier (SEM) has 17 discrete stages and focusing dynode geometry is a fast ion current amplifier between the quadrupole filter and the rods system is reduced.

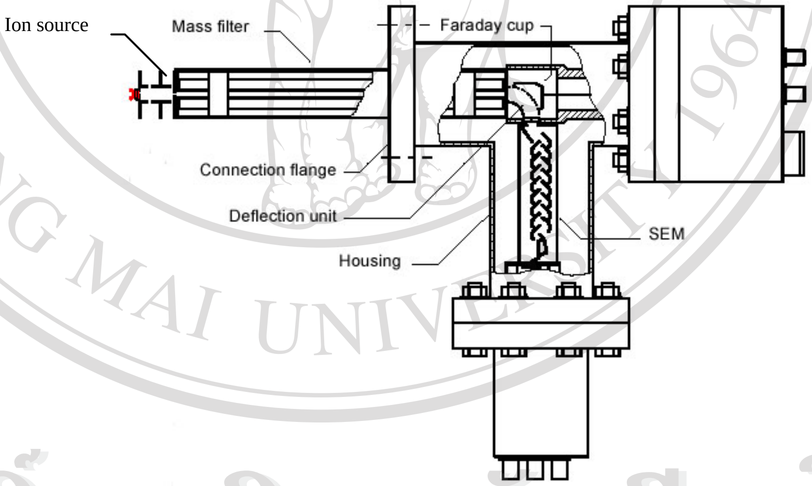


Figure 4.2 Schematic drawing of QMA with 90° off axis SEM (Balzers instruments)

4.2 Resolution (*R*) and peak width (ΔM)

Resolution is the parameter that tells us the ability of quadrupole to separate an analyze peak from a spectral interference. When the energy of inject ion is ≤ 10 eV.From section 2.3.5, two important characteristics of quadrupole are mass range and the maximum resolution. Both of them bring us to design the range of three parameters which used to control the quadrupole. In this project, the mass range is 1 to 1000 amu. The resolution can find from $R = M_m/\Delta M$, when this project aim to detect the injected ion with the maximum mass at 1,000 amu, then $R = 1000/\Delta M$. To simplify this calculation, ΔM is used instead of the resolution.

Compare the normal resolution when ΔM is 1 amu (R = 1,000) and high resolution when ΔM is 0.3 amu ($R \sim 3{,}300$). From Equation 2.32, the value of radio frequency at ΔM = 1 and 0.3 when the energy of inject ion (eV) varies from 1 to 10 eV are shown in Table 4.1.

Table 4.1 The value of Radio Frequency when the energy of inject ion varies from 1 to 10 eV at ΔM = 1 and 0.3 amu.

Energy of inject ion (eV)	Radio frequency (MHz)	
	ΔM=1 amu	ΔM=0.3 amu
1	0.32	0.58
2	0.45	0.82
3	0.55	1.00
4	0.63	1.15
5	0.71	1.29
6	0.77	1.41
7	0.84	1.53
8	0.89	1.63
9	0.95	1.73
10	1.00	1.83

From Table 4.1, the frequency at the good resolution (ΔM = 0.3 amu) is in the range of 0.5-2 MHz, and normal resolution (ΔM=1 amu), the RF is in the range of 0.5-1 MHz. That means the higher resolution the higher frequency at the same energy of injected ions.

4.3 Calculation of operating parameters

The designed resolution can lead to find the maximum value of the a.c. voltage (V_m) from Equations 2.30 after that find the d.c. voltage (U_m) from Equation 2.29, by consider at the point of the stability area is a/q = 0.336, the best point that just one mass to charge ratio can pass though the quadrupole, this point can get the relation U/V = 0.168. The value of V and U, when a length of rods is 0.2 m, rods diameter is 4 mm, and the energy of the inject ion varies from 1-10 eV are in the Table 4.2.

Table 4.2 The value of V and U, when L = 200 mm, r = 4 mm, and the energy of the inject ion varies from 1-10 eV.

Energy of inject ion (eV)	m = 1,000 amu		m = 1 amu	
	V (volt)	U (volt)	V (volt)	U (volt)
1	580	97	0.58	0.10
2	1160	195	1.16	0.19
3	1740	292	1.74	0.29
4	2320	390	2.32	0.39
5	2900	487	2.90	0.49
6	3480	585	3.48	0.58
7	4060	682	4.06	0.68
8	4640	780	4.64	0.78
9	5220	877	5.22	0.88
10	5800	974	5.80	0.97

From Table 4.2, the value of U which use to analyze m = 1 amu is lower than 1 V. The lower limits of operation voltage U and V are order of 1 V (Dawson, 1995). To operate at this mass have to operate at higher frequency**.** The values of V and U are 6.96 V and 1.17 V respectively when the radio frequency is 2.0 MHz and 10.88 V and 1.83 V when the radio frequency is 2.5 MHz. To operate all mass range, the system should has the maximum frequency at 2.5 MHz. The most practical frequency range for operating quadrupole mass spectrometer is 0.5 MHz to 6 MHz (Dawson, 1995). Then the frequency range of this system is 0.5 MHz to 2.5 MHz.

For maximum value of V_m is about 5,700 volt and maximum value of U_m is about 1,000 volt when design at peak width equal to 0.3 amu. The conclusion of this design is in the Table 4.3.

Table 4.3 Characteristics of a Quadrupole Mass Spectrometer for precision mass determinations.

rods length (L)	20 cm
rods diameter	0.8 cm
Mass range	1-1,000 amu
Maximum DC voltage (*U*)	1,000 volt
Maximum AC voltage (*V*)	5,700 volt
Radio frequency	0.5-2.5 MHz
Peak width	0.3 amu

4.4 Electrical connections

There are two modes of electrical connections (Balzers instruments, 1989) of analyzer with 90° ion deflection and off-axis SEM, connection with electrometer amplifier (EP) as shown in Figure 4.3 and connecting as oscilloscope directly to the SEM as shown in Figure 4.4. Table 4.4 shows the connection made between the analyzer and the electronics. The quadrupole mass spectrometry system is shown in Figure 4.5.

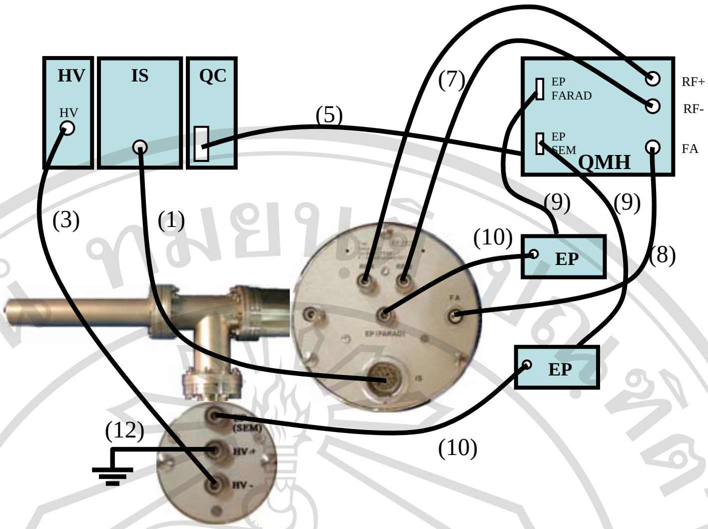


Figure 4.3 The connections made between the analyzer and the electronics with electrometer amplifier (EP).

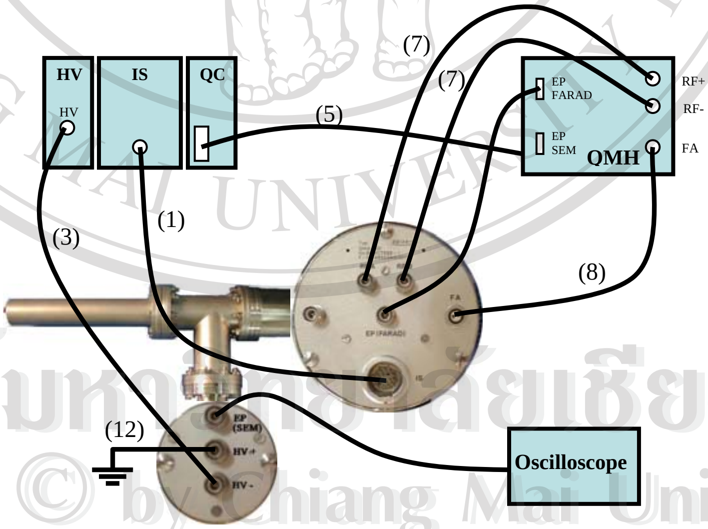


Figure 4.4 The connections made between the analyzer and the electronics with connect an oscilloscope directly to the SEM.

Table 4.4 The connections made between the analyzer and the electronics.

Connection	Purpose
1	Ion source supply
3	SEM high voltage
5	Control cable
7	Radio Frequency line
8	Field axis cable
9	Electrometer
10	Electrometer preamplifier input
12	Short circuit jumper

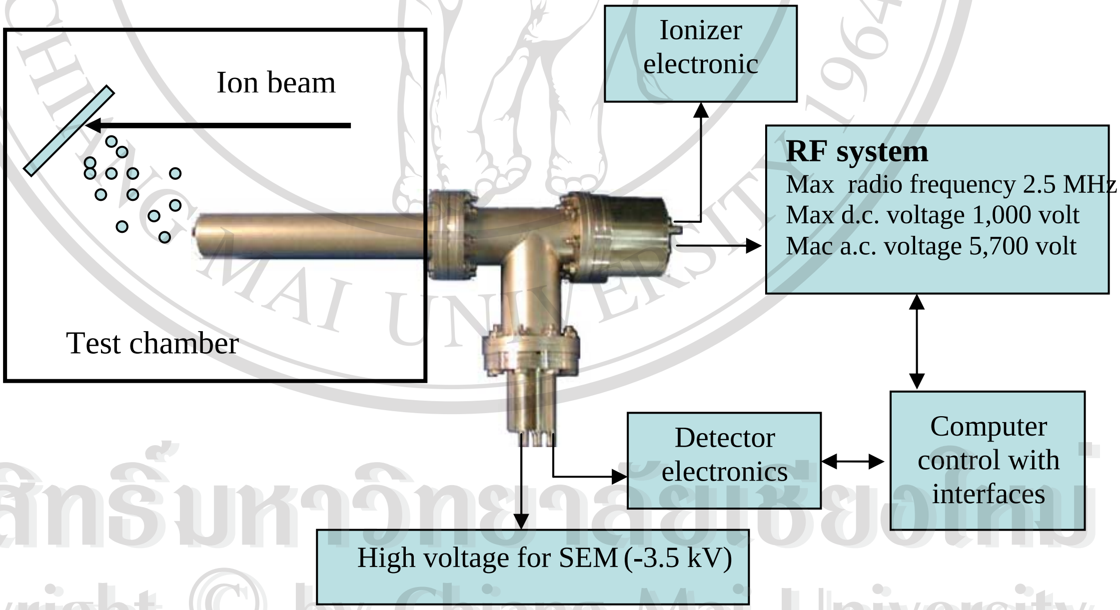


Figure 4.5 Quadrupole mass spectrometer system.

Part II: Experiment using a quadrupole gas analyzer

In this part, the experiment aims to use a mass spectrometer with a quadrupole gas analyzer to study the interaction of energetic ions and the biological cell (onion cell) from the sputtering which occurs during ion bombardment of onion cell.

4.5 Quadrupole gas analyzer

4.5.1 General description

A Dycor^{TM} quadrupole gas analyzers (series M100, AMETEK, Pittsburgh, PA. USA) consist of the following items:

- The CONTROL UNIT with operation controls and CRT screen for data output.
- The POWER SUPPLY for the analyzer head.
- The ANALYZER HEAD that connects to a vacuum system.
- The ELECTROMETER that connects to the power supply to the analyzer head.
- The CONTROL CABLE that connects the power supply to the control unit.

For residual gas analysis in a vacuum chamber, the analyzer head is to be installed in the user's vacuum system. The analyzer comes with a filament installed in the factory. The electrometer connects directly to the analyzer head in order to the best signal to noise ratio. There are two of three cables attached to the electrometer, a coaxial cable to supply the RF. to the mass filter, a second flat cable coaxial to supply numerous other voltages and signals to the analyzer head and, for the multiplier versions of the instrument, a coaxial cable to supply the high voltage to the electron multiplier. All of these cables should be plugged into the power supply at the appropriate locations.

Figure 4.6 shows box diagram of quadrupole gas analyzers system and Figure 4.7 is shows the control unit with operation controls and CRT screen which interface with computer. The mass spectrum can be collected and saved by Mass Spectrometer Data Collection code, developed by Mr. Michael W. Rhodes as shown in Figure 4.8.

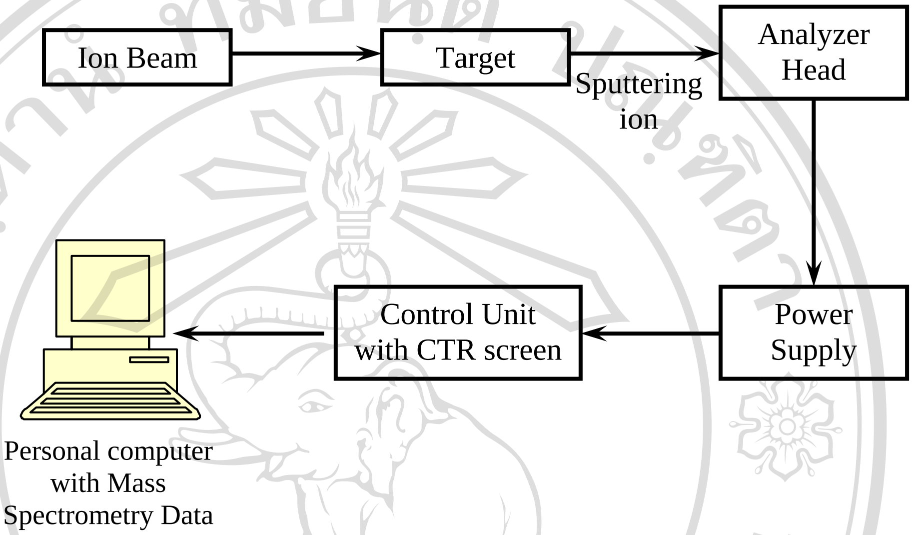


Figure 4.6 Box diagram of quadrupole gas analyzer system.

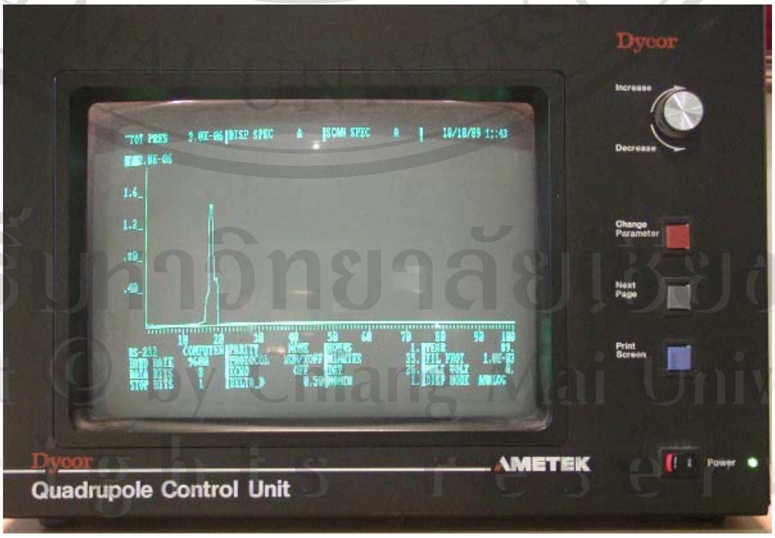
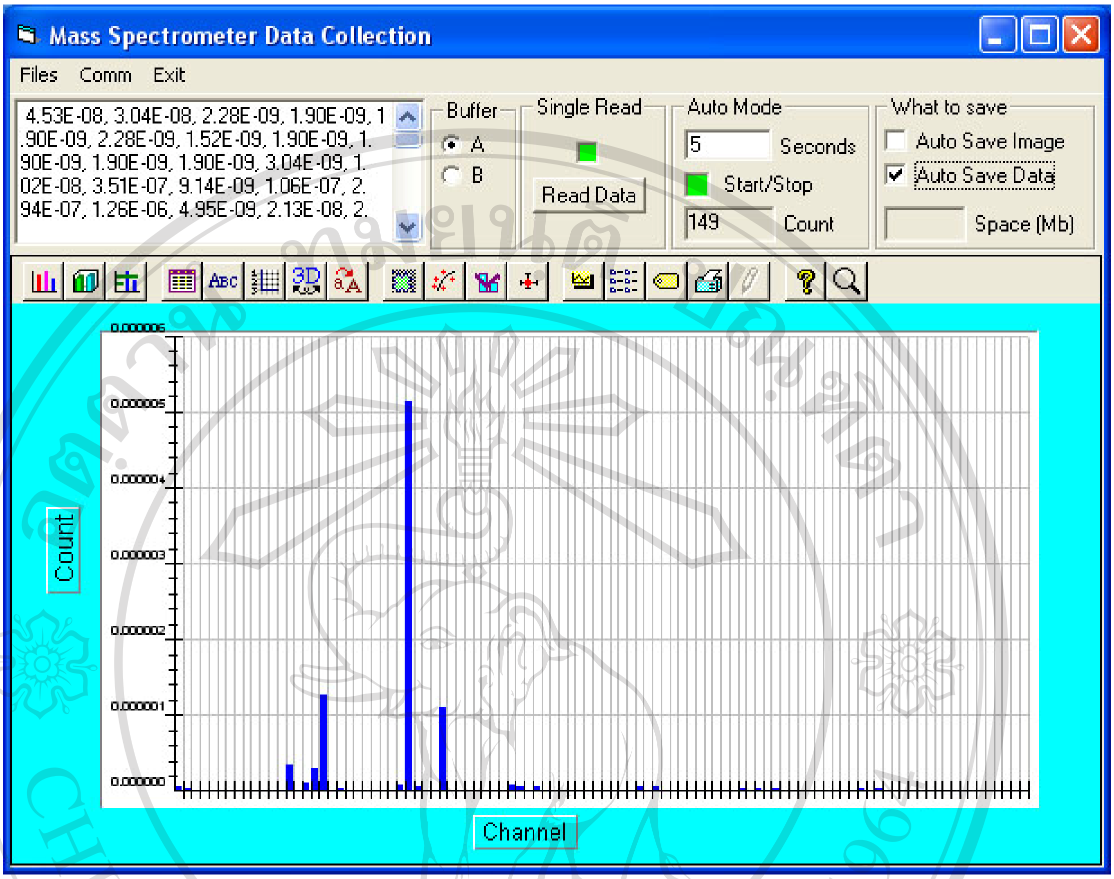


Figure 4.7 The control unit with operation controls and CRT screen.



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94E-07, 1.26E-06, 4.95E-09, 2.13E-08, 2.
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Figure 4.8 Mass Spectrometer Data Collection code.

4.5.2 Principle of operation

When gas is evacuated into the quadrupole housing, electrons emitted from a hot filament collide with gas molecules in the ionizer region of the analyzer head producing ions of the parent molecules and ion fragments also. These ions are directed toward the mass filter by the electric fields produced by a focus electrode. The mass filter rejects the passage of all ions except those with a specific mass-to-charge ratio. The mass filtered ions are converted to electric current which is proportional to the corresponding molecular partial pressure in the source.

This is done in one of two user selected detection modes. In the faraday cup mode, the ions are directed to a cup shaped element and the ion current it self is measured. In the electron multiplier mode, the ions are directed to a multiplier structure where they produce a cascade of electrons. These electrons are in turn directed to faraday cup. The electron multiplier, therefore, acts as a fast current amplifier.

4.5.3 Calibration of quadrupole gas analyzer

To calibration of quadrupole gas analyzer can be done from the front panel controls and the settings will be stored digitally in memory even if the power is interrupted. The calibration is done in the Faraday Cup mode and will require the introduction of gasses at known pressures into the analyzer and adjusting certain parameters until the readings from the analyzer are correct. Calibration can be done by doing the following:

1. Adjust the frequency of the R.F. power source to match the resonant frequency of the R.F. transformer in Electrometer housing by doing the following:
   - A. Set the instrument to the ANALOG mode.
   - B. Set the NO. SCAN to -1.
   - C. Turn the filament on.
   - D. Set the EMISSION at 1E-3, EL ENERGY at -70 and Focus at -20. (set to where they will be operated at during normal service)

E. Set TOTAL PRS to ON and allow the instrument to warm up at least ½ hour.

F. Change the FREQUENCY parameter until the R.F. TUNE is at its lowest value possible which get FREQUENCY at 2.752 MHz where R.F. TUNE is 7.190.

2. Introduce a gas; adjust the LO RES to obtain the required resolution of mass peak at low mass.
3. Next do the same; adjust HI RES to obtain the required resolution of mass peak at high mass.
4. Repeat step 2 and 3 until the resolution is correct, get LO RES at 4100 and HI RES at 2650.
5. Adjust the LO POS and HI POS to make the peaks appear at their correct place, get LO POS at -0.10 and HI POS at -2.65.

Each parameter will be described in the following:

NO SCANS

This is the number of times to scan, before each scan this number is decreased by one until it zero. The instrument will stop scanning when this parameter is zero. If this parameter is set to -1 then the scanning will continue indefinitely.

EMISSION

The electron emission current can be change to suit the user. The filament power will be adjust until the actual emission current equals this value.

EL ENERGY

This is the energy of the ionizing electrons in the ion source in electron-volt. Most of the data available on the ionizing efficiencies and cracking pattern of various molecules are taken at -70 volt and rarely will there be a need to change this parameter.

FOCUS

The focus electrode voltage is normally at -20 volt.

FIL

This can be turned on or off. When it is off there will be a small voltage applied to the filament, but not enough to heat it.

FREQUENCY

This is the actual frequency that the mass filter operates at and cad be varied by changing this parameter.

LO RES, LO POS, HI RES and HI POS

Adjust these parameters to get good resolution of mass spectrum.

Argon was used for calibration; the mass spectrum is shown in Figure 4.9. Figure 4.9(a) shows the mass spectrum of Ar before the calibration; there are many peaks, but no correct ones. Figure 4.9(b) shows the mass spectrum of Ar from a library of spectra in the NIST Chemistry - WebBook, a data correction of the National Institute of Standards and Technology. The singly charged argon ion (Ar^+) is also the base peak at m/z = 40 and the doubly charged argon ion (Ar^{+2}) has an m/z = 20. Figure 4.9(c) shows the mass spectrum of argon after the calibration, which is consistent with the spectrum in Figure 4.9(b).

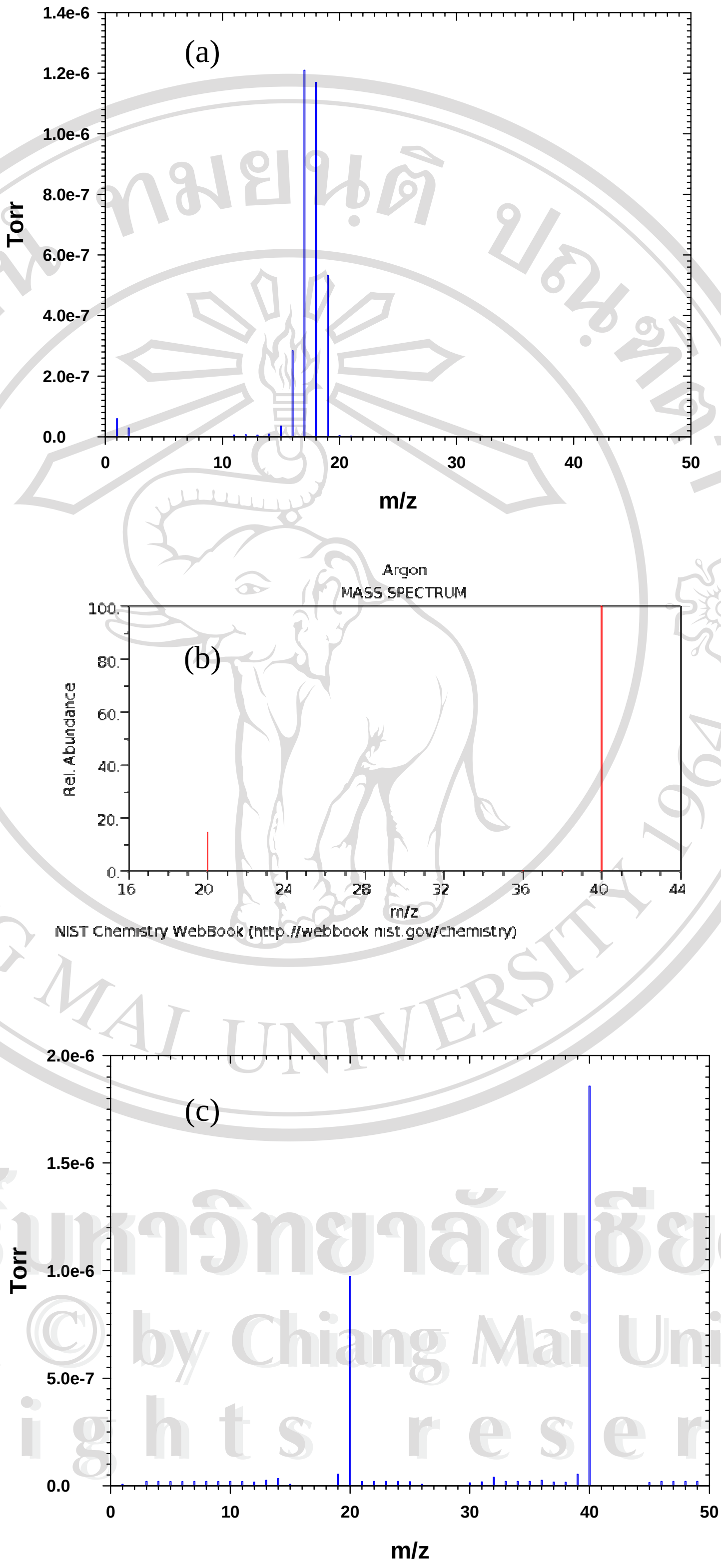

Figure 4.9 Mass spectrum of argon (a) before calibration, (b) a library of spectra in the NIST- WebBook (NIST-WebBook, 2003) (c) after calibration.

4.6 Sample and sample preparation

The experimental design for this research was divided into distinct phases:

- Analysis of gas residues of pure gas, argon (Ar) and nitrogen (N_2).
- Analysis of compounded gas, carbon dioxide (CO_2).
- Analysis of solid residues of ion-bombarded pure compounds, carbon (C).
- Analysis of ion-bombarded compounded solid, plastic scintillator or organic scintillator (BC–400) and silicon dioxide (SiO_2). The mass density of plastic scintillator 1.032 g/cm^3 and the ratio of H:C is 1.104.
- Specific analysis of ion-bombarded biological tissues, the inner surface membrane of onion.

Thin layers of onion epidermis are prepared from ordinary yellow onions. The onion is cut and the third layer form the outer shell obtained. From the middle part of this layer, a thin skin of onion epidermis was peeled and dried by a dryer to remove water in cell (fresh cells make the pressure of chamber too high to be analyzed by this quadrupole). This onion was attached to a flat holder using carbon tape. The composition of the onion samples was measured by element analysis equipment and the ratio of C:H:O in this kind of sample is approximately 1:2:1. Figure 4.10 shows four kinds of samples.

Nitrogen and Carbon dioxide are used in this experimental to test the operation of the quadrupole gas analyzer before the experiment with onion cell. The most common atoms in biological cell are Carbon(C), Hydrogen (H) and Oxygen (O). Sputtering of solid carbon, plastic scintillator (compound of C and H) and silicon dioxide (SiO_2) before the experimental with the biological cells was studied to test the system.

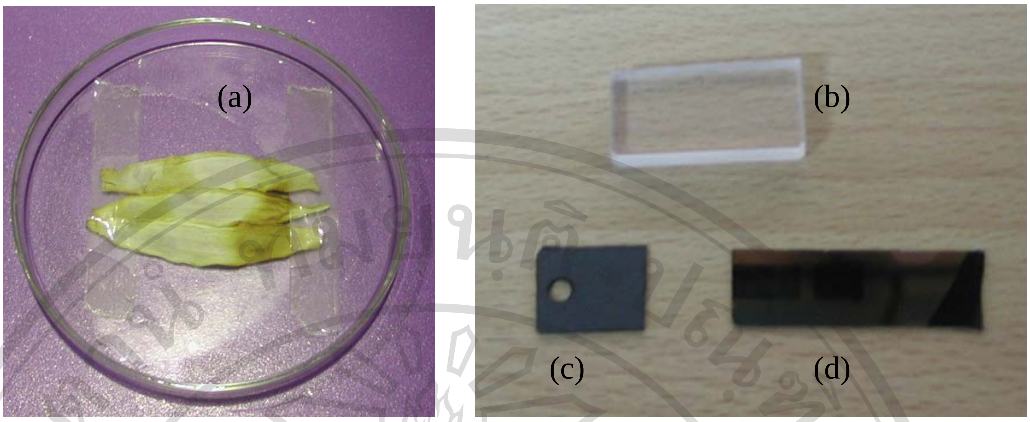

Figure 4.10 Four kinds of sample, (a) onion, (b) plastic scintillator, (c) carbon and (d) silicon dioxide.

4.7 Ion bombardment

Figure 4.11 shows the schematic diagram of the experimental system. The main parts are the accelerator, test chamber and quadrupole analyzer. The low energy incident N ions at 30 keV used in this experiment were produced by CMU2 heavy ion-implantation facility at Chiang Mai University as shown in Figure 4.12. The beam current is up to a few microamperes. The samples were tilted by an angle about 45^o with respect to the beam axis and bombarded about 40 minutes for onion cell. The quadrupole gas analyzer installed in the target chamber is shown in Figure 4.13. The pressure of the target chamber was approximately 6 x 10^{-5} mbar during the experiment.

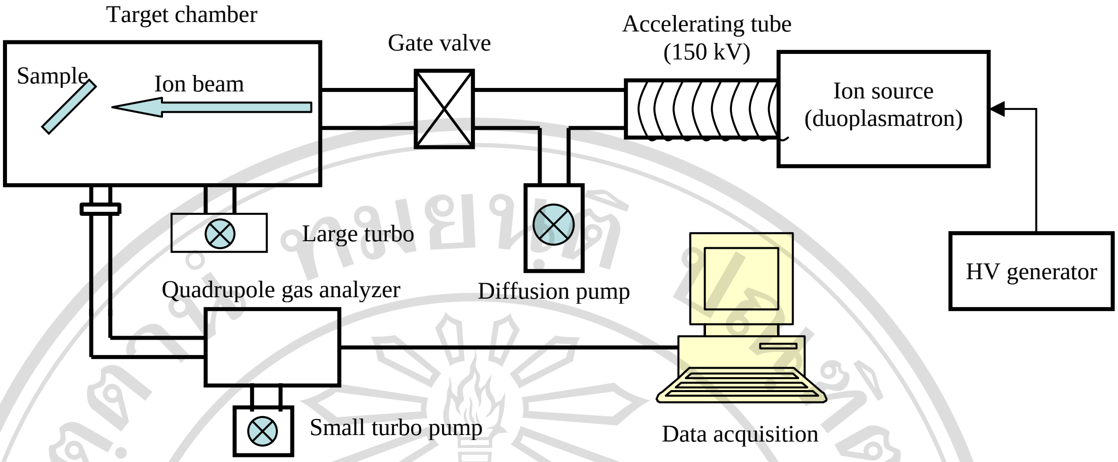

Figure 4.11 Schematic diagram of the ion beam sputtering process.

Figure 4.12 CMU2 heavy ion-implantation facility at Chiang Mai University.

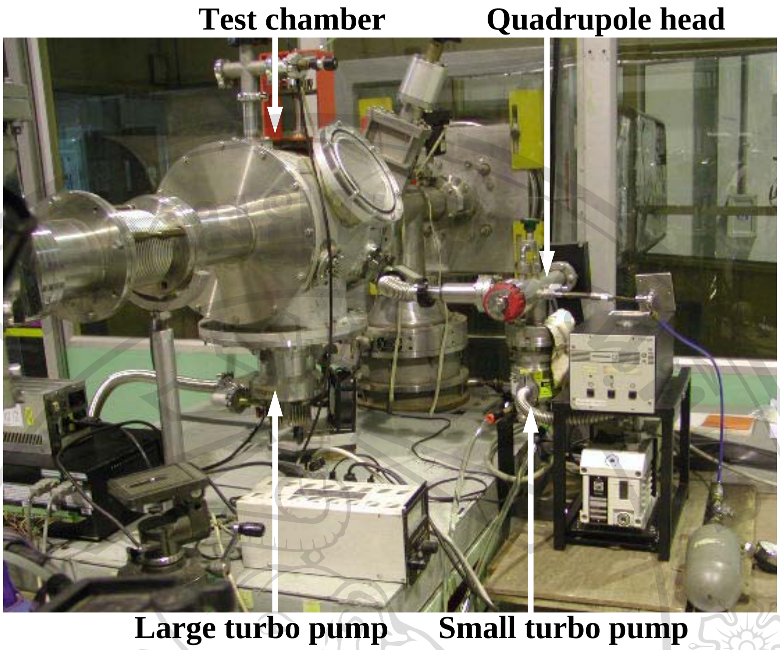

Figure 4.13 Installation of quadrupole gas analyzer to target chamber.

4.8 Mass spectrum

The fundamental operation of the quadrupole gas analyzer is basically a mass spectrometer. The mass spectrum is shown in a graph of partial pressure versus mass to charge ratio (m/z). Figure 4.14 shows the mass spectrum of nitrogen and it has a nominal mass of 28 amu. The molecule of nitrogen is composed of only two atoms; its mass spectrum is very simple. The molecular ion (N_2^+) is also the base peak at m/z = 28, and the only fragment ion is N^+ having an m/z = 14. Figure 4.15 shows the mass spectrum of carbon dioxide and it has a nominal mass of 44 amu. A molecule of carbon dioxide is composed of only three atoms. The molecular ion (CO^{2+}) is also the base peak at m/z = 44, and the fragment ions are CO^+ (m/z = 28), O^+ (m/z = 16) and C^+ (m/z = 12).

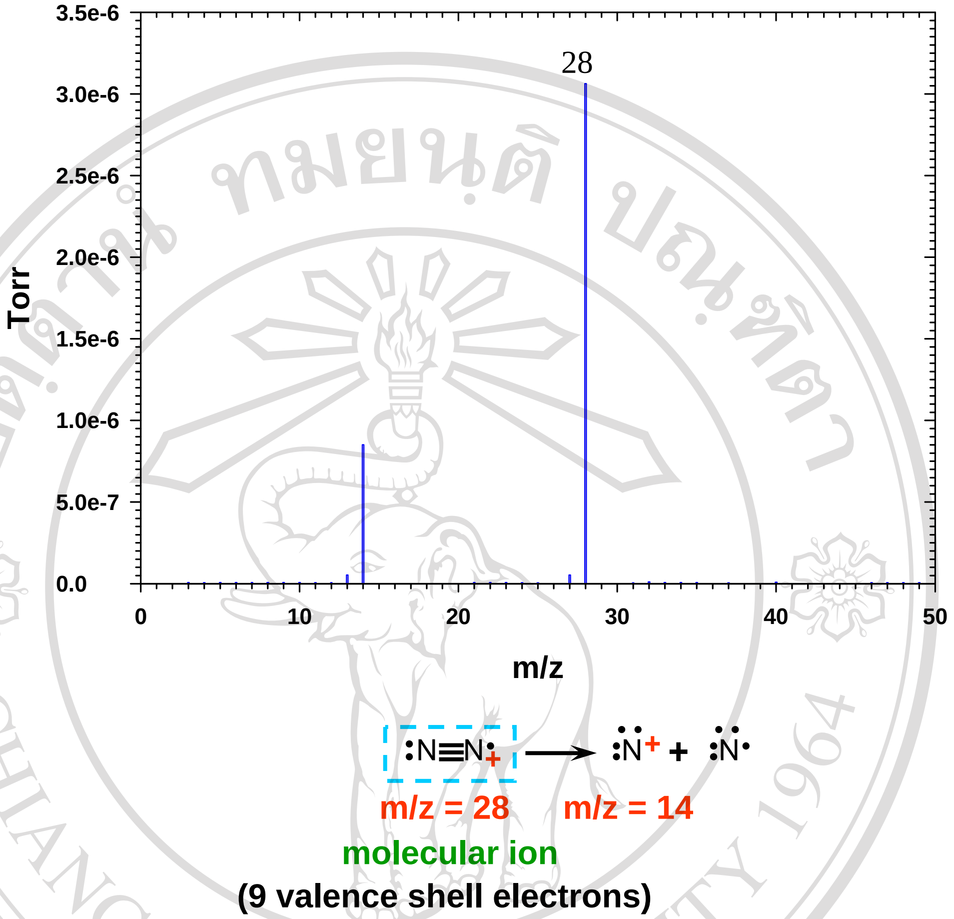

Figure 4.14 Mass spectrum of nitrogen and diagram of fragmentation.

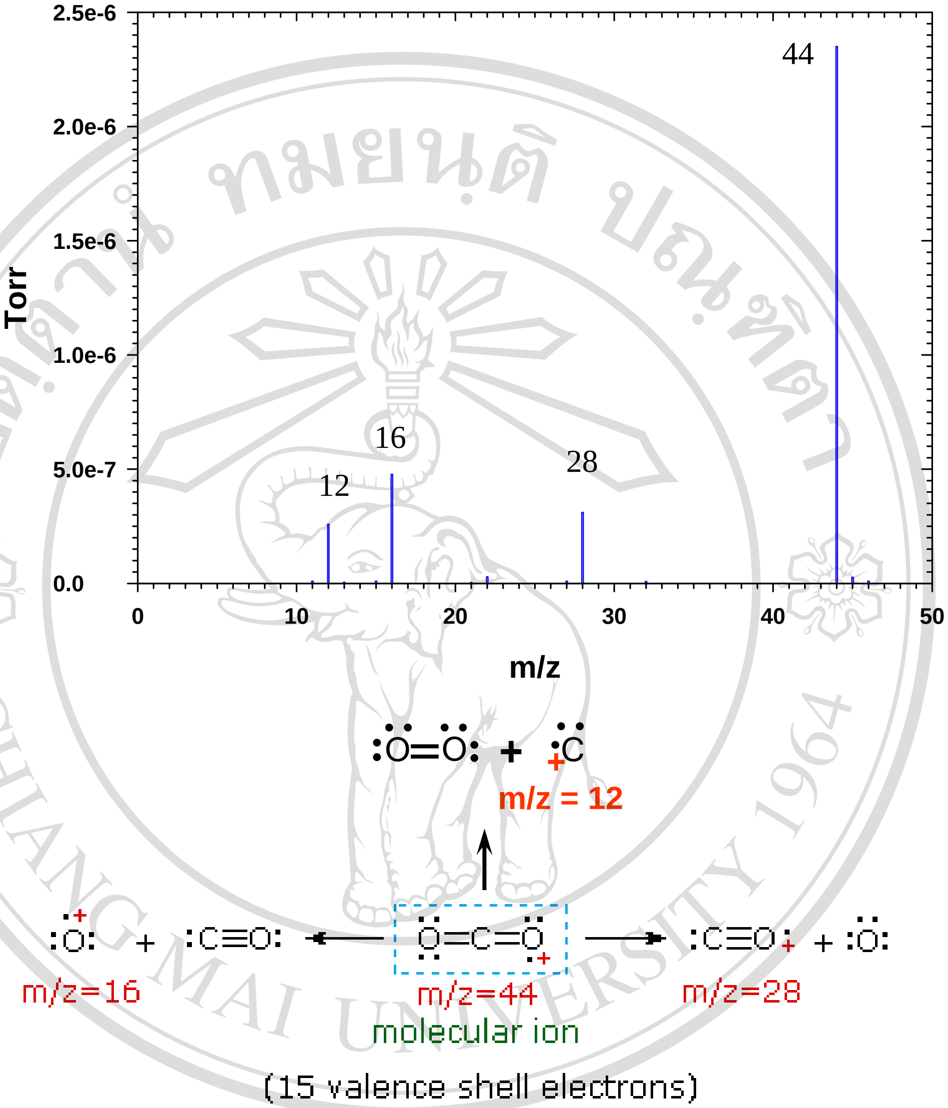

Figure 4.15 Mass spectrum of carbon dioxide and diagram of fragmentation.

The mass spectrum of vacuum chamber is shown in Figure 4.16. This scan from m/z = 1 to 60, shows some gases commonly present in vacuum chamber. There are many peaks, but they are caused mainly by seven species. Hydrogen (H_2^+) is at 2. Water gives primary peaks at 16, 17 and 18 due to the species O^+, HO^+ and H_2O^+. The smaller peaks at 19 and 20 are due to ^{18}O which is naturally present at 0.2 %. Nitrogen is at 28 and also causes the peaks at 14 by atomic N^+ and the doubly ionized N^{2+}. Molecular oxygen shows a peak at 32. Argon shows a peak at 40. Carbon dioxide (CO_2^+) shows a peak at 44 and peaks for C^+ at 12. Table 3.5 shows mass-to-charge ratios (m/z) of argon, nitrogen, oxygen, carbon dioxide, water vapor and hydrogen. The peaks at m/z 39, 41, 43, 55 and 57 are caused by mechanical pump oil back streaming into the vacuum chamber as shown in Figure 4.17.

The mass spectrum of each sample which is bombarded with the nitrogen beam at 30 keV is shown in Figure 4.18 – 4.21. Figure 4.18 shows the mass spectrum of carbon. This spectrum has no peak at 12 which is the peak of C^+. Figure 4.19 shows the mass spectrum of plastic scintillator. The mostly common atoms in plastic scintillator are carbon and hydrogen (H/C = 1.104). From the mass spectrum, there is only a molecular peak of H_2^+ at 2. Figure 4.20 shows the mass spectrum of SiO_2. There are two peaks of oxygen at 32 and 16. Figure 4.21 shows the mass spectrum of dry onion skin cell wall. There are peaks of hydrogen and oxygen. The peak of water is higher than other samples because of too much water in the onion cells.

Table 4.5 List of mass to charge ratio (m/z).

Gas	Ion	Mass to Charge (m/z)
Argon	Ar^+	40
	Ar^{+2}	20
	Ar^{+3}	13.3
Nitrogen	N_2^+	28
	N^+	14
Oxygen	O_2^+	32
	O^+	16
Carbon dioxide	CO_2^+	44
	CO^+	28
	O^+	16
	C^+	12
Water vapor	H_2O^+	18
	OH^+	17
Hydrogen	H_2^+	2

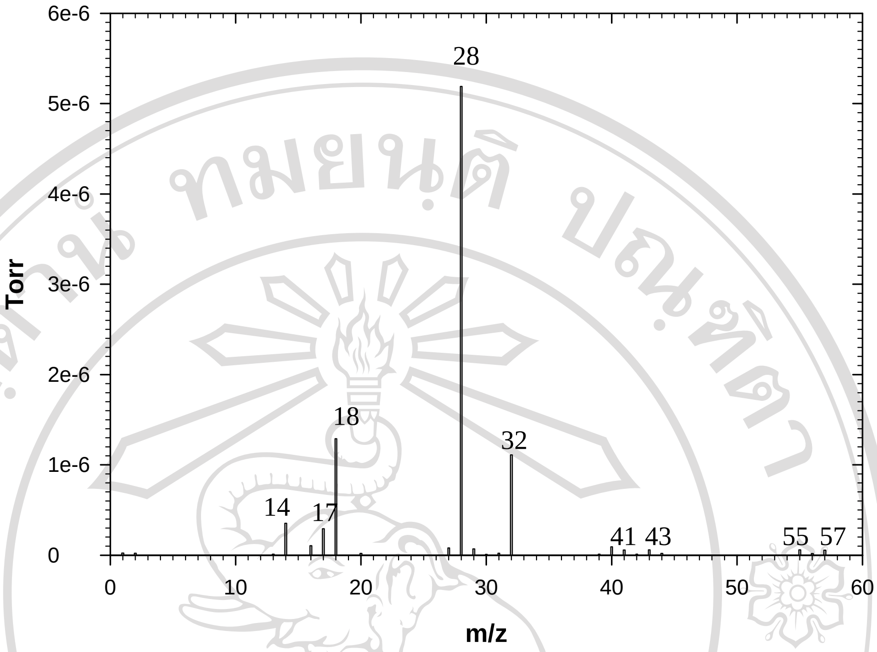

Figure 4.16 Mass spectrum of vacuum chamber.

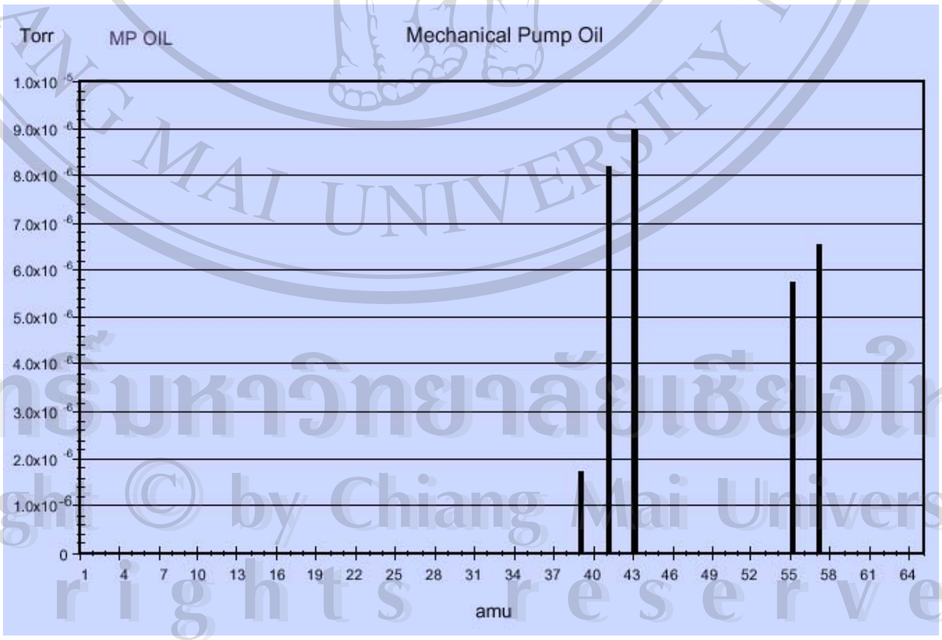

Figure 4.17 Mass spectrum of mechanic pump oil (Stanford Research Systems, No date).

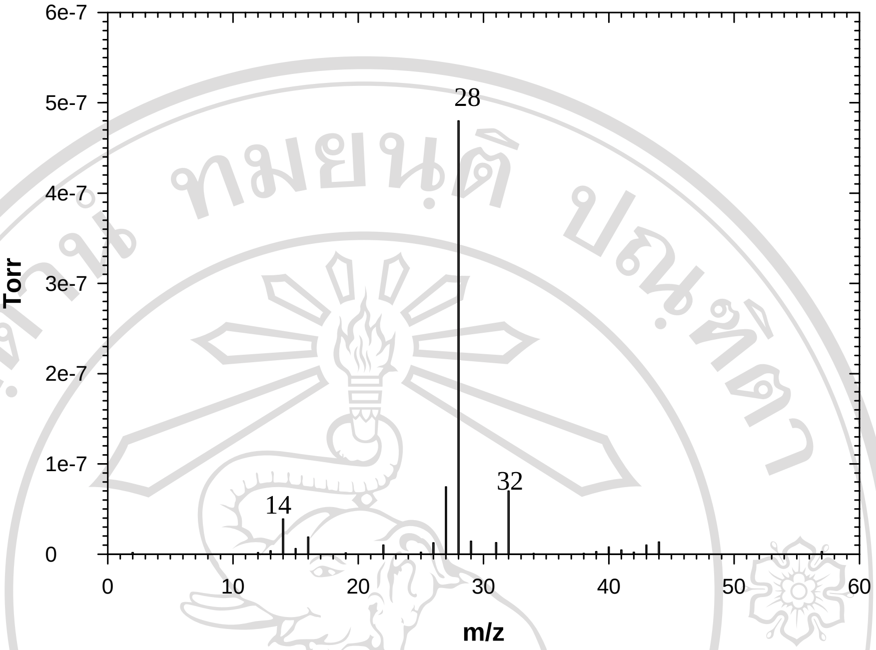

Figure 4.18 Mass spectrum of carbon.

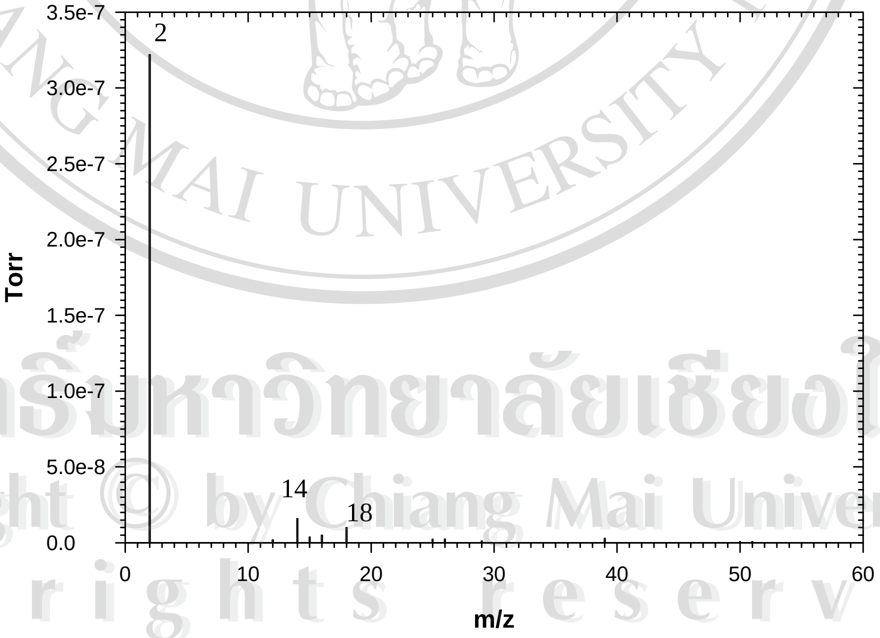

Figure 4.19 Mass spectrum of plastic scintillator.

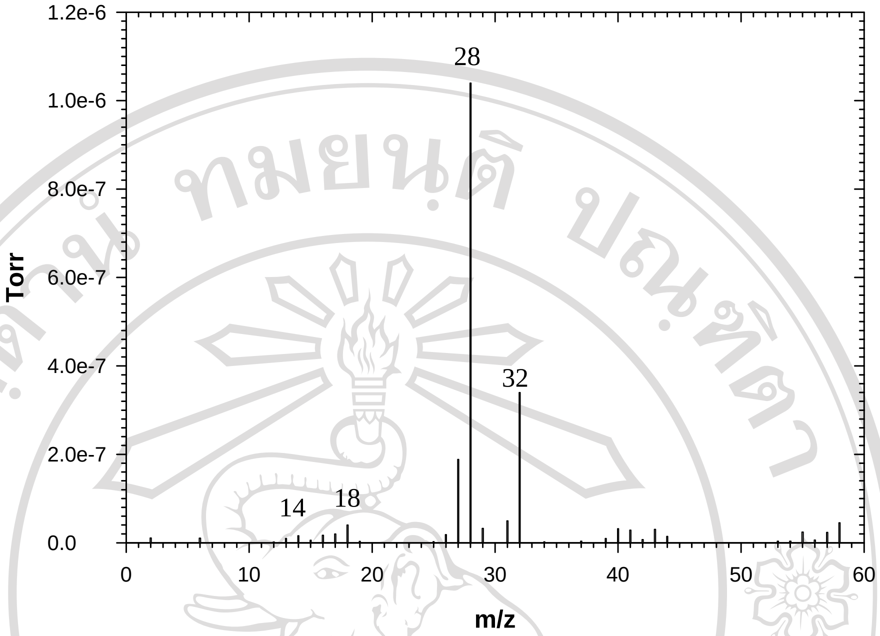

Figure 4.20 Mass spectrum of SiO_2.

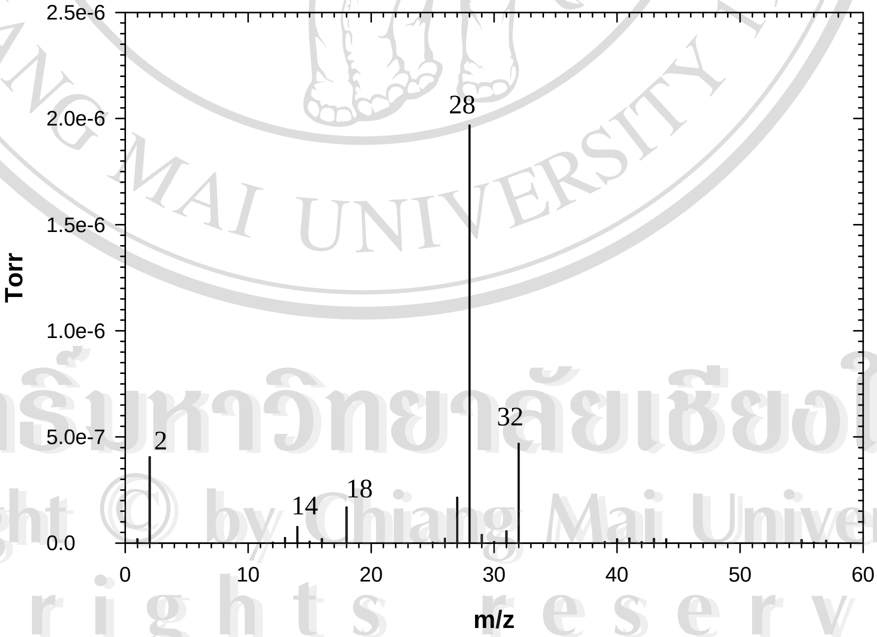

Figure 4.21 Mass spectrum of onion cell.