Radiation Environmental Safety and Health

Application of ICPMS, AAS, IC, NAA for environmental study

Malaysian Nuclear Agency
Bangi, Selangor

10-14 Ogos 2015

Application of ICPMS, AAS, IC, NAA for environmental study

- CONTENT
- Introduction: Analytical chemistry, Purpose of chemical analysis, Type of Chemical analysis, units of concentration, Accuracy and Precision etc

- PART I –non nuclear technique
- ICPMS, AAS, IC

- PART II – nuclear technique
- Measurement of Ambient Emission – Coal dust, road dust
- Measurement of Ambient Air -

"Characterization and source apportionment of particulate pollution in Klang Valley, Kuala Lumpur: A long term study between 2002-2011"

INTRODUCTION

- What is analytical chemistry?

- Analytical chemistry deals with separating, identifying and quantifying the amounts of the component of an analyte.

- Analyte: the component(s) of a sample that are to be determined.

- Several areas of analytical chemistry: Clinical analysis, pharmaceutical analysis, environmental analysis, forensic analysis, industrial quality control

- Purpose of chemical analysis?
- Process/quality control
- Monitoring/regulatory
- Validation of test methods/procedures
- Research- related to origin, sources, producer, impacts

- Type of Chemical analysis:
- Qualitative analysis: detection for presence of a component in a sample - by colour, smell, chemical reaction
- Quantitative analysis: quantify the concentration of an analyte in sample – gravimetry, titrimetry, spectrometry, instrumental methods.
- On the basis of sample size, analytical methods are classified as: macro(0.1g), semi macro(0.01-0.1), micro(<0.001g) and trace analysis.

- Common materials:
- Single/mixture of elements: metals, alloys, silverwares,
- Organic: plant materials, animal tissues, polymers, fats, petroleum
- Composite/mixture of minerals: ceramics, glass, cements, rocks
- Inorganic: salts, mineral acids,
- Gas/mixture of gases
- Environmental sample: air filter, water, soil, sediment

- Units of concentration
- Percent concentration (parts per hundred)
- Weight percent(w/w) = [weight solute/weight solution] x 100 %
- Volume percent(v/v) = [volume solute/vol. solution] x 100 %
- Weight/volume percent(w/v) = [weight sol./vol. soln] x 100 %

- 1% = 10000 ppm

- ppm: [weight of substance/weight of solution] $x10^6$
- 1 ppm = 1mg/L, 1ug/ml, 1 ug/g

- ppb: [weight of substance/weight of solution] $x10^9$
- 1 ppb = 1ug/L, 1ng/ml, 1ng/g

- Steps of analysis:
- Sampling
- Sample preparation (physical treatment): drying, crushing, cutting, pulverisation, filtration etc
- Sample preparation (chemical treatment): ashing, digestion, leaching
- Preparation of standard
- Measurement
- Calculation: calculator, computer
- Reporting: QC, statistical analysis

PART I –non nuclear technique
ICPMS, AAS, IC

Inductively Coupled Plasma Mass Spectrometer (ICP-MS)

- Definition
- Analytical technique to determine elements using mass spectrometry from ions generated by ICP

- Mass spectroscopy
- Separation of ion according to their mass and measurement of the mass of individual atoms making up a given material

ICP-MS ELAN 6000

Fig 1: ICP-MS ELAN 6000

ICP-MS ELAN 6000

- Components of ELAN ICP-MS system

1. Sample introduction system:
   - peristaltic pump
   - nebulizer
   - spray chamber
   - plasma torch and
   - injector

ICP-MS ELAN 6000

2. Ionization Source: RF Generator

- major part of the
- function: to convert AC power to RF power that is used for sustaining the argon plasma
- Ion extraction: interface vacuum
- Ion focusing system: lens assembly

ICP-MS ELAN 6000

3. ICP Torch
   - the region where plasma is formed by RF power

4. Mass filter: Quadrupole
   - Ion detection System: ETP detector
   - Control Software

ICP-MS ELAN 6000

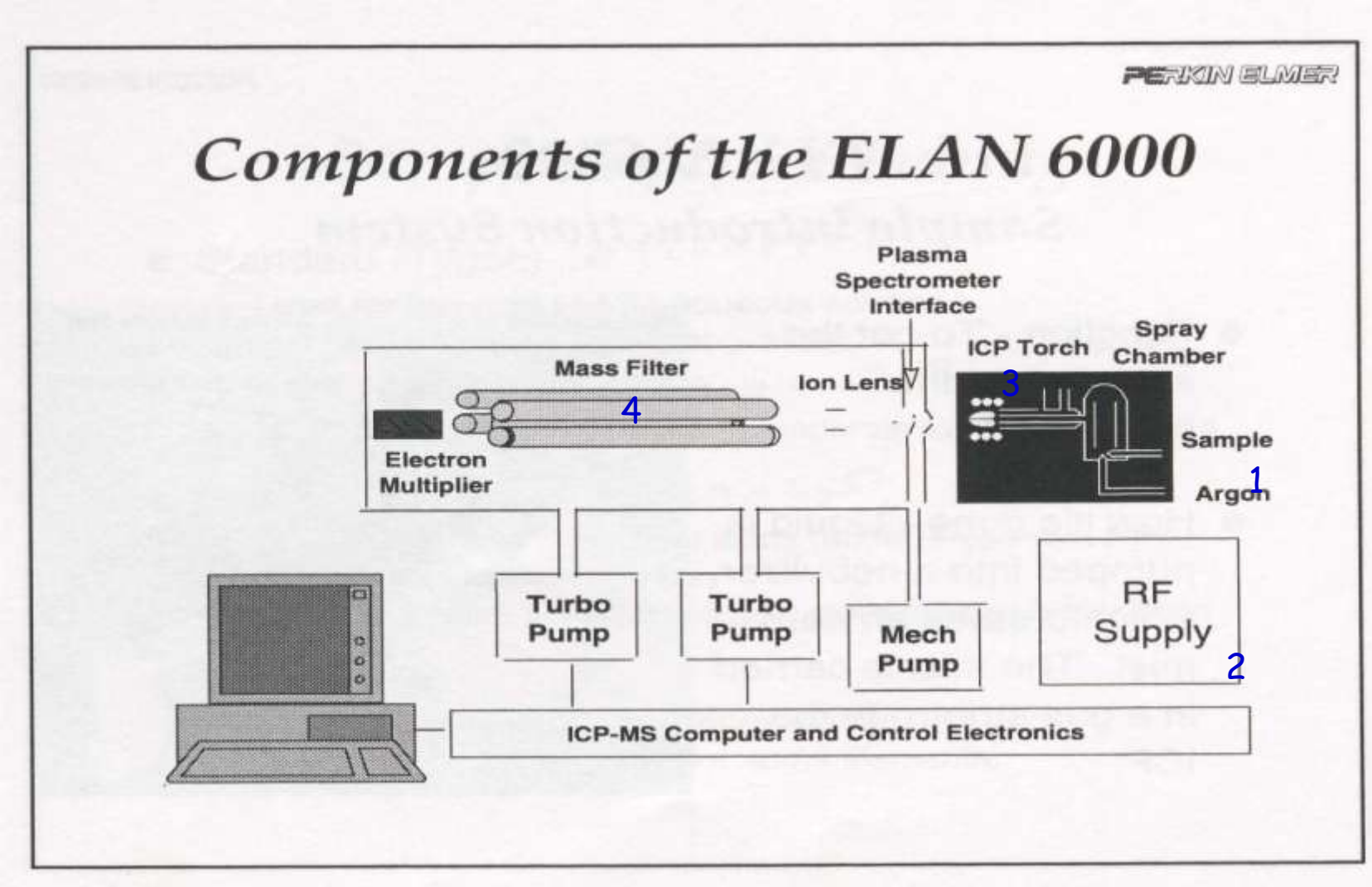
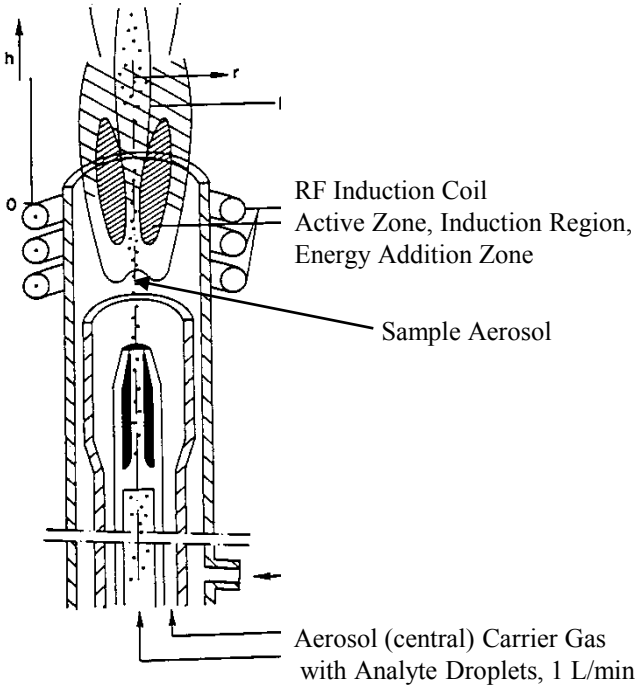


Fig 2: Components of ICP-MS ELAN 6000

ICP-MS ELAN 6000

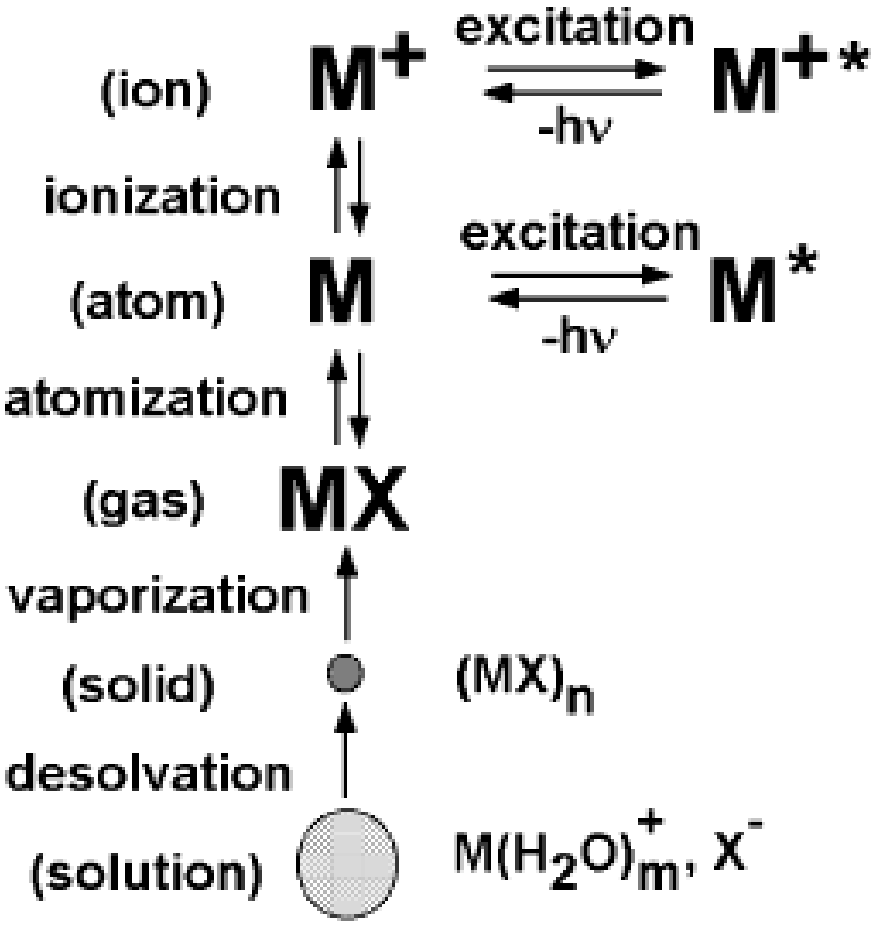
- What is Plasma?
  - Formed at ICP torch by RF power
- ICP Torch
  - quartz torch surrounded by copper induction coil
  - RF energy is supplied to the coil and inductively heats the argon gas to approx. 10,000°C

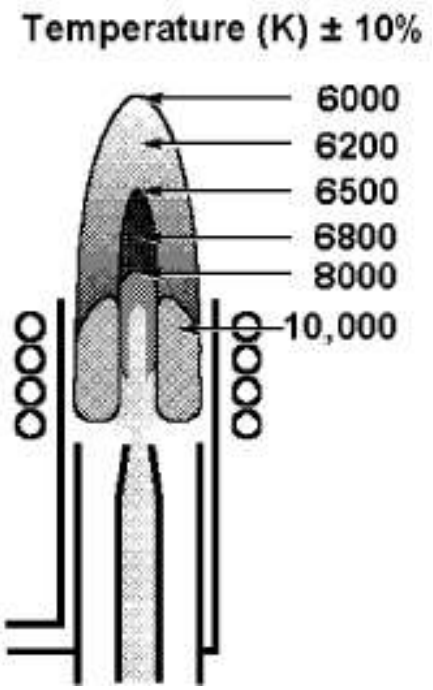
- When the gas heated at temperature 10,000°C it turns into plasma of positive ions and electrons (in approx. equal concentration)



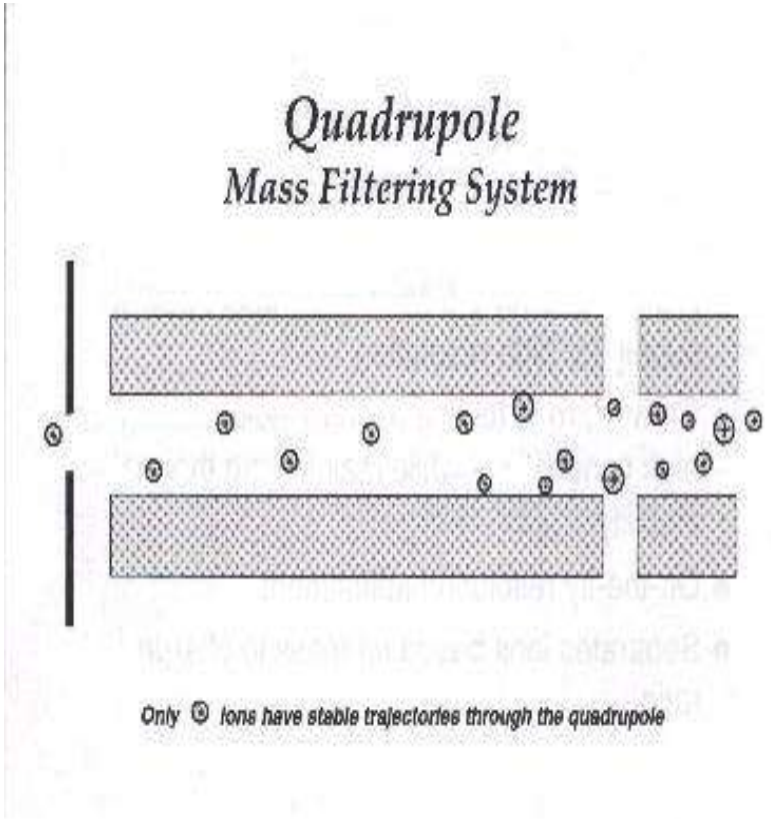
Processes in ICP plasma

- Most elements 90% ionized at 6000°C , the processes involve:
  Heat from 6000°C ICP dries aerosol, then atomize and ionize the components of the sample





- Processes in quadrupole (Mass filter)
  - four parallel conductive rods (ceramic) that operate in vacuum
  - mass filtering system which separates ions based on mass to charge ratio.
  - electro-magnetic field of the quadrupole rods allow only ions of particular mass can pass through the spectrometer.
  - ions leaving the mass filter will be counted at the detector



ICP-MS ELAN 6000

- Advantage of the ICPMS technique
  -Rapid multi-element quantitative analysis, 60-70 elements
  - Very low detection limit: most element <0.01ppb
  - Semi quantitative analysis (total quant)
  - Isotopic analysis
    the total number of isotope of an element determine the number of peaks in its mass spectrum

ICP-MS ELAN 6000

e.g: Element	Isotope masses	Abundance(%)
Al	27	100
Cu	63, 65	69, 31
Fe	54, 56, 57, 58	5.8, 91.7, 2.2, 0.28
Pb	206, 207, 208	24, 22, 52

- mass spectrum of Cu consist of 2 peaks
- mass spectrum of Fe consist of 4 peaks

Atomic Absorption Spectrometer (AAS)

- AAS Aanalyst 800
  - Flame AAS
  - Graphite furnance AAS
  - FIAS
- Principle:
  - An analytical technique to determine elements concentration in solution of the unknown sample by measurement of absorbed energy (at specific resonance wavelength) by free atoms

AAS AAnalyst 800

Fig 3: AAS AAnalyst 800

AAS AAnalyst 800

- Basic components of the system
  - Light source: hollow cathode lamp – made of the element to be determined
  - Absorption cell : flame, graphite furnace, FIAS cell
  - Monochromator (lens system): disperses the light and the specific wavelength of light
  - Detector: Photomultiplier, solid state detector
  - Computer

AAS AAnalyst 800

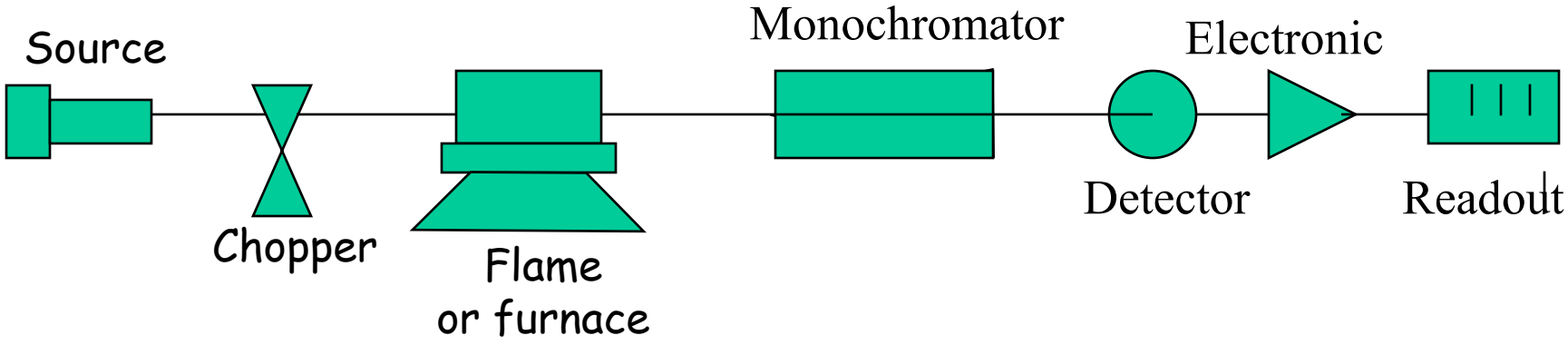
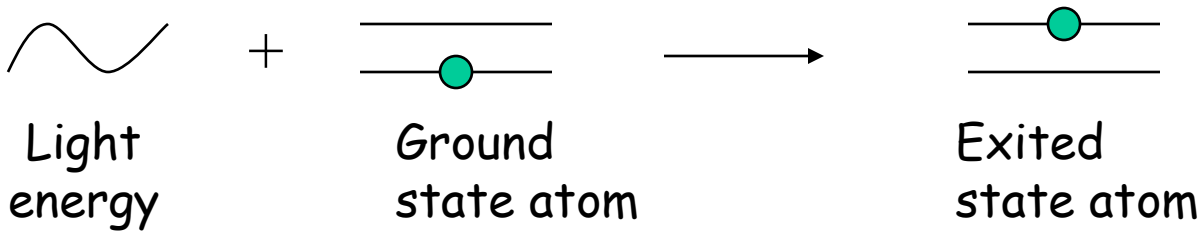


Fig 4: components of AAS AAnalyst 800 system

AAS AAnalyst 800

- Principle:



- ground state atom absorbs light energy of a specific wavelength as it enters the excited state

- quantitative determination of the amount of element can be made by measuring the amount of light absorbed.

AAS AAnalyst 800

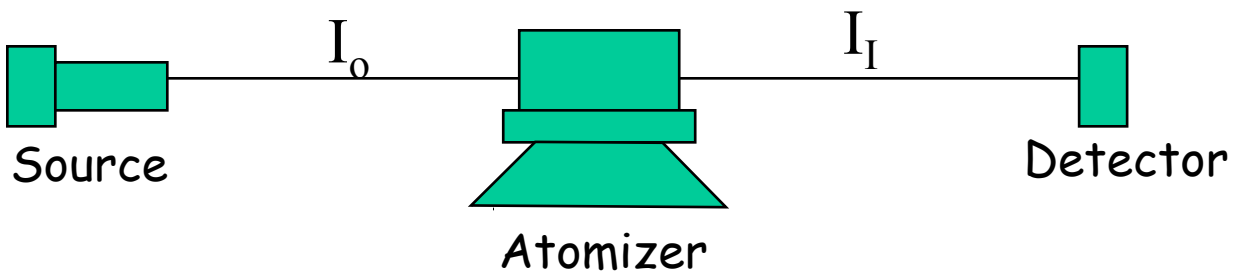


Fig 5: Principle of AAS

Absorbance, $A = \text{Log } I_0/I_1 = KLC_0$

Where I_0 = initial intensity,
I_1 = final intensity
K = absorption coefficient
L = path length
C = concentration of atom

HCL: with a cathode made of the analyte element

AAS AAnalyst 800

Process in a Flame:

- Sample in form of solution is introduced into the flame as an aerosol:

Evaporation - solution → fine particles

Atomization - vaporization of fine particles into atoms

$$MA \rightarrow M^o + A^o$$

Excitation - absorption of light by atoms

$$M^o \xrightarrow{+E} M^*$$

Ionization - $M^* \rightarrow M^+ + e^-$

Measurement of light intensity

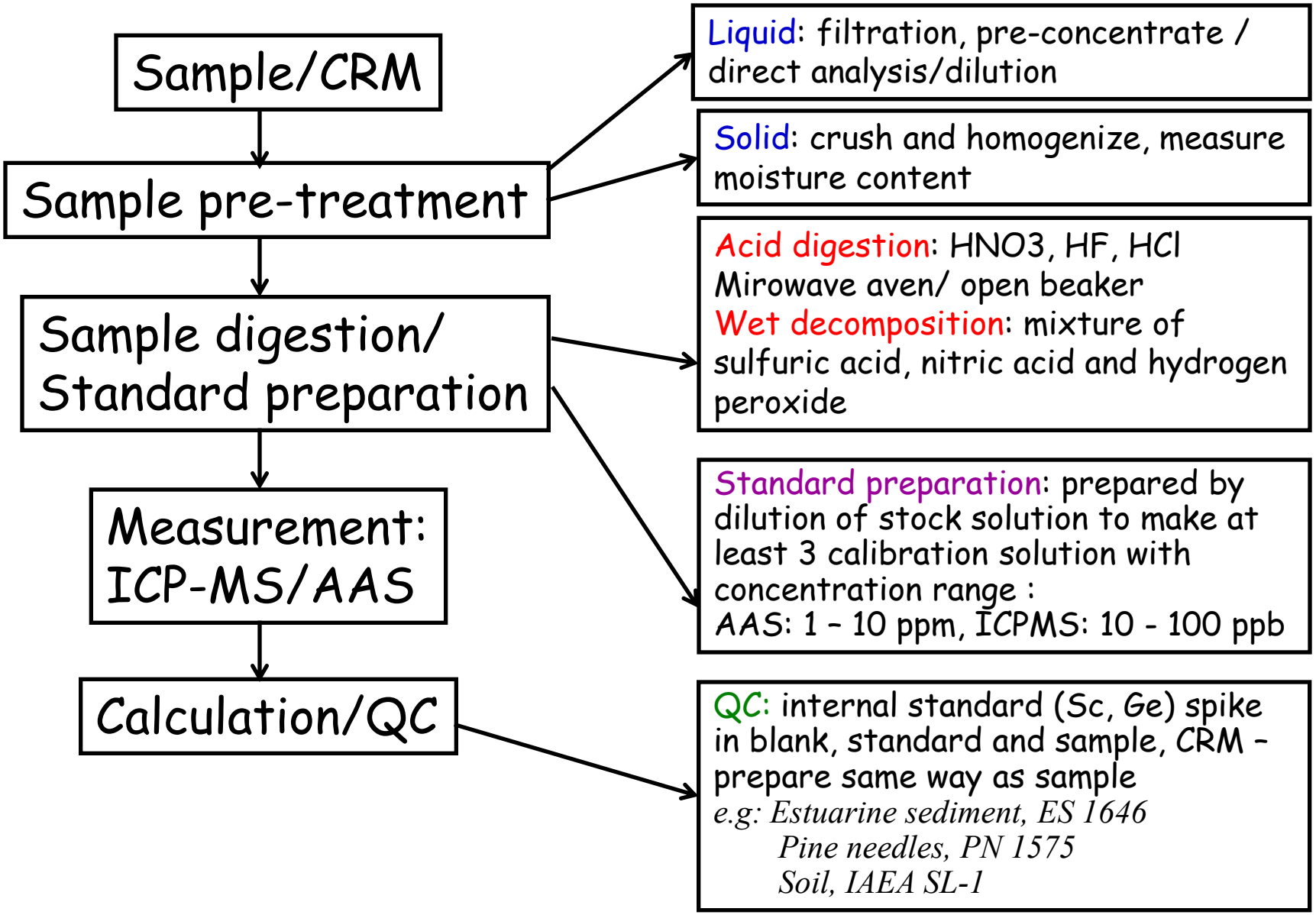


Fig 6: Steps in Analysis of Samples by ICPMS/AAS

Table 1. Comparison of AAS and ICP-MS techniques

Properties	AAS	ICP-MS
Multielemental capability	Yes (sequential)	Yes (rapid sequential)
Sample form	Liquid/solution	Liquid/solution
Detection limit	ppm (flame AAS) ppb (flameless AAS)	ppb -ppt
Speed of analysis	Medium-fast	Fast
Light source	Yes (hollow cathode lamp)	No
Excitation medium	Flame	Plasma
Cost of analysis	Medium	High
Concept of measurement	Absorption of light	No of ions

Ion Chromatography

Ion Chromatography – DX500

Chromatography – Based on differential distribution of the sample components between two phases

Stationary phase: Remains fixed in the system – ion-exchange resin

Mobile phase: percolates over the surface of the fixed phase – eluent

Ion Chromatography –DX 500

Fig 7: Ion Chromatography –DX 500

Ion Chromatography –DX 500

Major components of the system:

Pump: Eluent delivery system to blend and pump eluent and control the flow rate

Injector: To introduce sample into the eluent stream

Column: Guard column

Analytical column/separator column

Suppressor: reduce the background conductivity enhance the peak area and sensitivity

Detector: Analyte (anion/cation) detection

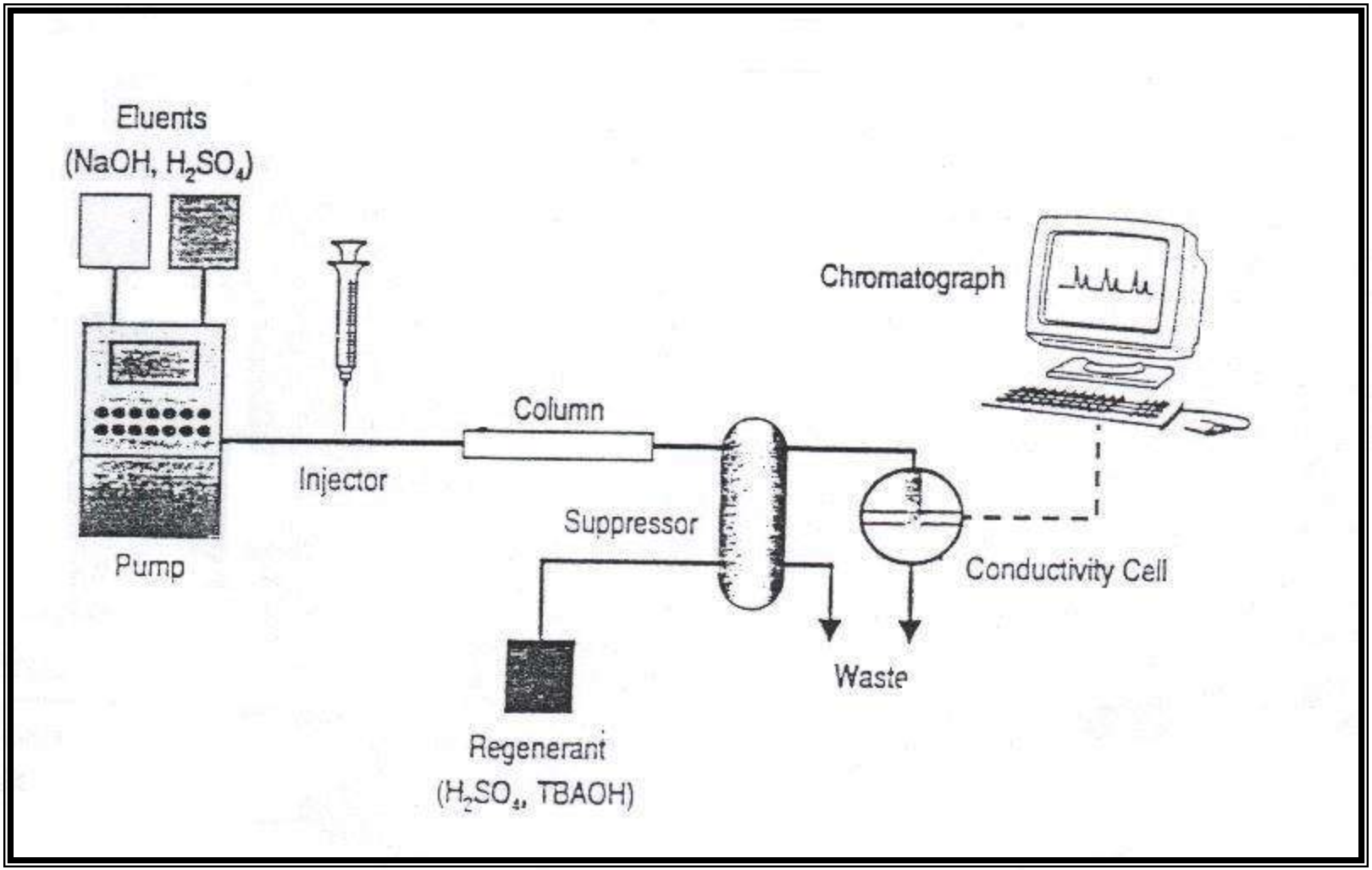


Fig 8: Components of Ion Chromatography

Ion Chromatography –DX 500

- Ion exchange separation

- Based on the relative affinity of the analyte ion in competition with the eluent ion
- The greater the affinity, the longer the retention time
- Eluent: the mobile phase used to elute components from stationary phase

  Anion eluent: e.g borate, hydroxide, bicarbonate
  Cation eluent: e.g HCl, HNO3, MSA (methane sulfonic acid)

- Ion exchange separation

Elution sequence for common anions:

Shorter elution time

←

$F^- < Cl^- < NO_2^- < Br^- < NO_3^- < PO_4^{2-} < SO_4^{2-}$

→

Stronger affinity

Elution sequence for common cations:

Shorter elution time

←

$Li^+ < Na^+ < NH_4^+ < K^+ < Mg^{2+} < Ca^{2+} < Sr^{2+}$

→

Stronger affinity

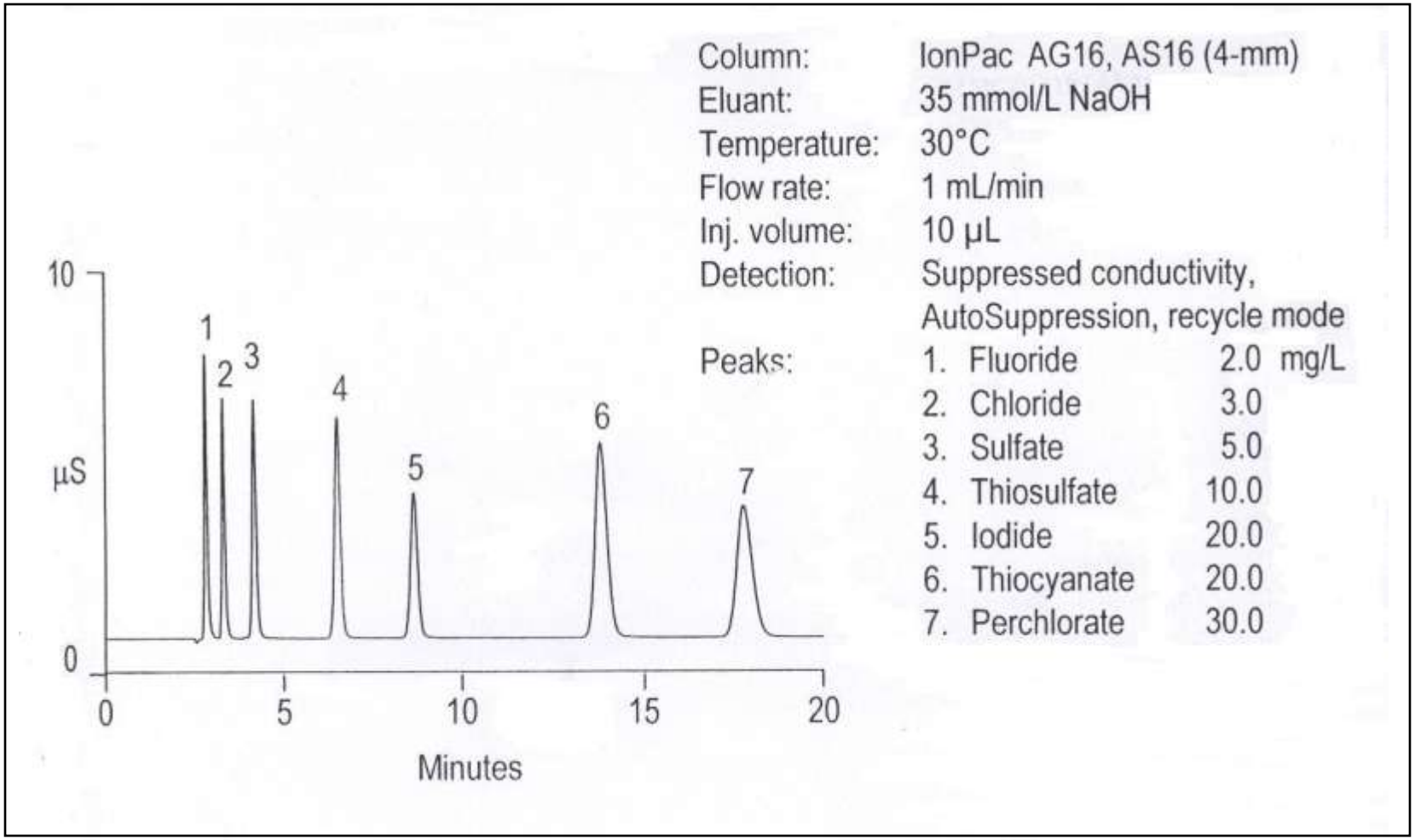


Fig 9: Chromatogram of Ion Chromatography

Ion Chromatography –DX 500

Table 2. Sample and sample preparation for IC

Sample	Preparation
Natural water	Filter
Drinking water	Filter
Waste water	Filter
Air dust on filter	Dissolved in deionized water and filter
Solid sample	Dissolved in deionized water and filter

- Standard preparation
- Standard solution is prepared from the mix calibration solution (composition of the solution must be close to the anticipated to the samples)
- The solution diluted to make different concentration of working solution e.g 1, 2, 5, 10 ppm
- Data obtained is plotted (peak area Vs concentration)

- Calculation of sample concentration
- Direct comparison of the peak area
- Amount of the analyte in the unknown sample is compared to a known solution (standard) of the same substances

PART II – nuclear technique Neutron Activation Analysis (NAA)

Neutron Activation Analysis (NAA)

- What is NAA?
- The technique involves a nuclear reaction between nucleus atom of sample and neutron when sample is exposed for a period of time to a uniform flux of neutron. The product is radioactive nuclides.

- The radioactive products (gamma ray emitters) are identified by the energy of their gamma ray photo peaks in the energy spectrum of the activated samples.

- Amount of elements is proportional to the intensity of the characteristic gamma rays.

NAA technique: Production of a radioactive isotope in nuclear reactor (n, γ reaction)

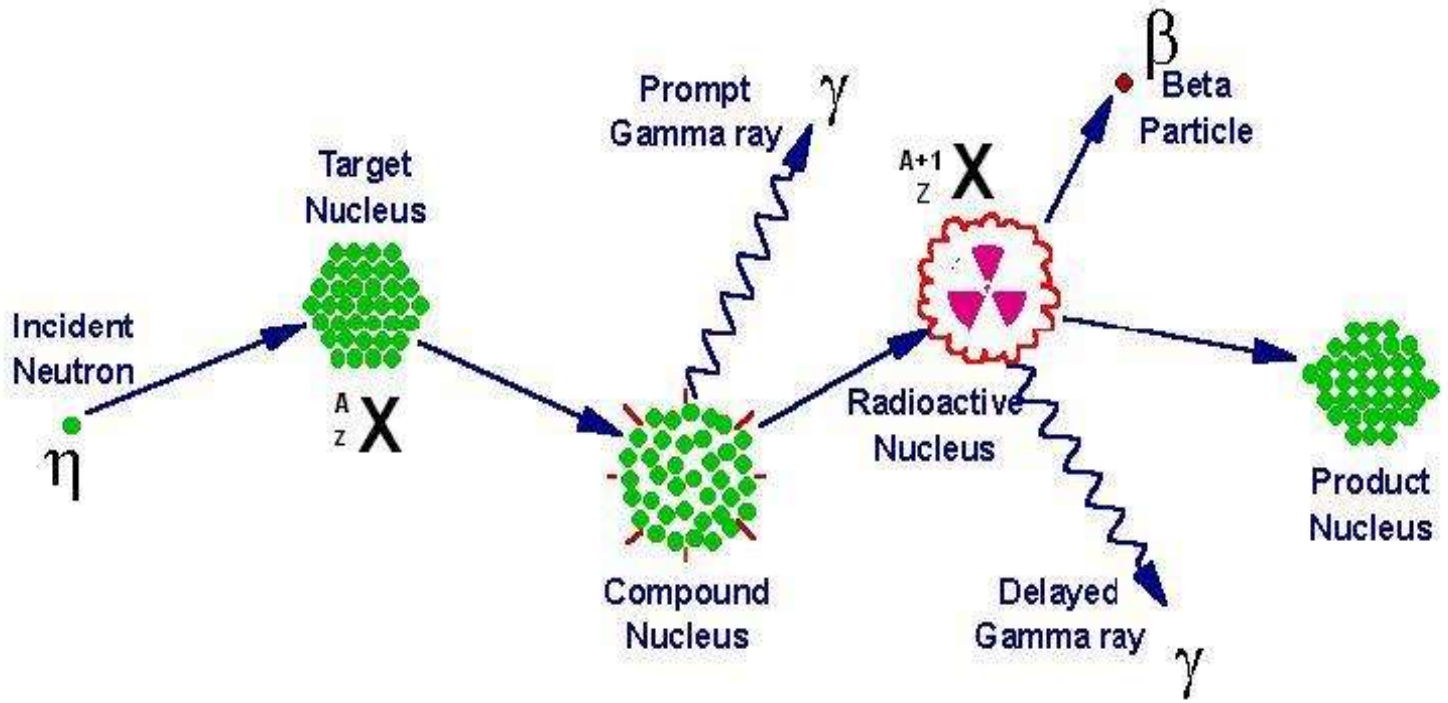


Fig 10: Principle of NAA technique

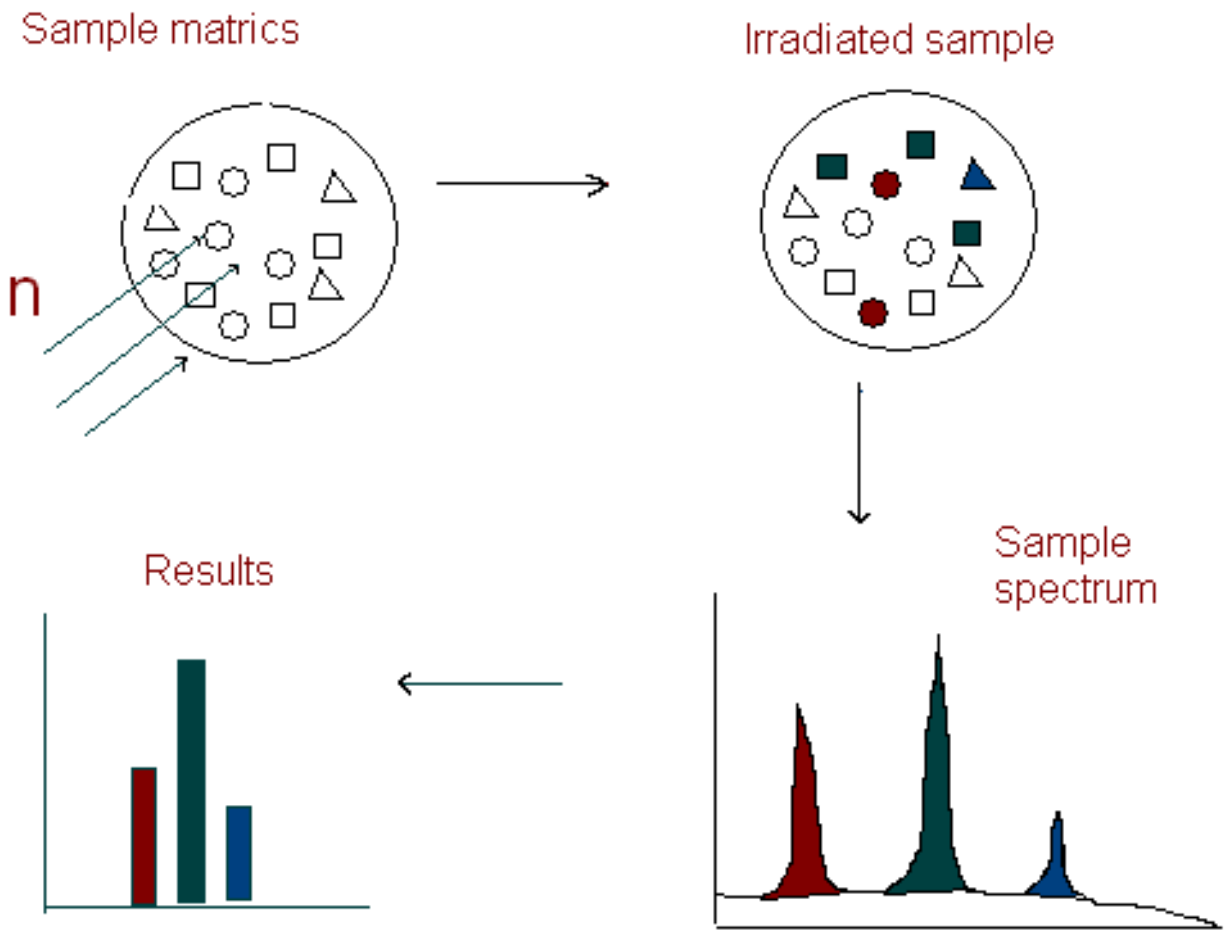


Fig 11. NAA: Schematic diagram

Facilities for NAA

- Neutron Source
  Triga Mk II Reactor: 1MW
  Rotary Rack: 1 x 10^{12} $n.cm^{-2}s^{-1}$
  PTS: 2 x 10^{12} $n.cm^{-2}s^{-1}$

- Detector system
  Gamma spectrometer (Hp(Ge) detector, amplifier, HV , spectrum analysis softwares (gamma vision and microsampo)

- NAA can be employed in two different forms:

- Purely Instrumental form (INAA)

  The irradiated samples are counted on the gamma ray spectrometer after suitable decay time, without prior chemical treatment.

  - Non-destructive method, minimum contamination
  - Simple: no chemistry is performed on the sample, no blank reagent

- Radiochemical separation (RNAA)

  Destruction of sample after irradiation

  Carrier amount of element of interest is added to the activated sample for high recovery of macro chemical separation

  Counting of separated portion on gamma detector

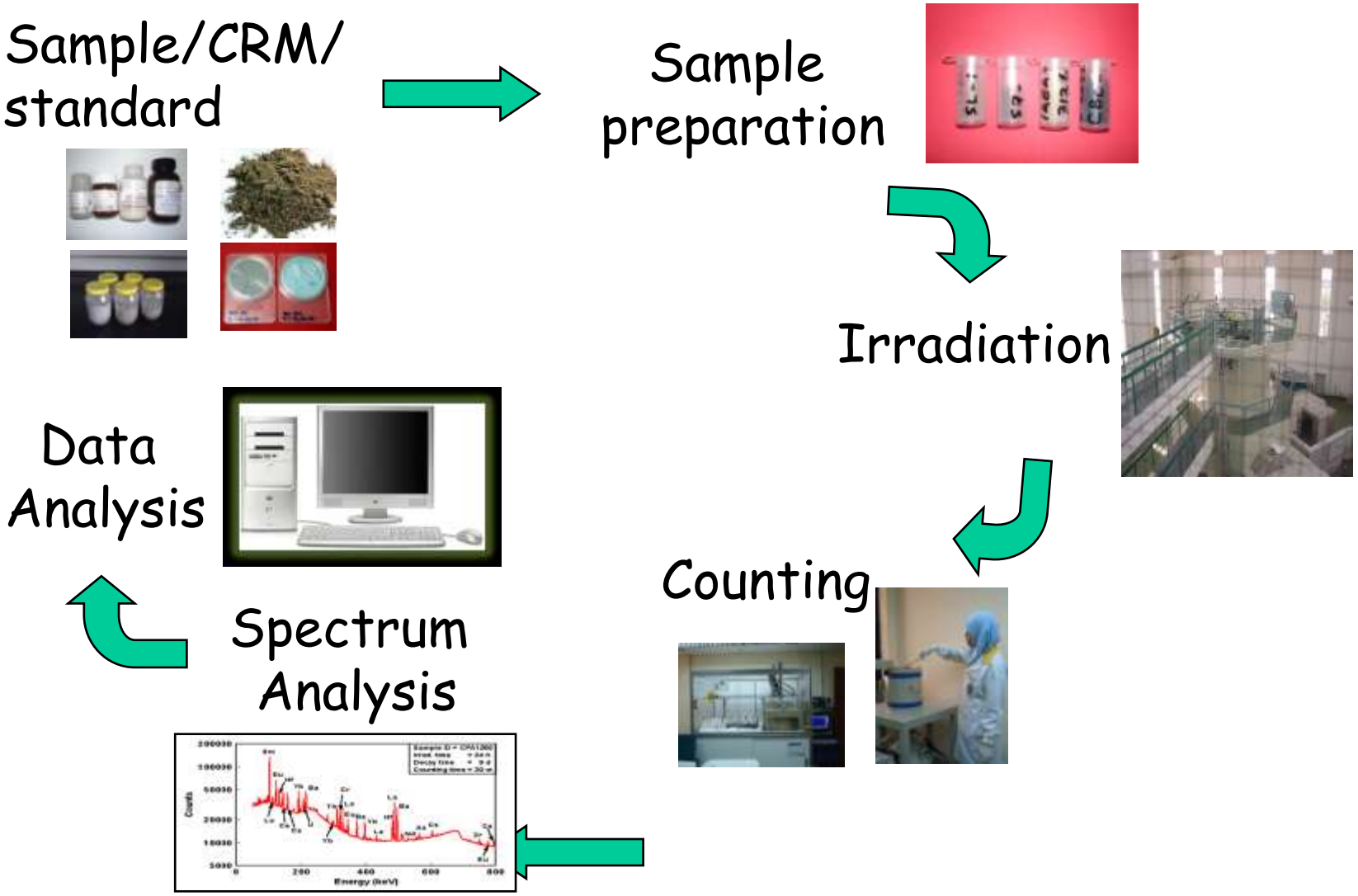


Fig 12. Steps in NAA (INAA)

Short Irradiation process

Standard/sample/
CRM
↓
Irradiation
1-5 minute
ϕ: 1 x 10^{12} n.$cm^{-2}s^{-1}$
↓
Decay time &Measurement – 1st count
(10-20 minute, 5 min)
Al, Ti, Mg, Mn, V, Ca,
↓
Decay time &Measurement – 2nd count
24hrs, 1200–3600s)
K, Na

Long Irradiation process

Standard/sample/
CRM
↓
Irradiation
6 hrs
ϕ:1 x 10^{12} n.$cm^{-2}s^{-1}$
↓
Decay time &Measurement – 1st count
(5-7 days, 3600-7200s)
As, Br, Au, La, U
↓
Decay time &Measurement – 2nd count
(20 -30 days, 3600-7200s)
Ba, Cr, Zn, Fe, Co, Sc

Table 3. Short irradiation procedure

Procedure	Elements	Nuclides	Half-life	γ-ray Energies (keV)
1. Irradiation 1-5 min	Al	^{28}Al	2.32 min	1779
	V	^{52}V	3.75 ”	1434
Cooling 10-20 min	Ti	^{51}Ti	5.79 ”	320
Counting 5 min	Ca	^{49}Ca	8.80 ”	3083
	Mg	^{27}Mg	9.46 ”	1014
	Br	^{80}Br	17.60 ”	617
	I	^{12}8I	25.00 ”	443
	Cl	^{38}Cl	37.32 ”	2168
	Ba	^{13}9Ba	1.38 hr	166
	Dy	^{165}Dy	2.32 ”	95
	Mn	^{56}Mn	2.58 ”	847, 1811
	Sr	^{87}Sr	2.83 ”	388
Cooling 24hrs	Eu	^{152m}Eu	9.20 hr	122
Counting 1200 – 3600s	K	^{42}K	12.40 ”	1525
	Ga	^{72}Ga	14.10 ”	834
	Na	^{24}Na	15.00 ”	1368, 2754

Table 4. Long irradiation procedure

Procedure	Elements	Nuclides	Half-life	γ-ray Energies (keV)
2. Irradiation 6-12 hr	W	^{187}W	24.00 hr	686
	As	^{75}As	26.40 ”	559
Cooling 3-5 days	Br	^{82}Br	32.40 ”	555,776
Counting 3600 – 7200s	La	^{140}La	40.20 ”	1596
	Sm	^{153}Sm	46.80 ”	103
	U	^{239}Np	2.35 days	228,278
	Au	^{198}Au	2.70 ”	412
	Sb	^{122}Sb	2.70 ”	564
	Yb	^{175}Yb	4.20 ”	396
	Lu	^{177}Lu	6.70 ”	208
	Nd	^{147}Nd	11.10 days	531
	Ba	^{131}Ba	12.00 ”	496
Cooling 20-30 days	Rb	^{86}Rb	18.70 ”	1077
Counting 3600 – 7200s	Th	^{233}Pa	27.00 ”	312
	Cr	^{51}Cr	27.80 ”	320
	Yb	^{169}Yb	32.00 ”	177,198
	Ce	^{141}Ce	32.50 ”	145
	Hf	^{181}Hf	42.50 ”	482
	Fe	^{59}Fe	45.10 ”	1099,1293
	Sb	^{124}Sb	60.90 ”	603
	Zr	^{95}Zr	65.50 ”	757
	Tb	^{160}Tb	72.10 ”	879
	Sc	^{46}Sc	83.80 ”	889
	Ta	^{182}Ta	115.00 ”	1121
	Zn	^{65}Zn	244.00 ”	1221
	Cs	^{134}Cs	2.05 yr	1116
	Co	^{60}Co	5.25 ”	796
	Eu	^{152}Eu	12.70 ”	1173,1332 122,1808

The Application of Neutron Activation Analysis (NAA) for Air pollution Study

- MEASUREMENT OF AMBIENT EMISSION
- Sample: Coal dust (41L/05-NAA/143)

- Emission from coal power plant
- Request: to measure all possible elements in the samples (esp toxic elements)
- Purpose of analysis: research
  (The were complaints from the people/residential area nearby on the production of their prawn fry and farm)
- The analysis of samples (by NAA) was combine with another method, ICP-MS

Table 5: Concentration of elements in coal dust

RESULT OF ANALYSIS

Elements	Coal – Lati	Coal - Banggala	Coal- Hunter Valley
Al (%)	0.97 ± 0.07	1.39 ± 0.04	1.63 ± 0.07
Ca (%)	0.57 ± 0.02	0.07 ± 0.05	0.08 ± 0.04
Fe (%)	0.67 ± 0.07	0.44 ± 0.04	0.45 ± 0.01
K (%)	0.18 ± 0.04	0.133 ± 0.004	0.12 ± 0.03
Mg (%)	0.05 ± 0.01	0.078 ± 0.002	0.031 ± 0.002
Na (%)	0.21 ± 0.01	0.054 ± 0.003	0.040 ± 0.001
Ti (%)	0.042 ± 0.003	0.12 ± 0.05	0.092 ± 0.006
As (ppm)	2.9 ± 0.4	1.1 ± 0.1	1.6 ± 0.1
B (ppm)	147 ± 10	26 ± 2	24 ± 2
Ba (ppm)	129 ± 7	97 ± 8	145 ± 40
Cd (ppm)	0.25 ± 0.05	0.30 ± 0.05	0.20 ± 0.05
Co (ppm)	2.1 ± 0.2	9.4 ± 0.2	6.1 ± 0.5
Cr (ppm)	8.2 ± 0.3	6.4 ± 1.4	4.5 ± 0.1
Cs (ppm)	1.37 ± 0.04	1.21 ± 0.05	0.81 ± 0.10
Cu (ppm)	9.5 ± 0.8	17.5 ±10.5	11.4 ± 1.0
Hg (ppm)	<0.2	<0.2	<0.2
Mn (ppm)	26.9 ± 0.9	50.3 ± 18.4	2.0 ± 0.2
Ni (ppm)	9.6 ± 1.0	9.2 ± 0.9	39.1 ± 1.3
Pb (ppm)	14.8 ± 1.3	16.3 ± 1.5	9.7 ± 0.8
Rb (ppm)	12.0 ± 1.3	10.9 ± 1.7	9.0 ± 1.8
Sb (ppm)	2.3 ± 0.03	0.75 ± 0.03	0.75 ± 0.10
Sc (ppm)	2.0 ± 0.2	3.80 ± 0.05	3.6 ± 0.1
Se (ppm)	<2	<2	<2
Th (ppm)	2.3 ± 0.3	<0.5	3.1 ± 0.3
U (ppm)	0.90 ± 0.17	0.90 ± 0.14	1.00 ± 0.07
V (ppm)	17.6 ± 0.5	37.8 ± 2.3	30.3 ± 8.5
Zn (ppm)	<10.0	21.2 ± 2.1	22.4 ± 2.8

The Application of Neutron Activation Analysis (NAA) for Air pollution Study

- MEASUREMENT OF AMBIENT EMISSION
- Sample: Road dust

(Shamsiah Abd Rahman, Mohd Suhaimi Hamzah, Md Suhaimi Elias, Wee Boon Siong, Nazaratul Ashifa Salim and Ezwiza Sanuri, Elemental determination and source apportionment of road dust in Klang Valley, Kuala Lumpur. *Japan Association of Activation Analysis 29 (2013), 29-44)*

The Application of Neutron Activation Analysis (NAA) for Air pollution Study

- Why road dust?
- Road dust is earthen material or dirt/particles that deposited on the road
- It is easily re-suspended back into the atmosphere esp during dry conditions with significant traffic or wind.
- Can contributes certain amount of trace elements (eg. Cd, Cu, Pb, Zn and Ni) into the atmosphere
- Freely inhaled by those traversing the streets and those residing within the area of the streets.

The Application of Neutron Activation Analysis (NAA) for Air pollution Study

- Objective of study:
- To identify the levels of heavy metal in road dust (NAA+ICP-MS)
- To identify sources of heavy metal contamination in road dust particles (Statistical method, factor analysis - statgraphic)
- Study area: Five different routes (R1, R2, R3, R4 and R5) of Klang Valley, Kuala Lumpur.
- Each route covers at least 50 Km of 6 to 7 areas including highway, residential area, business centre and industrial area.

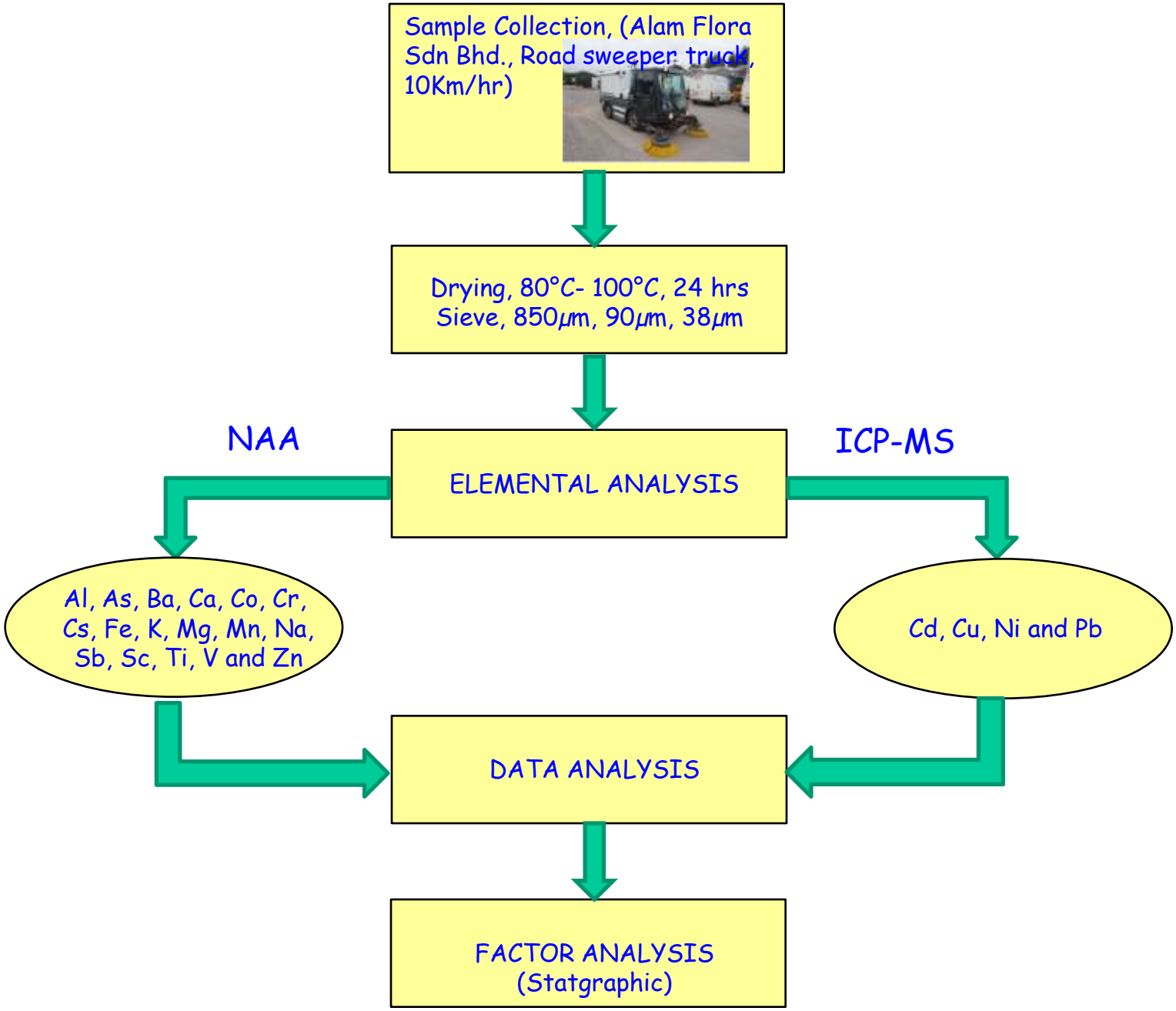


Fig 13: Flow chart for methodology

Table 6: Factor loading for Klang Valley road dust (R_{38} and R_{90})

Element	Factor Loading			
	F1	F2	F3	F4
Al	**0.939**	0.203	0.197	0.007
As	-0.113	**0.744**	**0.473**	0.009
Ca	**0.495**	-0.734	-0.295	-0.200
Cd	**0.349**	**0.328**	**0.820**	0.069
Cr	**0.484**	-0.324	**0.705**	0.260
Cu	0.017	-0.091	**0.868**	-0.052
Fe	0.037	-0.225	0.320	**0.876**
K	0.136	**0.956**	0.001	-0.192
Mn	**0.854**	0.257	0.140	-0.384
Na	-0.163	**0.926**	-0.226	-0.156
Ni	0.028	0.152	**0.925**	0.097
Pb	**0.408**	-0.116	**0.503**	-0.631
Sb	**0.831**	-0.443	-0.131	0.143
Ti	**0.851**	-0.345	0.222	-0.120
V	**0.745**	-0.591	0.197	0.029
Zn	**0.607**	-0.479	**0.517**	**0.320**
Eigenvalue	6.651	4.093	2.659	1.108
Var. (%)	41.567	25.584	16.617	6.926
	Industrial activities, tyre bearing wear and brake dust	Biomass combustion process	Electrical industrial emission, engine abrasion	Abrasion of vehicle wheels and tyres

Table 7: Factor loading for Klang Valley road dust (R_{850})

Element	Factor Loading			
	F1	F2	F3	F4
Al	-0.137	-0.180	**0.883**	-0.126
As	**0.347**	-0.227	**0.674**	0.267
Ca	0.265	**0.495**	-0.361	**0.652**
Cr	0.170	**0.651**	**0.490**	-0.167
Cu	**0.904**	0.091	-0.220	0.090
Fe	-0.452	-0.081	0.056	**0.816**
K	-0.656	0.050	**0.654**	0.063
Mg	-0.519	**0.630**	0.042	0.212
Mn	0.229	**0.886**	-0.018	0.238
Na	-0.035	0.348	**0.873**	-0.183
Ni	**0.818**	0.133	0.256	-0.456
Ti	**0.870**	0.084	-0.004	-0.009
V	0.163	**0.859**	-0.157	-0.180
Zn	**0.767**	**0.414**	0.129	-0.203
Eigenvalue	4.596	3.120	2.716	1.221
Var. (%)	32.825	22.283	19.401	8.719
	Brake dust and engine abrasion	Oil combustion and construction activity	domestic industrial and biomass combustion	Local soil

The Application of Neutron Activation Analysis (NAA) for Air pollution Study

- INTRODUCTION
- IAEA/RCA project – Nuclear Malaysia which was carried out in Klang Valley, Kuala Lumpur since 1997 – present

Objective

- To demonstrate the applicability of nuclear and related analytical techniques (mainly NAA, XRF, PIXE) in studies of pollution caused by APM

- To establish the database and source identification for particulate air pollution in the Asian region - A-PAD project
  www.rcaro.org:The IAEA Fine and Coarse Particle Ambient Air Quality Database for the Asian Region

- To establish the database and source identification for particulate air pollution in the country (Klang Valley, Kuala Lumpur) – especially for PM2.5

The Application of Neutron Activation Analysis (NAA) for Air pollution Study

- METHODOLOGY
- Sampling station:

  Universiti Teknologi Malaysia (UTM), Kuala Lumpur (3° 10′ 30″N, 101° 43′ 24″E) - rooftop of a two storey building at approximately 10 meters height.

Sample Collection, Gent stack sampler, 1-2x /week, 15L/min

Measurement of total mass

Measurement of black carbon

ELEMENTAL ANALYSIS by NAA

Short irradiation (PTS)

Long irradiation (RR)

1st Count - (10 -20 min)
Elements measured: Al, V, Ti, Ca, Mg, Br, I, Cl, Ba, Dy, Mn, Sr

2nd Count - (24 hours)
Elements measured: Eu, K, Ga, Na

Decay = 2 weeks

1st Count - (3-5days)
Elements measured: W, As, Br, La, Sm, U, Au, Sb, Yb, Lu)
2nd Count - (20 – 30 days)
(Elements measured: Nd, Ba, Rb, Th, Cr, Yb, Ce, Hf, Fe, Sb, Zr, Tb, Sc, Ta, Zn, Cs, Co, Eu)

DATA ANALYSIS

POSITIVE MATRIX FACTORIZATION analysis (EPA-PMF3)

Fig 14: Flow chart for methodology

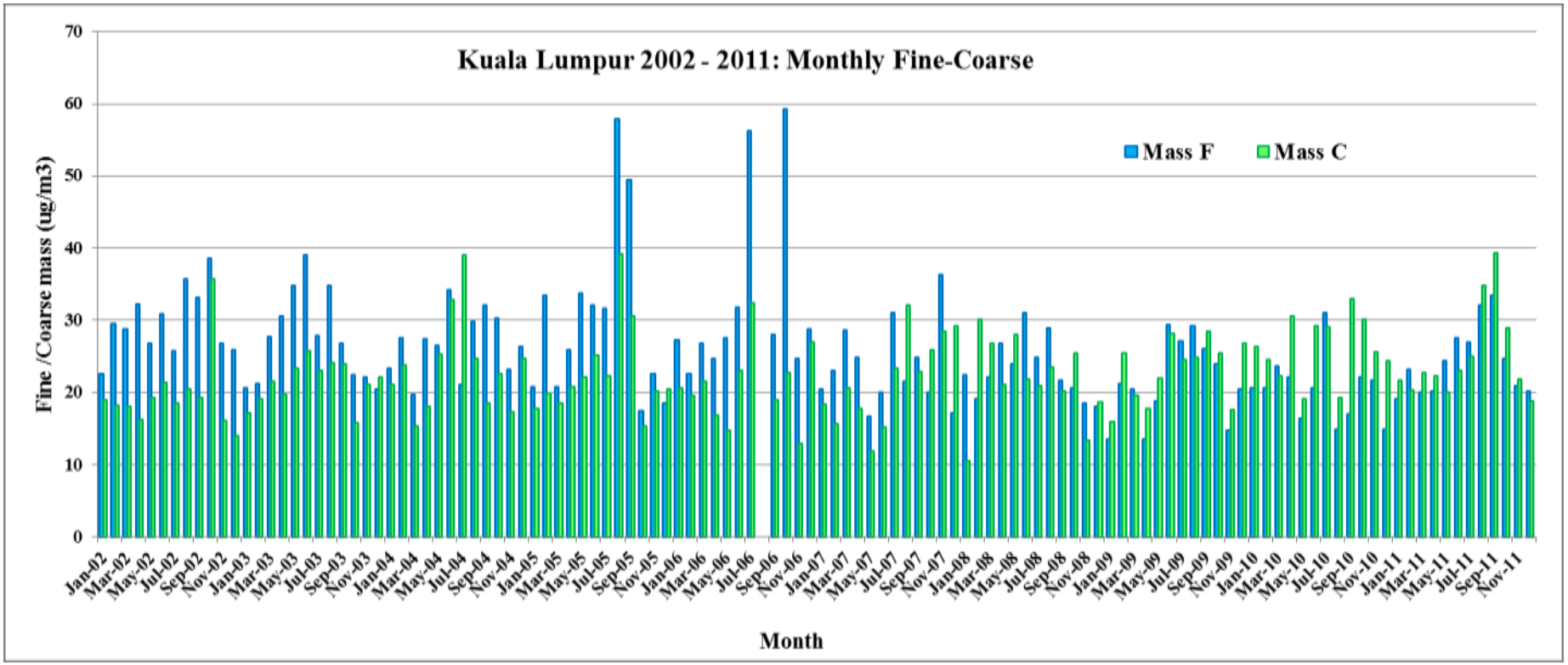


Figure 15: Monthly average of fine and coarse particle mass 2002-2011

- Low concentration in Nov-Jan: during the middle of northeast monsoon.
- High concentration in May-Sep: during the south west monsoon.

Table 8: Annual average of air particulate at Kuala Lumpur, Klang Valley, 2002-2011

DATA ANALYSIS

Year	$PM_{2.5}$ ($\mu g\ m^{-3}$)	$PM_{2.5-10}$ ($\mu g\ m^{-3}$)	PM_{10} ($\mu g\ m^{-3}$)
2002	29.5	18.1	47.6
2003	25.4	20.9	46.3
2004	26.6	22.6	49.2
2005	31.4	23.3	54.7
2006	34.8	20.7	55.5
2007	23.7	21.8	45.5
2008	23.2	22.1	45.4
2009	21.4	23.0	44.4
2010	20.5	26.1	46.6
2011	24.0	24.9	48.9
Average	26.1	22.3	48.4
Guidelines/ standard	USEPA NAAQS 15$\mu g/m^3$(annually) 35 $\mu g/m^3$ (24 hour)		Malaysian AAQ 50 $\mu g/m^3$ (annually) 150 $\mu g/m^3$ (24 hour)

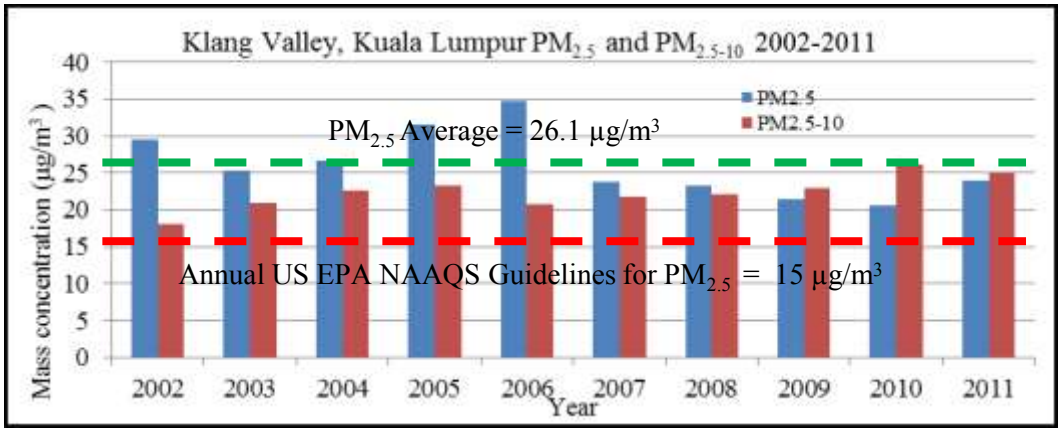


Fig 16. Annual average of $PM_{2.5}$ and $PM_{2.5-10}$ mass at Klang Valley, Kuala Lumpur 2002-2011

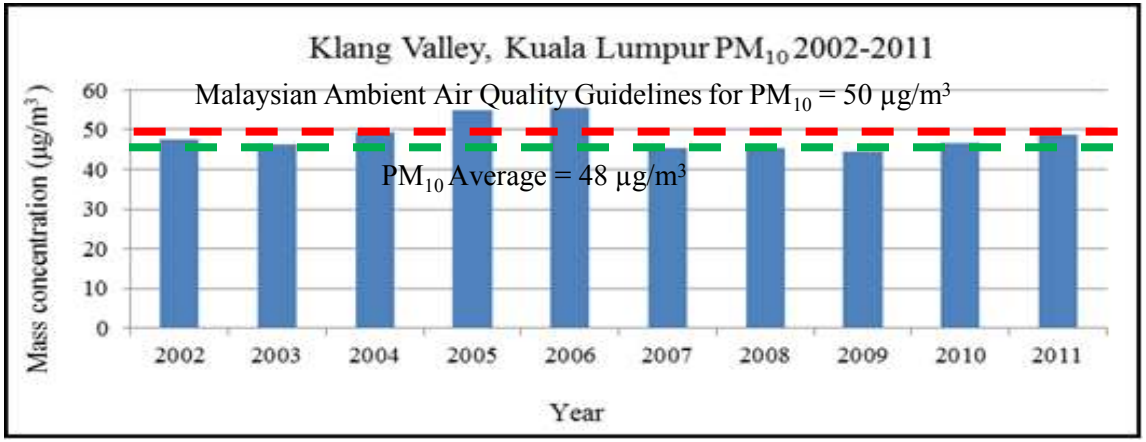


Fig 17. Annual average of PM_{10} mass at Klang Valley, Kuala Lumpur 2002-2011

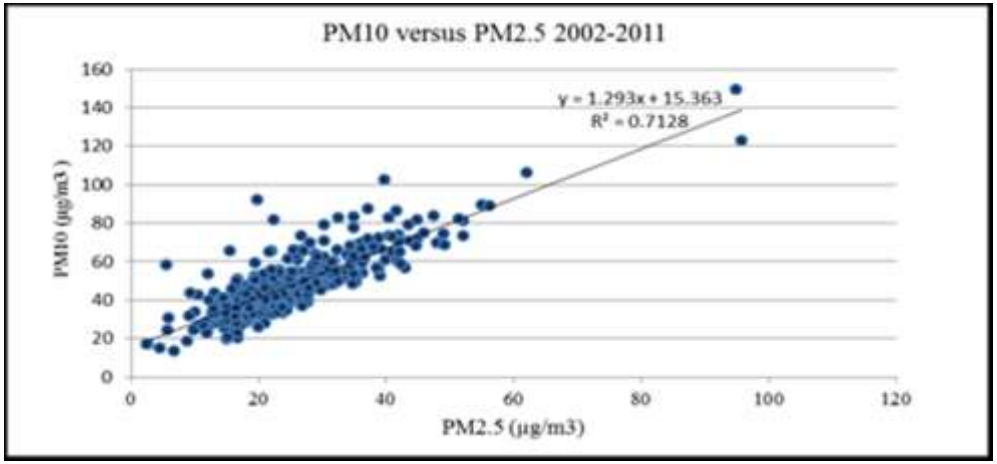


Fig 18. Plot of PM_{10} versus $PM_{2.5}$ at Klang Valley, Kuala Lumpur 2002-2011

DATA ANALYSIS

Table 9. Average of elemental concentration and statistic for $PM_{2.5}$ at Klang Valley, Kuala Lumpur , 2002-2011

Mass/ elements	Average (ng/m^3)	Max (ng/m^3)	Min (ng/m^3)	Median (ng/m^3)	StdDev (ng/m^3)	Average MDL (ng/m^3)	No of samples >MDL	Percentage (%)
Mass	25145	95750	2420	232454	10760	2184	380	100
BC	4080	13201	170	3948	1687	200	381	16.2
Na	556	4056	0	304	559	570	166	2.21
Mg	157	1144	0	102	185	66	289	0.62
Al	185	2560	7.9	108	258	37	366	0.74
Si	460	5696	76	259	541	26	382	1.83
P	50	728	10	21	99	35	144	0.20
S	2138	23830	10	1114	3121	19	381	8.50
Cl	150	1196	2.6	66	209	18	356	0.60
K	422	5064	0	259	556	15	377	1.68
Ca	127	2552	5.5	63	204	14	373	0.51
Ti	8.0	152	0	3.6	16	12	85	0.03
V	5.2	65	0	2.6	8.8	9.4	62	0.02
Cr	6.7	84	0	3.8	11	6.9	130	0.03
Mn	6.7	152	0	3.4	14	6.3	144	0.03
Fe	140	1552	2.4	79	195	4.3	380	0.56
Co	3.6	44	0	2.2	5.8	5.0	132	0.01
Ni	23	380	0	8.1	47	5.4	270	0.09
Cu	47	980	0	25	83	7.2	344	0.19
Zn	5.7	133	0	0	15	18	35	0.02
As	32	407	0	12	56	23	156	0.13
Pb	24	660	0	7.0	55	45	75	0.10

DATA ANALYSIS

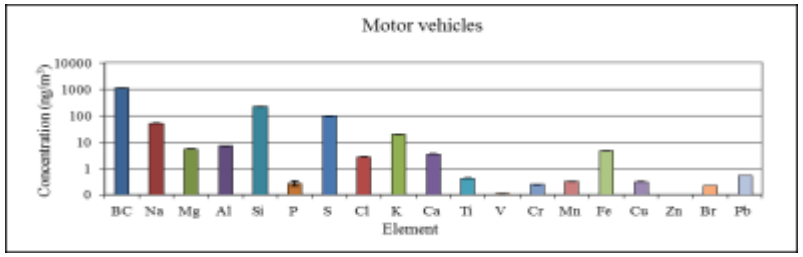
Table 10. Average of elemental concentration and statistic for $PM_{2.5-10}$ at Klang Valley, Kuala Lumpur , 2002-2011

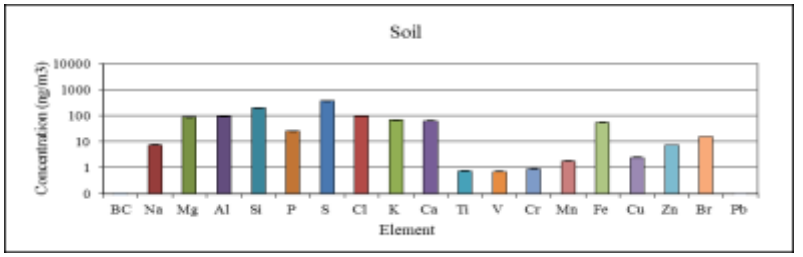
Mass/ elements	Average (ng/m^3)	Max (ng/m^3)	Min (ng/m^3)	Median (ng/m^3)	StdDev (ng/m^3)	Average MDL (ng/m^3)	No of samples >MDL	Percentage (%)
Mass	22730	72000	3190	21380	9376	2116	382	100
BC	561	5399	54	469	474	200	344	2.47
Na	835	11310	0	502	1142	542	203	3.67
Mg	323	3204	8.5	187	454	62	368	1.42
Al	1043	23958	15	440	2076	37	381	4.60
Si	2210	58971	102	954	4498	25	382	9.72
P	149	2860	0	53	328	30	303	0.66
S	745	19020	22	423	1425	21	379	3.28
Cl	411	8570	11	187	890	19	365	1.81
K	471	8580	5.1	247	775	17	372	2.07
Ca	1060	12958	12	585	1643	14	380	4.66
Ti	62	2013	0	25	150	11	307	0.27
V	5.2	143	0	2.2	13	11	38	0.02
Cr	16	297	0	5.7	35	7.9	188	0.07
Mn	12	220	0	5.0	23	7.1	187	0.05
Fe	584	6740	3.5	291	995	5.9	381	2.57
Co	3.9	44	0	2.6	6.0	5.9	128	0.02
Ni	18	341	0	8.2	34	6.1	265	0.08
Cu	42	920	0	22	84	7.2	322	0.18
Zn	3.7	66	0	0	9.6	16	25	0.02
As	29	364	0	8.0	52	23	129	0.13
Pb	15	648	0	0	53	40	30	0.07

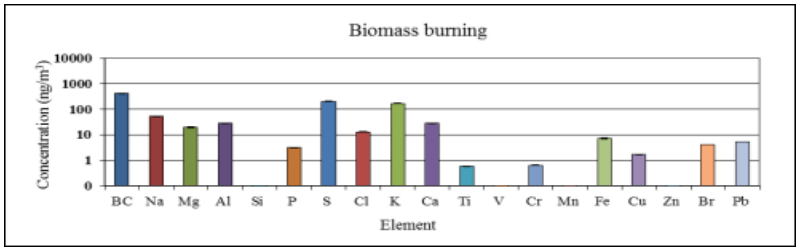
DATA ANALYSIS

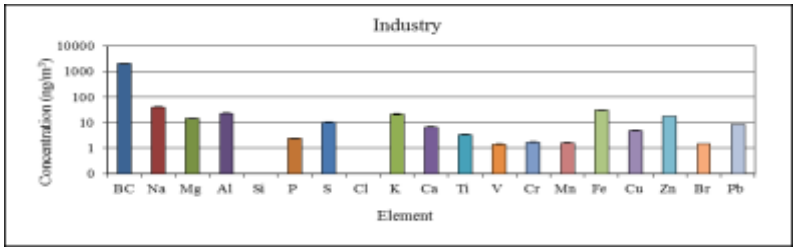
There are five (5) major factors that contribute to the fine particles of the Klang Valley area. These major sources identified as:

F1 = Motor vehicles (35.3%), F2= Soil (3.1%),
F3= Smoke/biomass burning (9.3%), F4= Industry (47.8%),
F5 = 2ndry sulphate (4.5%)









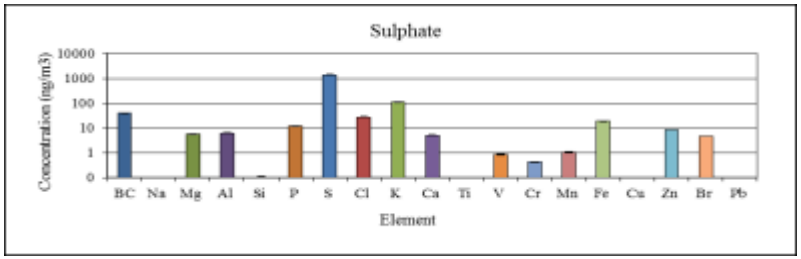
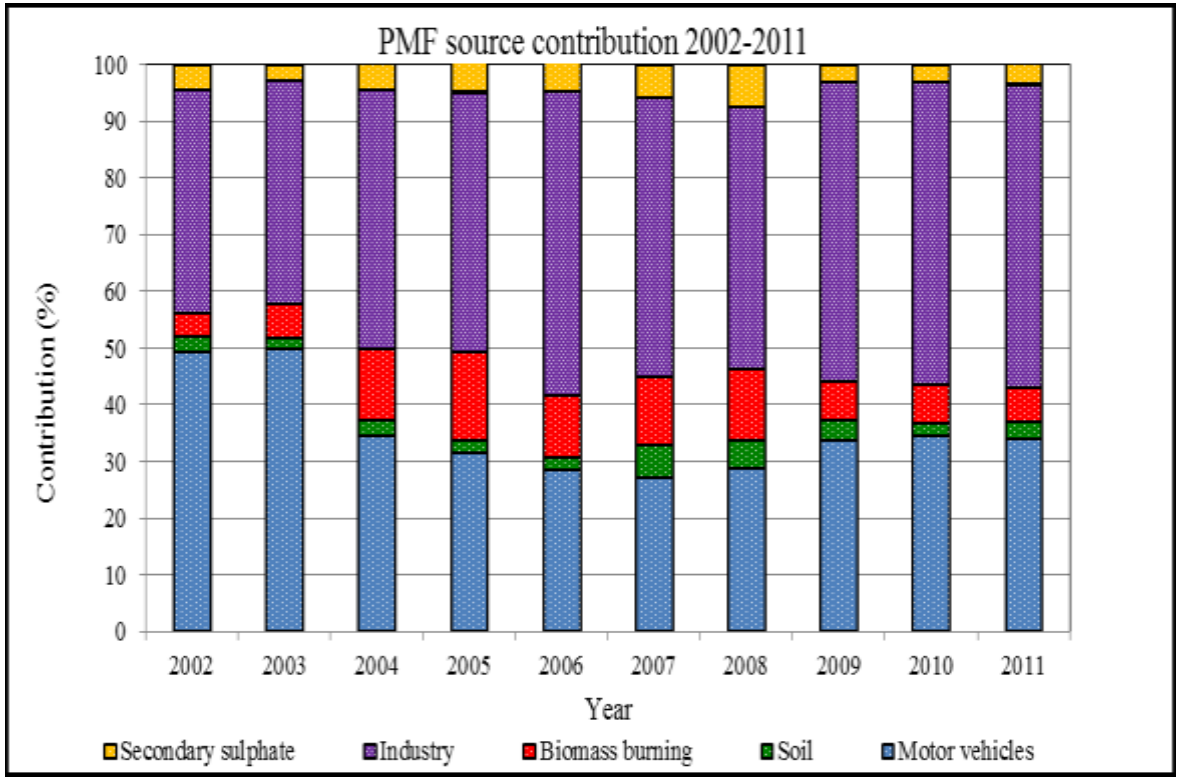


Fig 19. Source apportionment for the $PM_{2.5}$ mass measured at Klang Valley, Kuala Lumpur, 2002 -2011

DATA ANALYSIS



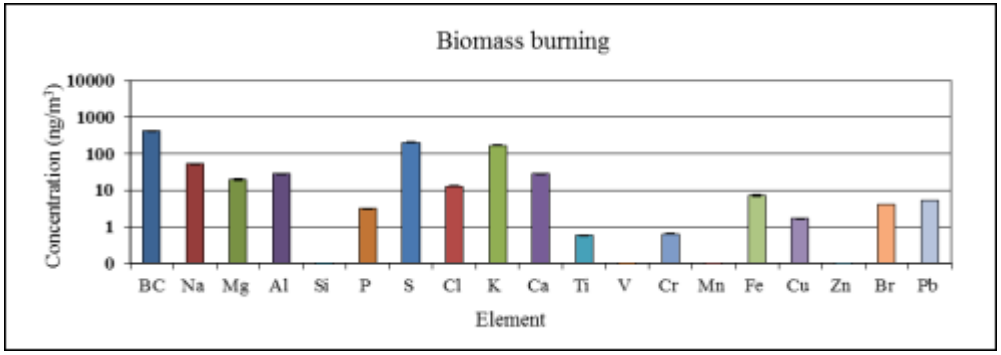
DATA ANALYSIS

Fig 20. Annual trend in source contributions of the PMF-modeled five factors in Klang Valley, Kuala Lumpur

- Approximately 35% and 48% of $PM_{2.5}$ emitted in Klang Valley, Kuala Lumpur came from motor vehicles and industry respectively.
- In 2002 and 2003 $PM_{2.5}$ mass was dominated by motor vehicles source with contribution of 49.5% and 50.0% respectively.
- After 2003 there was increasing of contribution from industry and has been the major source to $PM_{2.5}$ mass since 2004.

Trans-boundary pollution

- Smoke /biomass burning was identified based on potassium (K) loading



- Potassium often used as indicator of biomass burning and released especially under high temperatures in fires as potassium chloride and potassium sulfate

- In order to obtain a reliable smoke indicator from the fine potassium it is necessary to subtract the fine potassium associated soil.

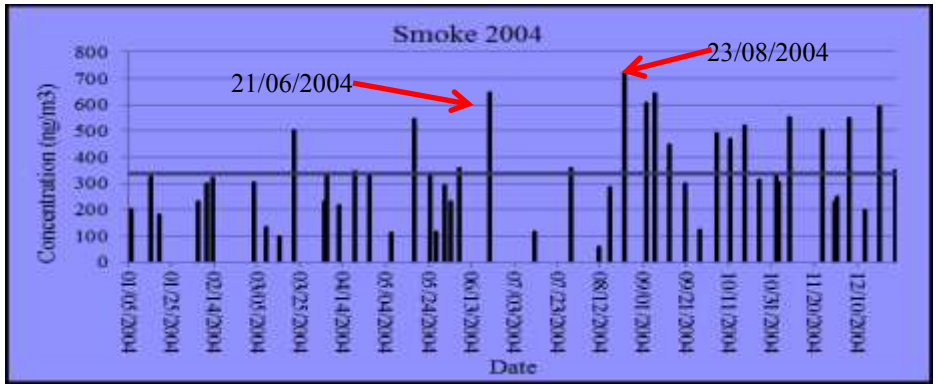
- Hence, smoke can be obtained by following equation:

$$\text{Smoke} = [K] - 0.6\,[Fe]$$

Table 11: Statistic and the smoke concentration for the selected studying period

Year	Date	Smoke ($ng.m^{-3}$)	Mean ($ng.m^{-3}$)	Median	2stdev
2004	21/06/04	646	335	316	337
	23/08/04	721			
2006	10/10/06	1102	477	336	662
	23/10/06	789			
2008	30/07/08	1551	684	517	1060
	04/08/08	1995			

- In this study, smoke trans-boundary events (with evidence) were identified based on the pseudo-element K during the southwest monsoon between May – Sep/Oct from the data base 2004 to 2008
- In order to investigate the source location that responsible for the long range transport of pollutant. Back trajectory model the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) was used to calculate the air mass backward trajectories up to 120 hours (5 days) for the days when fine particle were sampled.



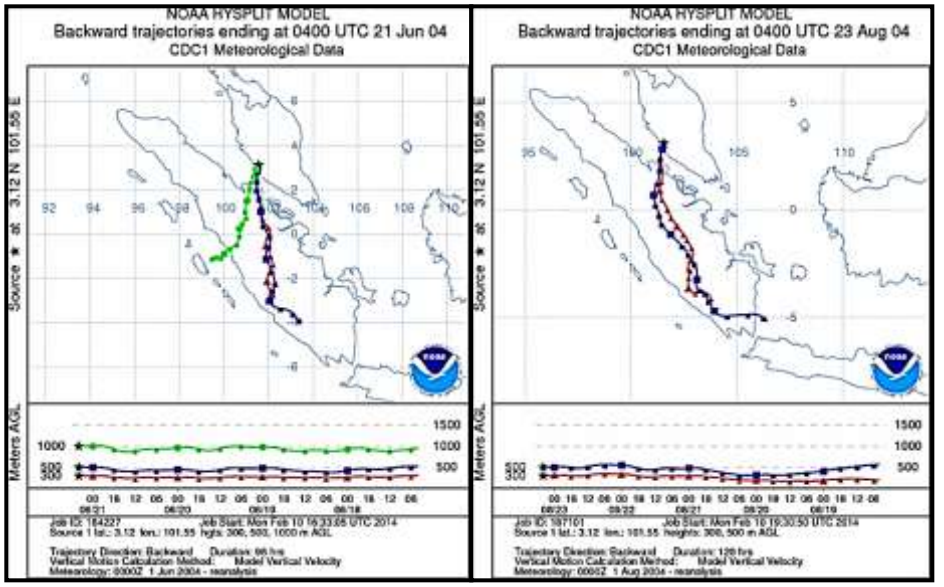


Fig 21. Four days (left) and five days (right) back trajectories calculated for Jun 21 and Aug 23, 2004

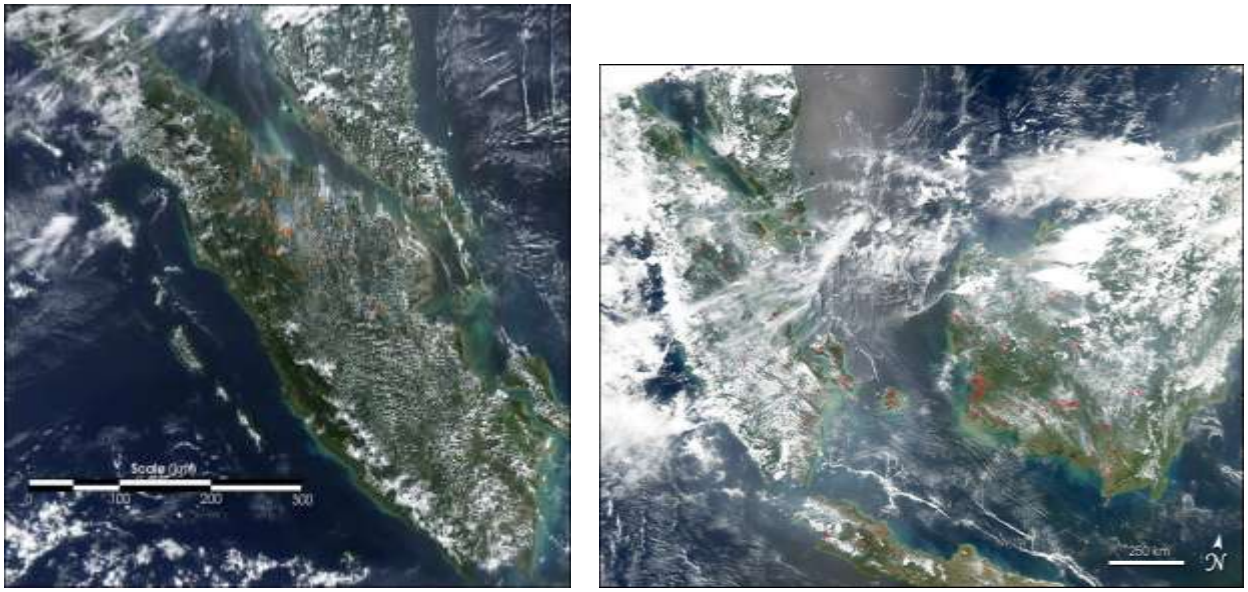
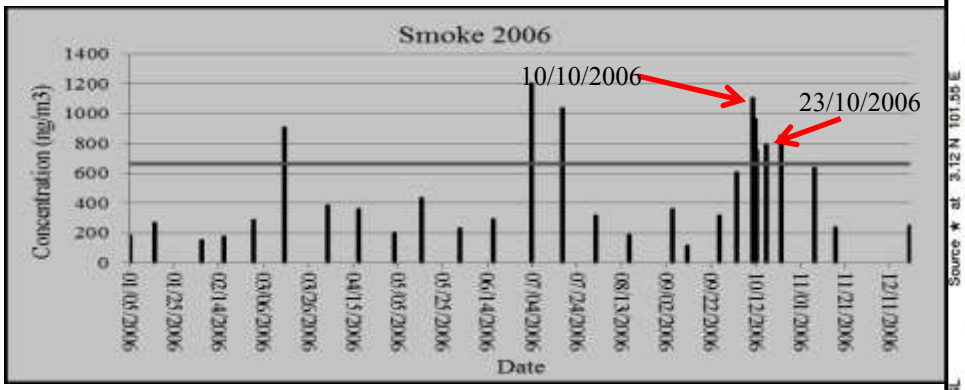


Fig 22. NASA satellite image of peninsular Malaysia shrouded in thick haze on Jun 17, 2004 (left) and image of fires burning across Sumatra and Borneo Island on Aug 22, 2004 (right). Active fires are marked with red dots



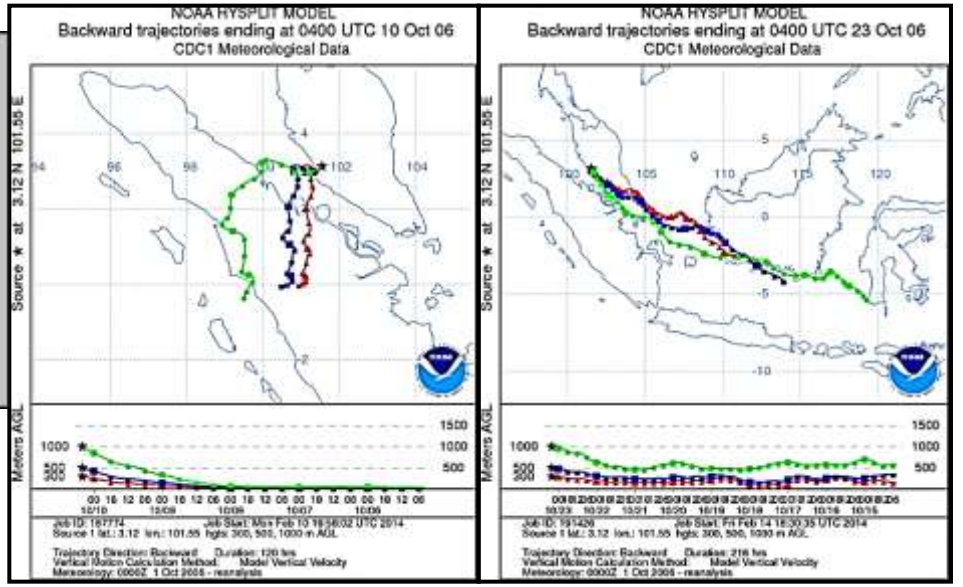


Fig 23. Five days (left) and nine days (right) back trajectories calculated for Oct 10, 2006 and Oct 23, 2006

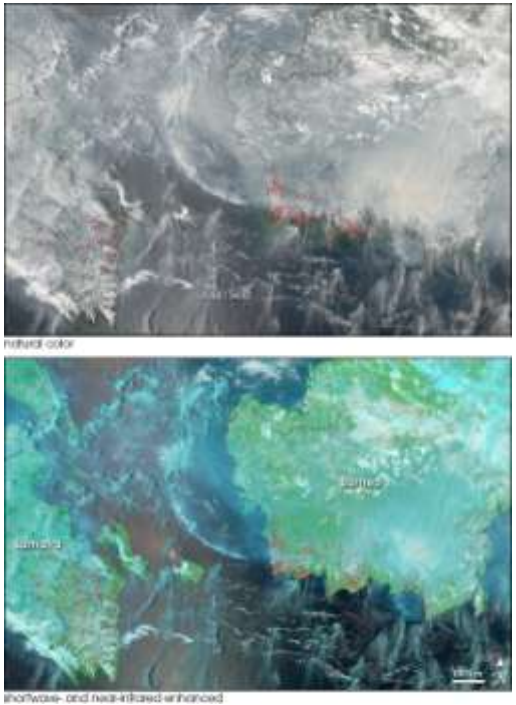
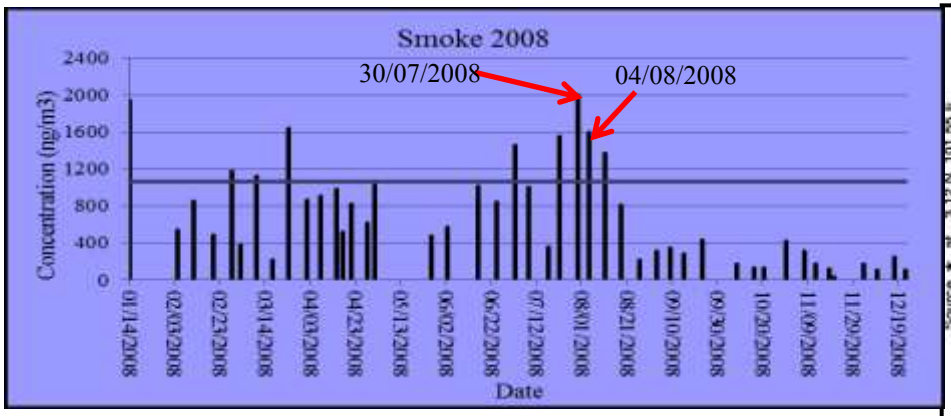


Fig 24. NASA satellite image of haze in the area of islands of Sumatra and Borneo on Oct 8, 2006 (left) and Oct 23, 2006 (right)



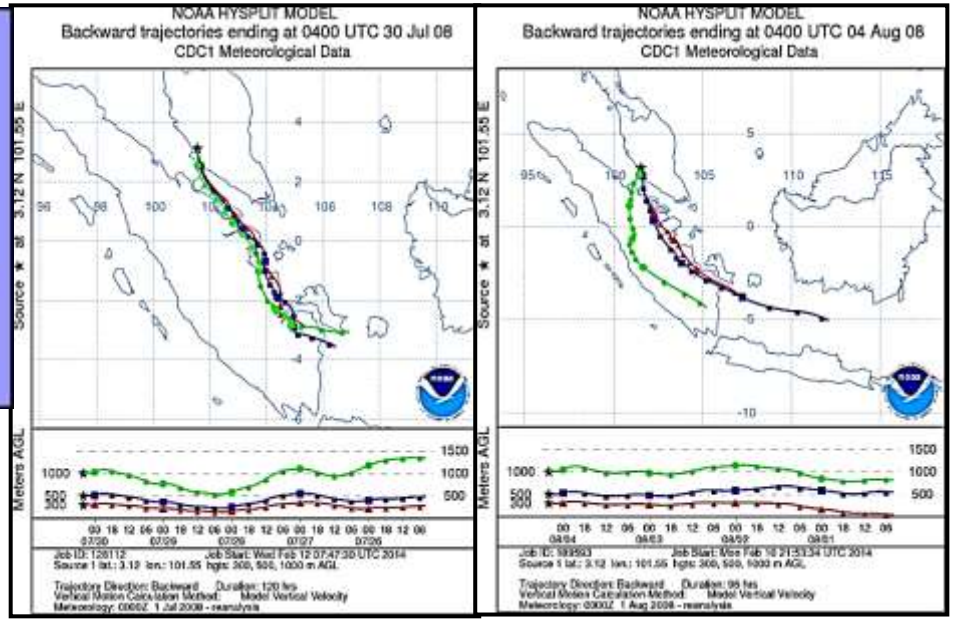
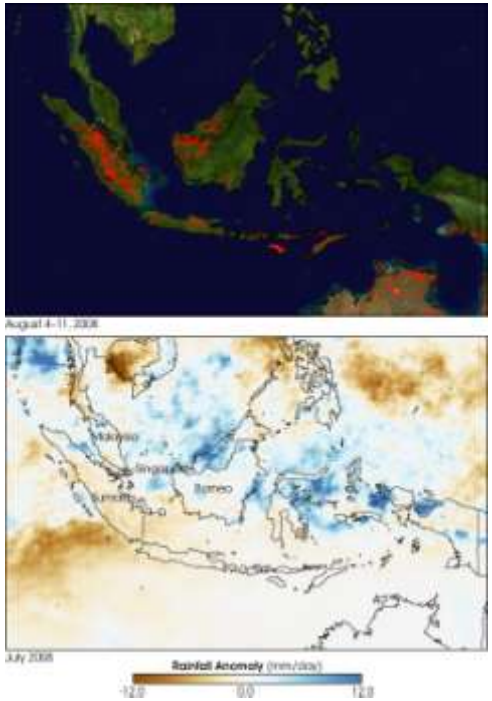


Fig 25. Five days (left) and four days (right) back trajectories calculated for Jul 30 and Aug 04, 2008



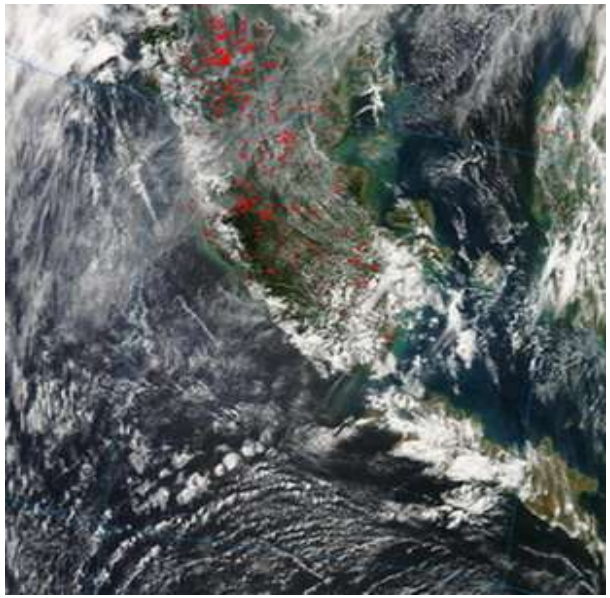


Fig 26. Fire locations from MODIS for the week of August 4, 2008 in the area of islands of Sumatra and Borneo (left) and active fires detected by MODIS on NASA's Aqua satellite on Aug 6, 2008 (right))

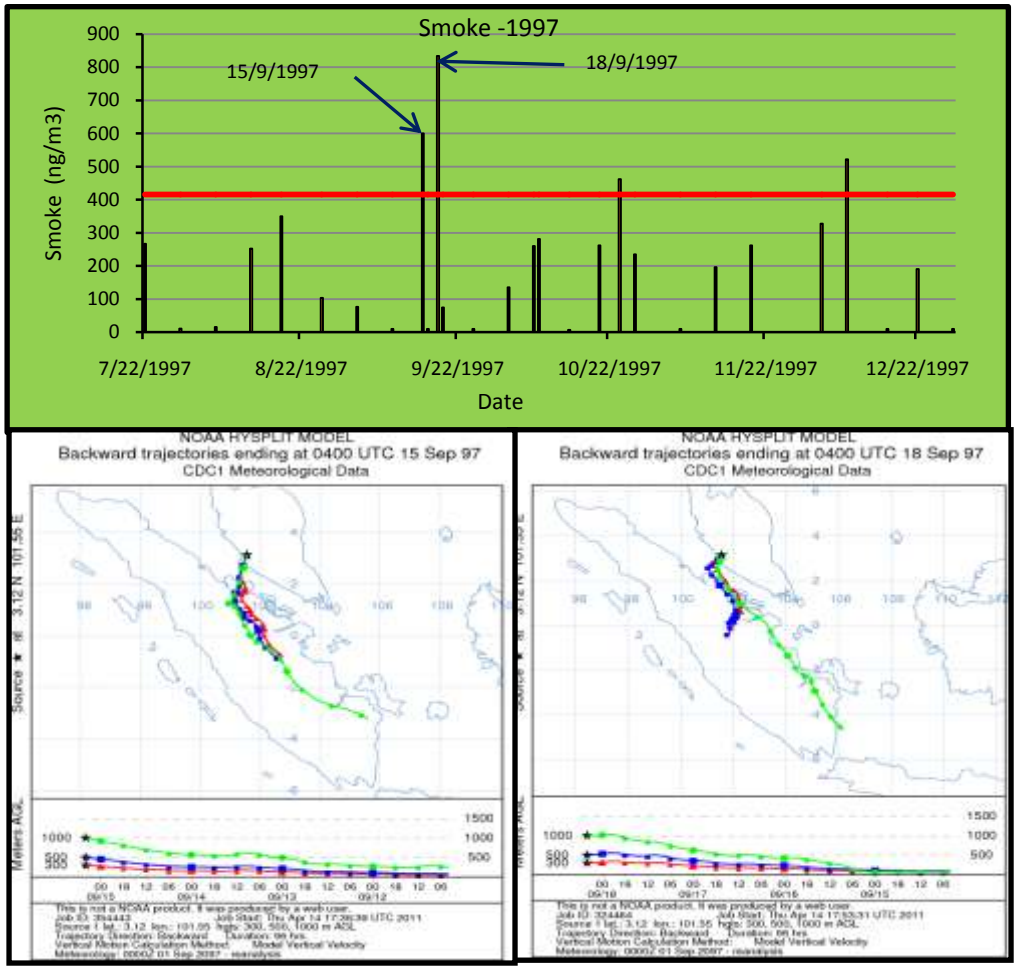


Figure 27: Back trajectories calculated for Sep 15 and Sep18, 1997

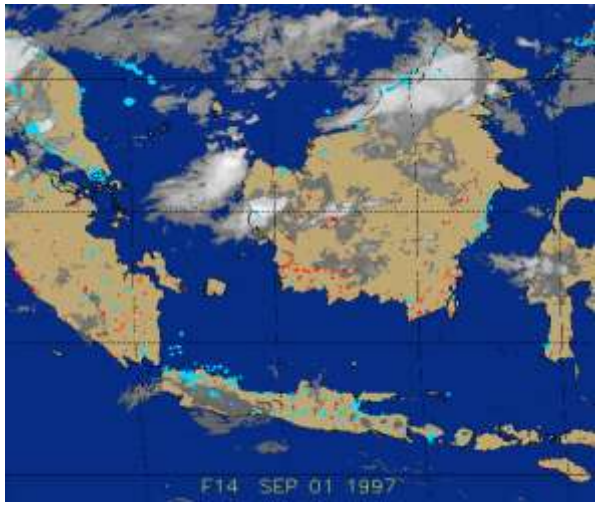


Figure 28: Fires and haze on Sumatra Island and Kalimantan in the beginning of Sep 1997 (Picture-NGDC)

Table 12: Analytical services

Sample Type	Elements Analysis	Technique Employed
Soil/Sediment	U, Th	INAA
Oil sludge	U, Th	INAA
Industrial Sludge	U, Th	INAA
Air filter	Multielement	INAA, ICPMS, IC
Herbs/traditional medicine	Pb, Cd, As, Hg	ICPMS
Rubber glove	Total Cl, Cl residue	INAA, IC
Soil/Sediment	Multielement	ICPMS, INAA
Water	NO_3^-, F^-, Cl^-, K^+, Mg^+	IC
Biological sample	Pb, As, Cd etc	ICPMS, INAA

Terima Kasih