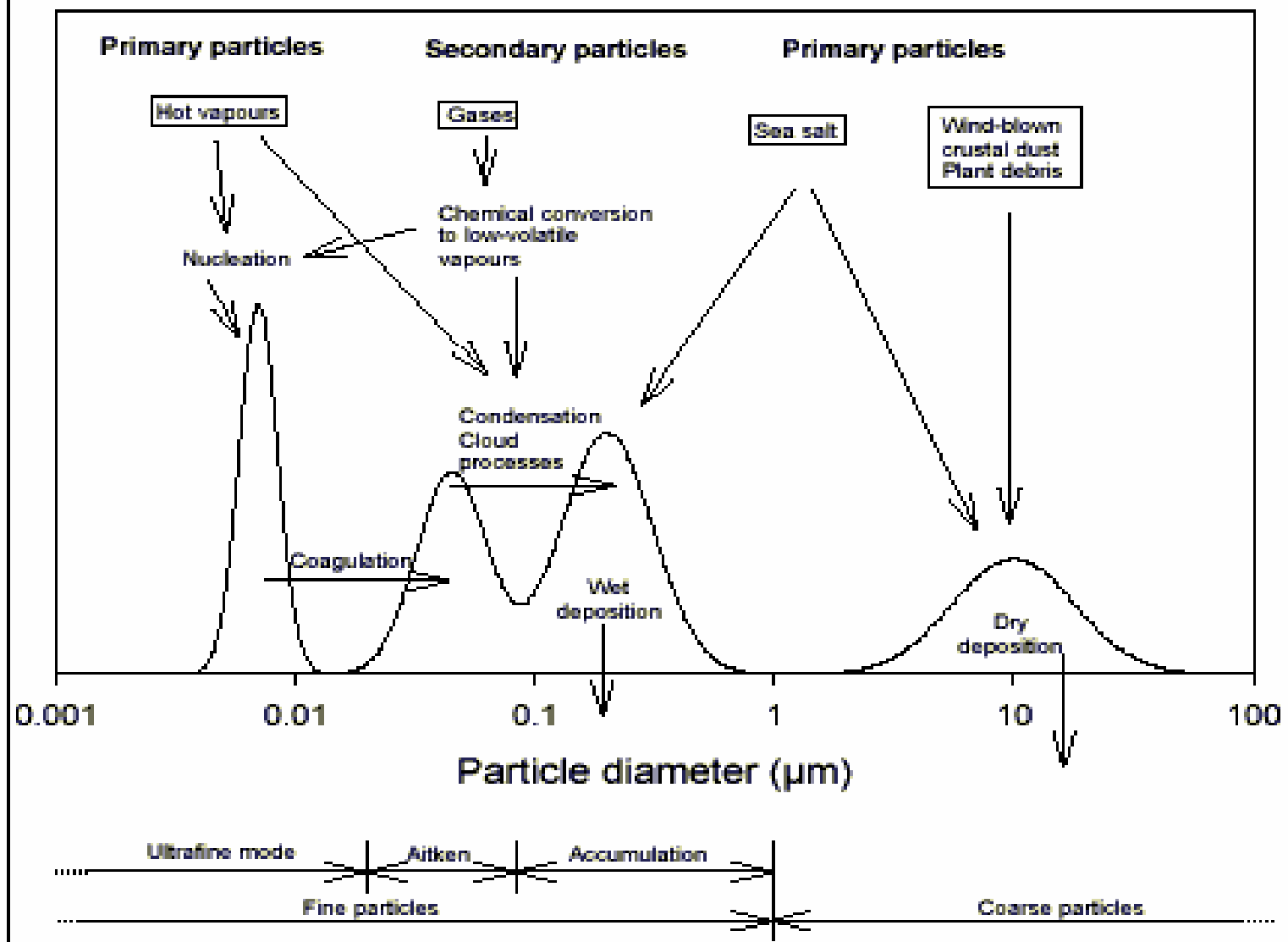


Atmospheric aerosols : Summary

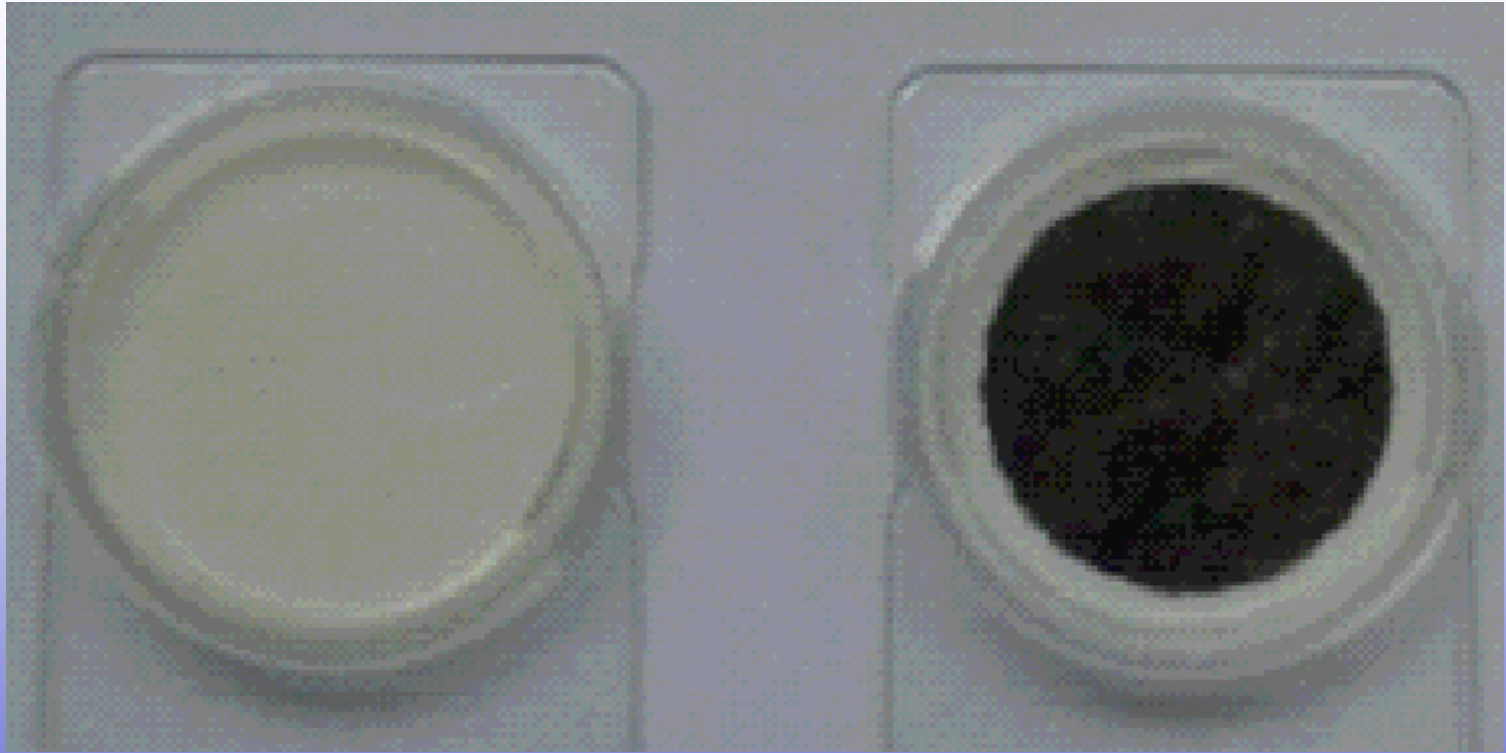
Suspension of solid or liquid in the atmosphere

- Wide range of size : from 1 nm to 100 μm
- 2 main classes : **fine** ($\text{\O} < 2.5 \mu\text{m}$) (PM_{2.5}) and **coarse** ($\text{\O} > 2.5 \mu\text{m}$) when considering surface area and volume/mass
- **Fine** particles mainly **man-made** and **coarse** particles mainly **natural**



Idealised and simplified schematic illustration of atmospheric aerosols, including sources, transformation and sinks. The different size ranges (modes) are also shown.

Atmospheric aerosol : chemical composition



Coarse fraction

Fine fraction

Atmospheric aerosols : Chemical composition

Inorganic species

- **Primary** : Metals, insoluble minerals, ammonium
- **Secondary** : Sulfates and nitrates

Organic species

- **Primary** : Soot (Impure graphite), polar (e.g. alkanolic acids), and non polar organics (PAH, alkanes...)
- **Secondary** : mainly polar organics (multi-functional compounds)

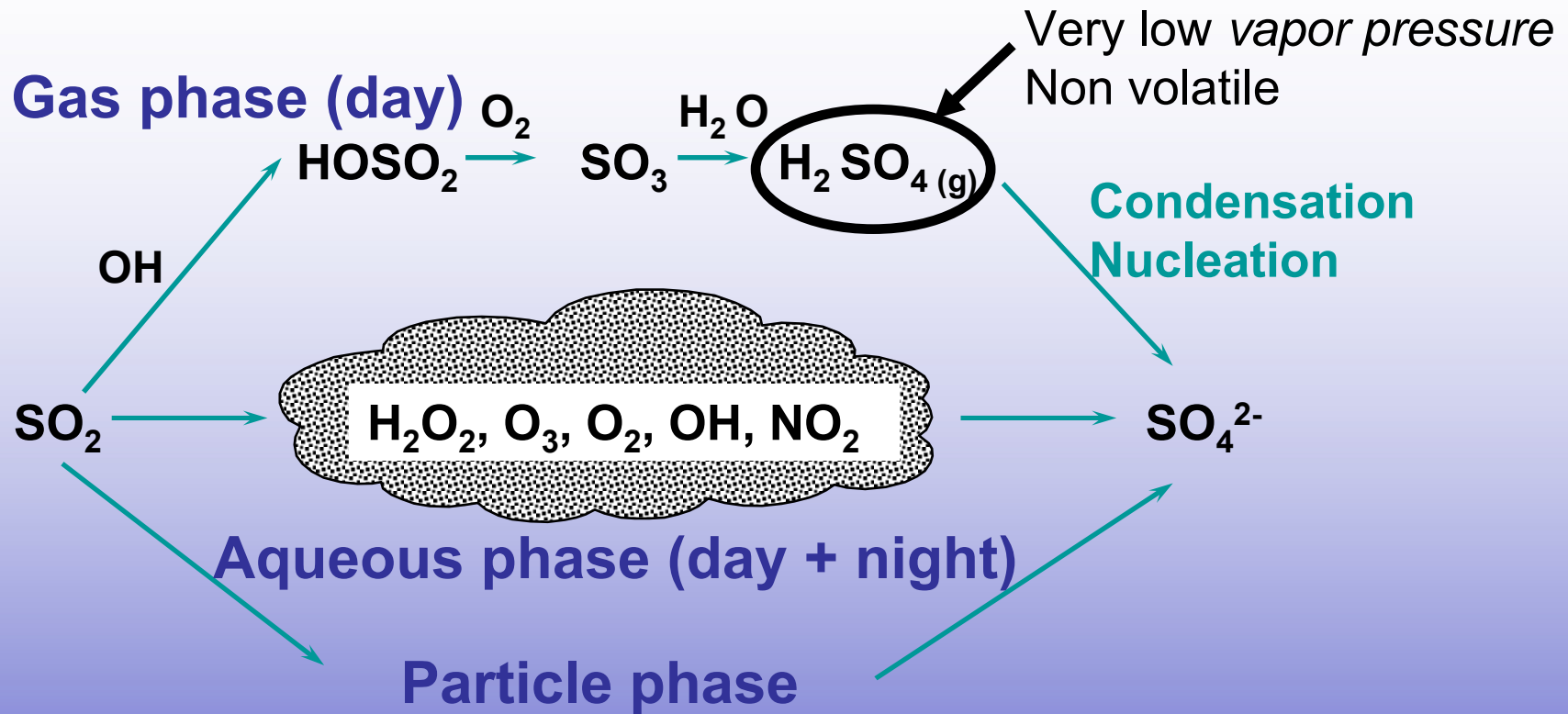
+ Water

Origin of Sulfates

- Oxidation of SO_2
- Over continents : SO_2 emissions from man-made activities (**fossil fuel combustion**) & **volcanoes**

Over oceans : **Marine phytoplankton** produces dimethyl sulfide (DMS) which oxidises in SO_2

Origin of Sulfates

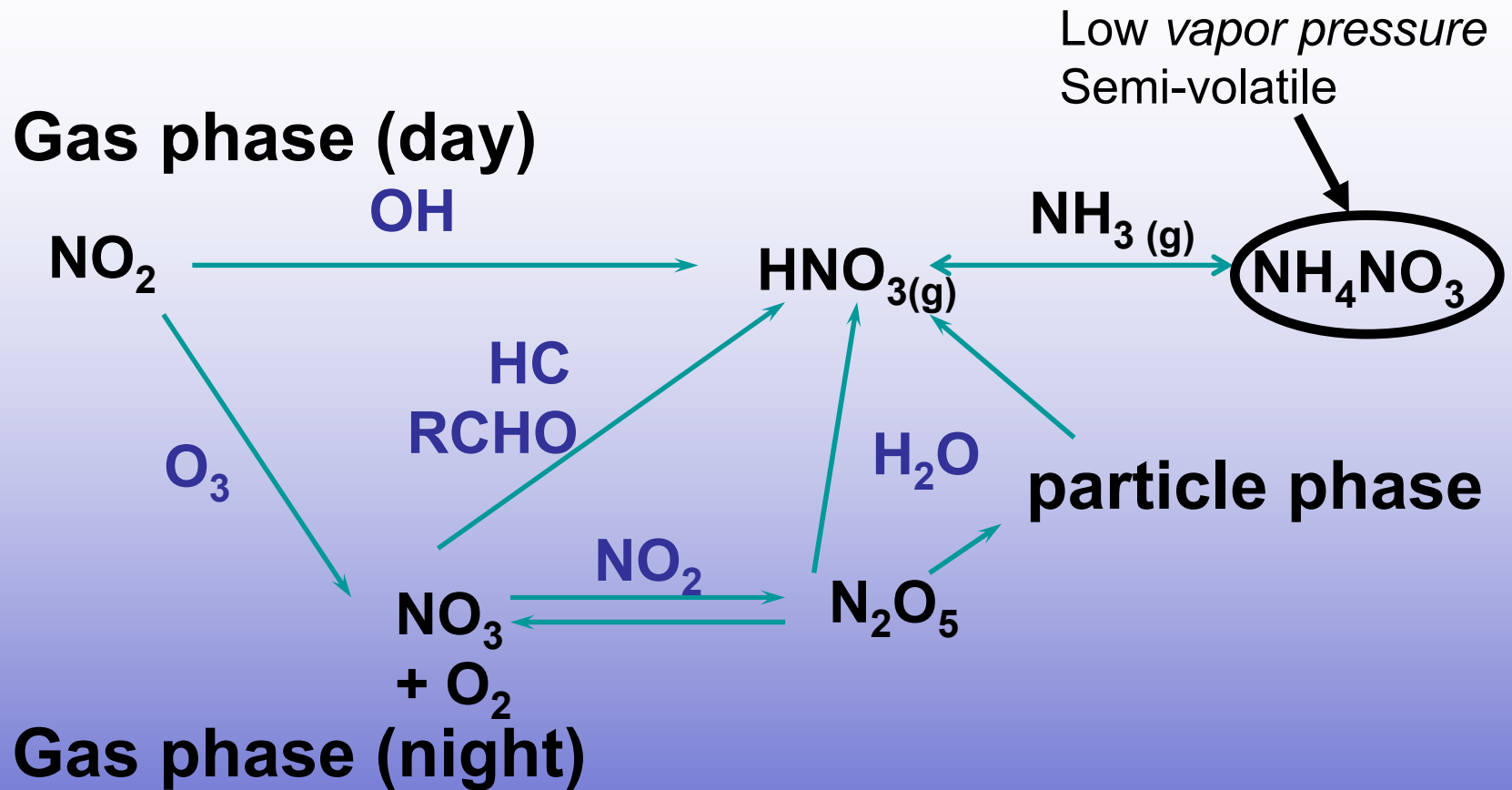


- Most SO_2 is converted in sulfate either in the **gas phase** or in the **aqueous phase**
- Both processes produce sulfate aerosol mainly in **fine mode** ($\text{Ø} < 2.5 \mu\text{m}$)

Origin of Nitrates

- Oxidation of NO_2
- Man-made origin : fossil fuel combustion
- Natural origin : soil, lightning

Nitrate ions (1)



- NO_2 is converted to HNO_3 mainly in the **gas phase**
- HNO_3 reacts with NH_3 to form ammonium nitrate
- Nitrates found in/on both **coarse** and **fine particles**: the origins are not the same. (Fine origin shown above)

Nitrate ions (2)

One origin of nitrate on **coarse** particles:



(This process is important in coastal areas)

Ammonium ions

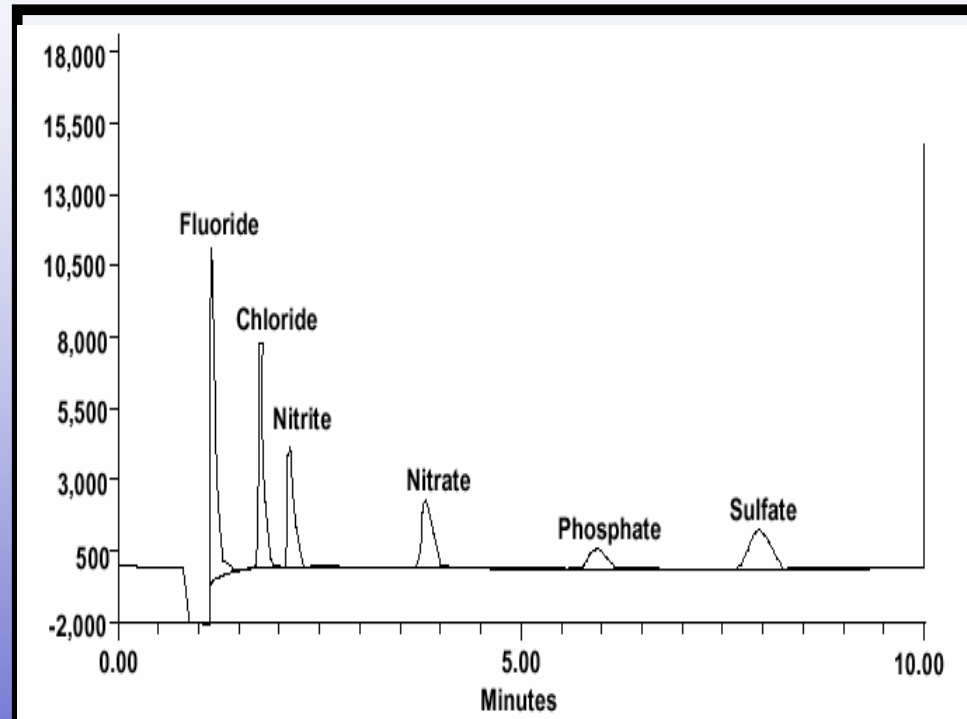
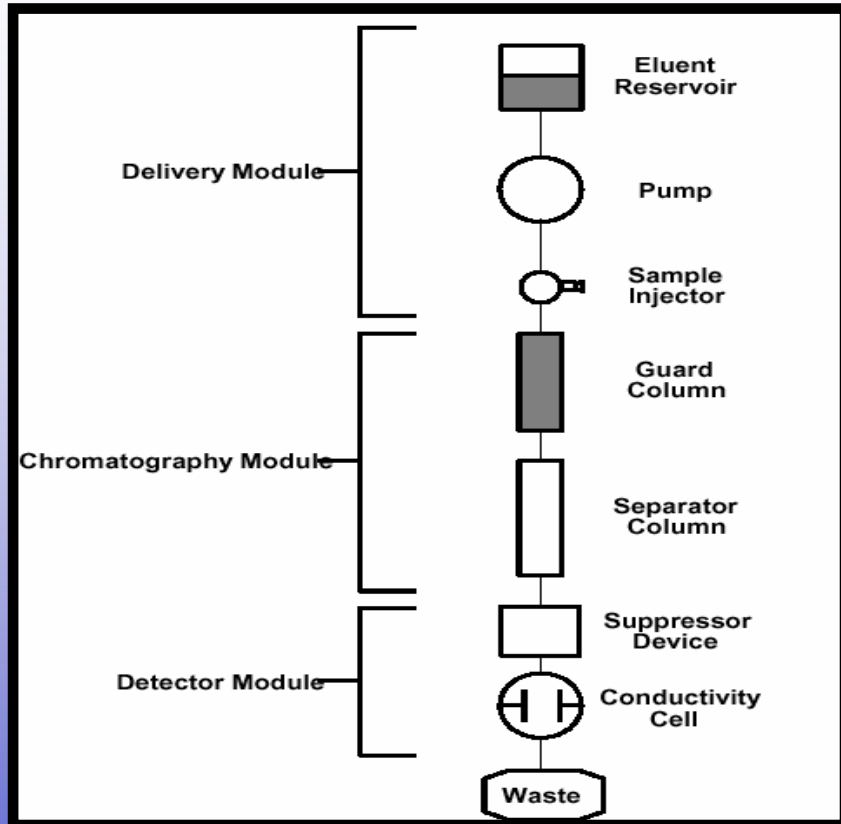
- NH_3 directly emitted in the atmosphere
- Man-made origin : sewage, fertilized lands
- Natural origin : soil, animals

- NH_3 reacts with sulfates & nitrates

- The preferred form for ammonium in the aerosol phase is ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$
 - Each sulfuric acid molecule is looking for two ammonia molecules (neutralization)
 - If there is not enough ammonia present, sulfuric acid exists either as H_2SO_4 (aq) or NH_4HSO_4

Analytical method for ions

Ion Chromatography (IC)



Separation of the species in an ion-exchange resin based on the interactions ion-column

Cations (Na^+ , K^+ , NH_4^+) & anions (SO_4^{2-} , NO_3^- , Cl^-) analysed separately

Metals

- Man made sources : incorporated in the particle in early stage of particle formation from combustion process
 - Natural sources : volcanoes + soil erosion
 - Fine mode : Pb, Zn, Fe, Cd, As...
 - Coarse mode : Ca, Mg, Al, Ti,
- Fine & Coarse mode : Na, K, Fe, V, Cr, Co, Ni, Mn, Cu

Current analytical methods : Metals

Inductively Coupled Plasma Emission Spectrometer (ICP)

All elements absorb and emit radiation at characteristic Wavelengths
Elements can be identified by their characteristic radiation and quantified by the intensity of the radiation

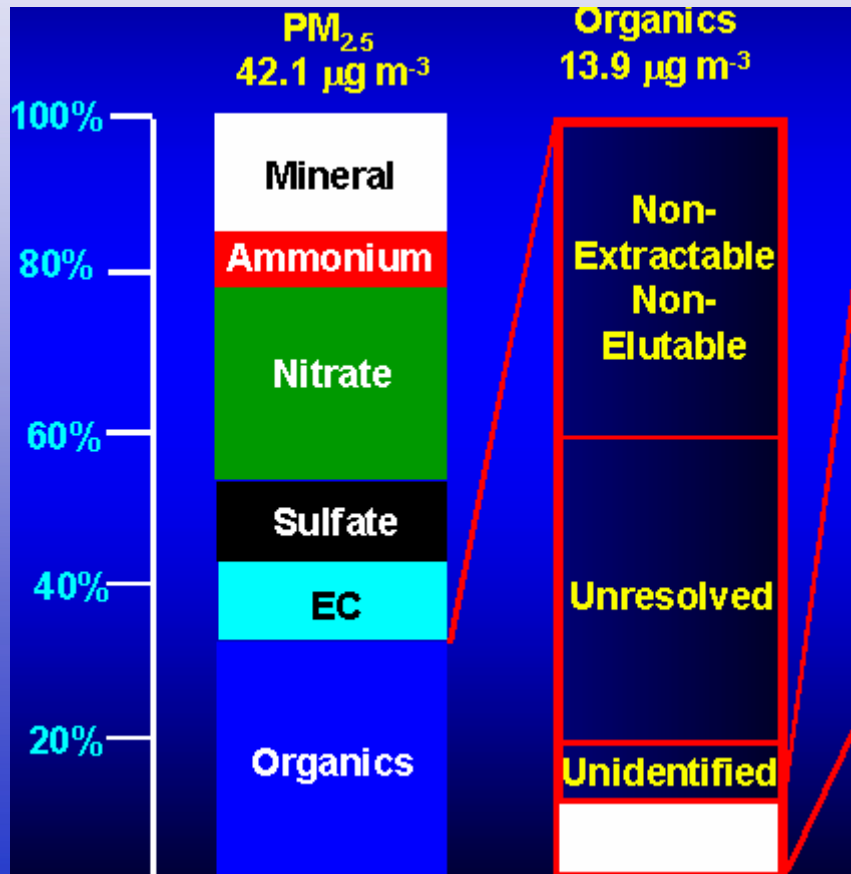


Temperature of Plasma = 7000-8000K used as an **Excitation Source**

**Simultaneous analysis of up to 20 Elements
from 11 (Na) to 92 (Uranium)**

Organic Compounds (OC)

- Man made : combustion processes + SOA from VOC
- Natural : SOA from biogenic VOC
- Complex mixture of 1000's of compounds



Only 10% identified with $n_c > 20$
(semi & nonvolatile):

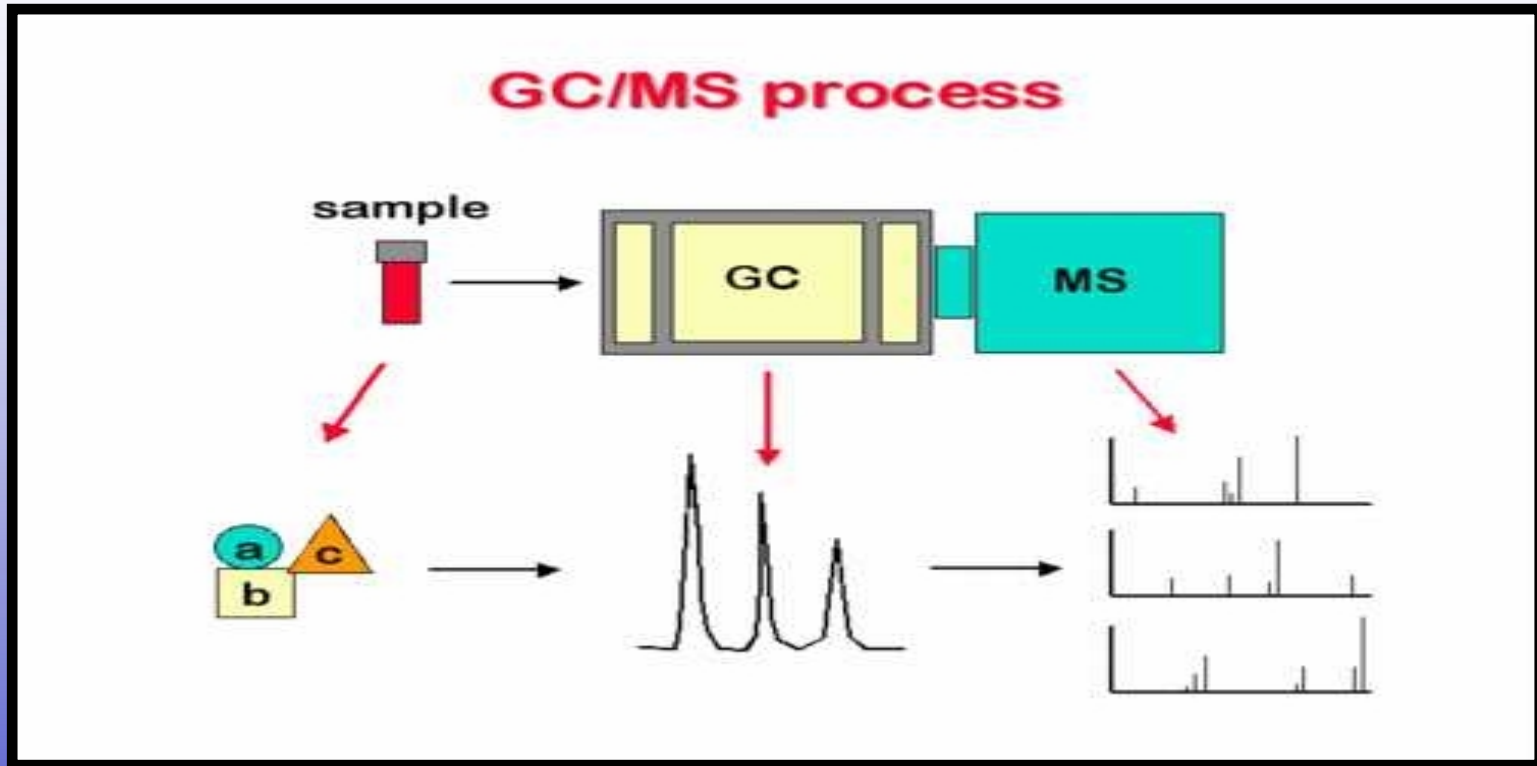
n-Alkanes

n-Alkanoic acids

Polycyclic aromatic compounds
(e.g. Polycyclic Aromatic
Hydrocarbons, PAH)

Current analytical methods : OC speciation

Gas chromatography coupled to mass spectrometer (GC-MS)



- Separation based on volatility and polarity
- Identification based on “Molecular ion” + characteristic fragments (e.g. loss of a methyl group = Molecular ion – 15)

Origin of secondary organics

High volatility products

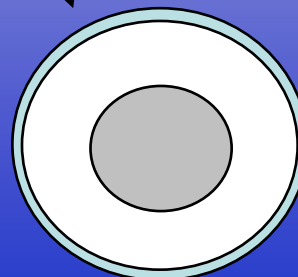
Low volatility products

**Acids, aldehydes,
ketones, organonitrates,
multi-functional
compounds
~1000 compounds**

Reaction with

- OH, O₃(day),
- O₃, NO₃ (night)

**Gas-particle partitioning
Nucleation**



**Emission of SOA Precursor
Volatile Organic Compounds
~100 compounds**

Secondary organic aerosols (SOA)

- The importance of a VOC as SOA precursor depends on:
 - The volatility of its products
 - Its emission rate (atmospheric abundance)
 - Its chemical reactivity
- Most important biogenics:
 - Terpenes : α -pinene, β -pinene, Δ^3 -carene, *d*-limonene, camphene, and myrcene.
- Most important anthropogenic VOCs:
 - Aromatics : Toluene, xylenes, trimethylbenzenes, diethylbenzenes, etc.

Secondary organic aerosols (SOA)

PREDICTED PERCENT CONTRIBUTION TO SECONDARY ORGANIC AEROSOL CONCENTRATIONS AT LOS ANGELES

Species	Contribution	
	Grosjean and Seinfeld (1989)	Pandis et al. (1992a)
Aromatics	58	65
Biogenic Hydrocarbons	10	16
Alkanes	21	15
Olefins	11	4

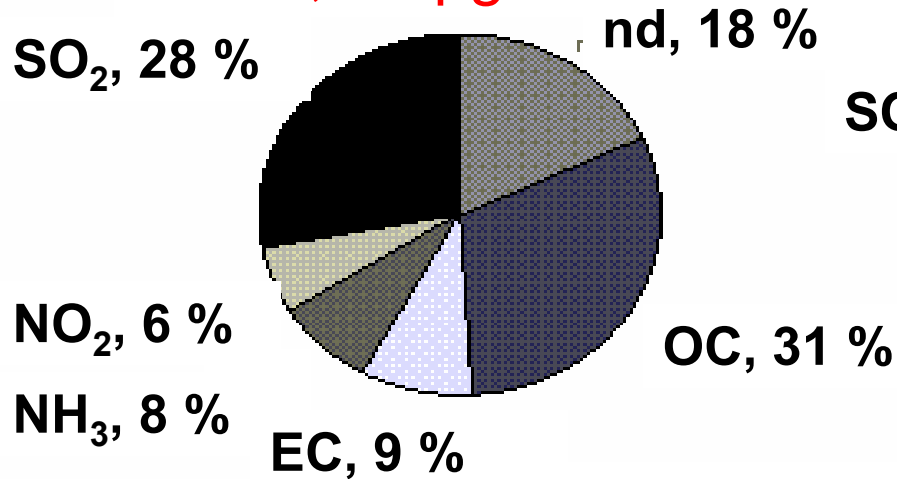
AMOUNT OF SECONDARY AEROSOL PRODUCED IN A TYPICAL LOS ANGELES SMOG EPISODE ACCORDING TO FUNCTIONAL GROUPS

Precursor	Aerosol produced (kg day ⁻¹)			
	Carbonyls	Aliphatic Acids	Nitrophenols	Aliphatic Nitrate
Alkenes	-	608	-	-
Cyclic olefins	62	131	-	9
Terpenes	295	623	-	41
Alkanes	243	-	-	121
Cycloalkanes	72	-	-	72
Aromatics	-	-	3118	-
TOTAL	672	1362	3118	243

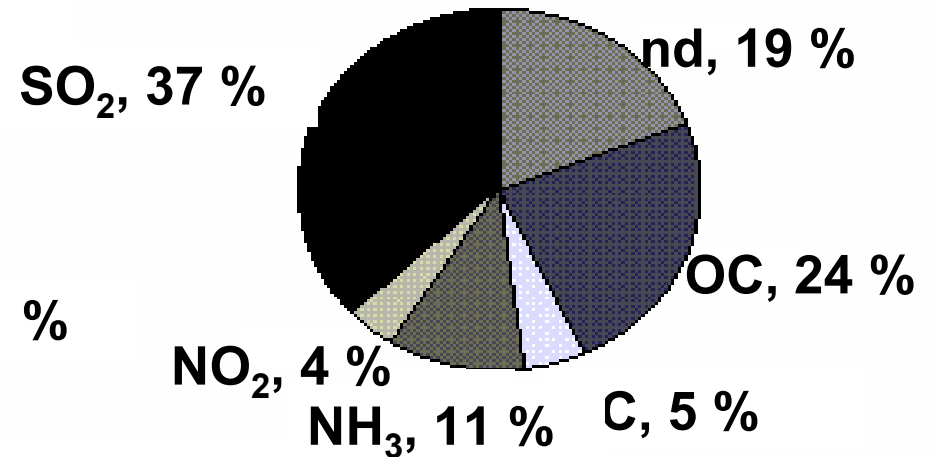
Tracers of aromatics

Major chemical components

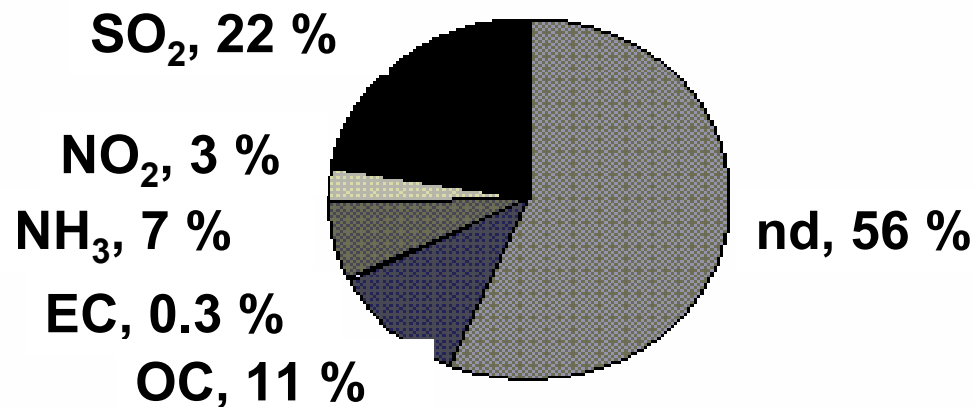
Urban, $35 \mu\text{g.m}^{-3}$



Non urban, $15 \mu\text{g.m}^{-3}$



Remote, $4.8 \mu\text{g.m}^{-3}$

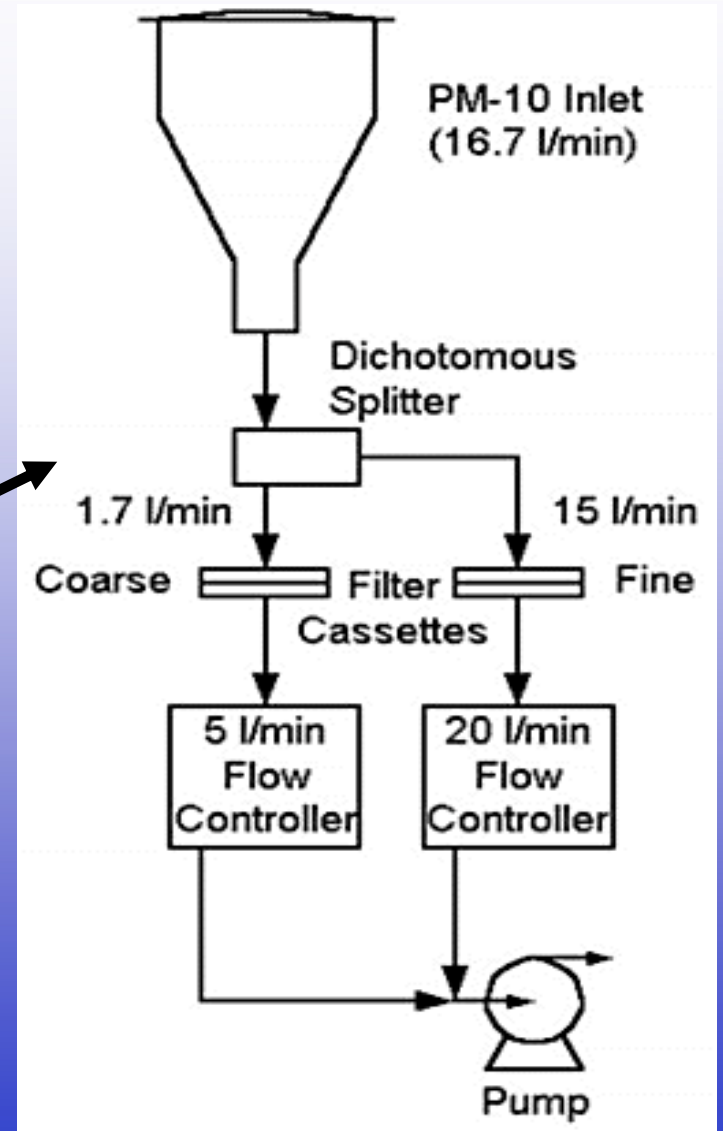


Composition strongly related to sources

Chemical composition and its dependence on aerosol size

- Sulfates, Ammonium, organic & elemental carbon, metals (lead, Iron, copper, nickel) are **principally** in the **fine mode**
- Minerals of geological origin, calcium, aluminum, magnesium, silicon, iron, sodium chloride (sea spray) + pollens, spores and coal fly ash are **principally** in the **coarse mode**
- Potassium and nitrate ions found **both in fine and coarse particles but with different origins**

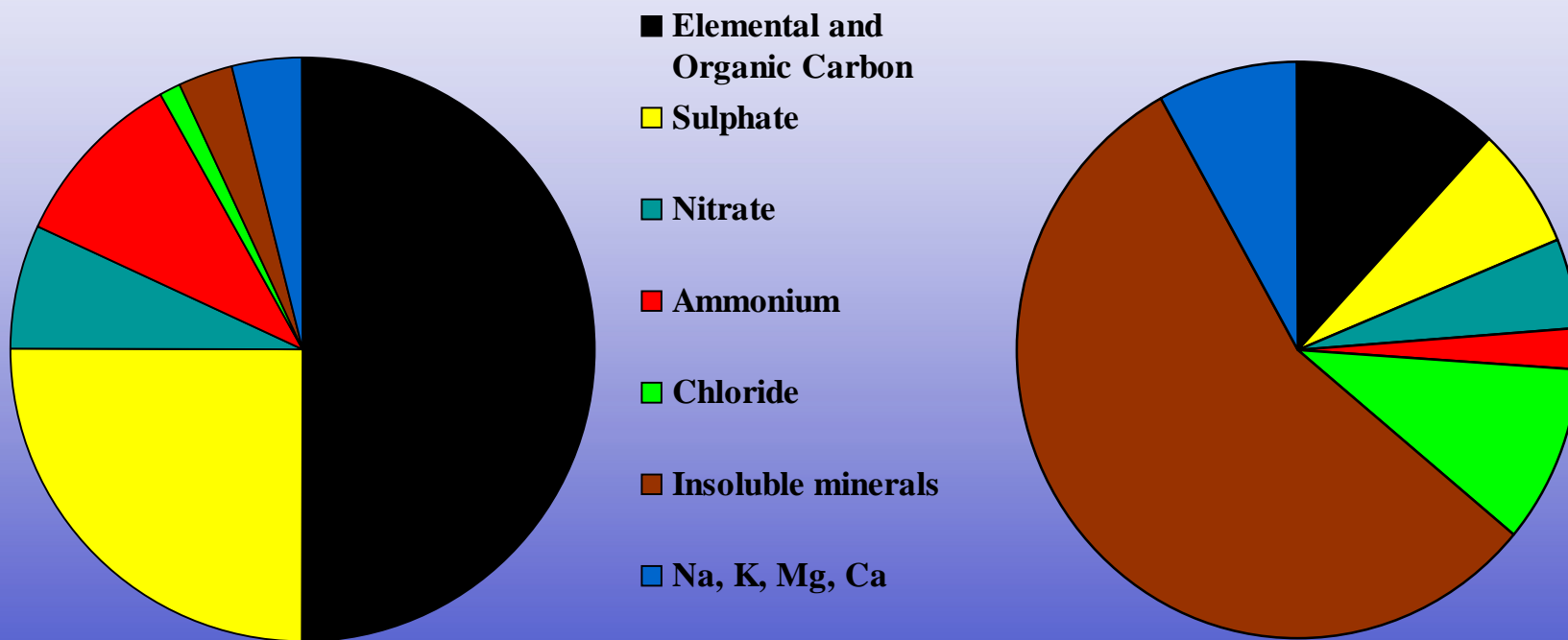
“Partisol” sampling of fine and coarse aerosols



Chemical composition : an example of its dependence on aerosol size

Fine fraction ($PM_{2.5}$)

Coarse fraction ($PM_{2.5}$ - PM_{10})

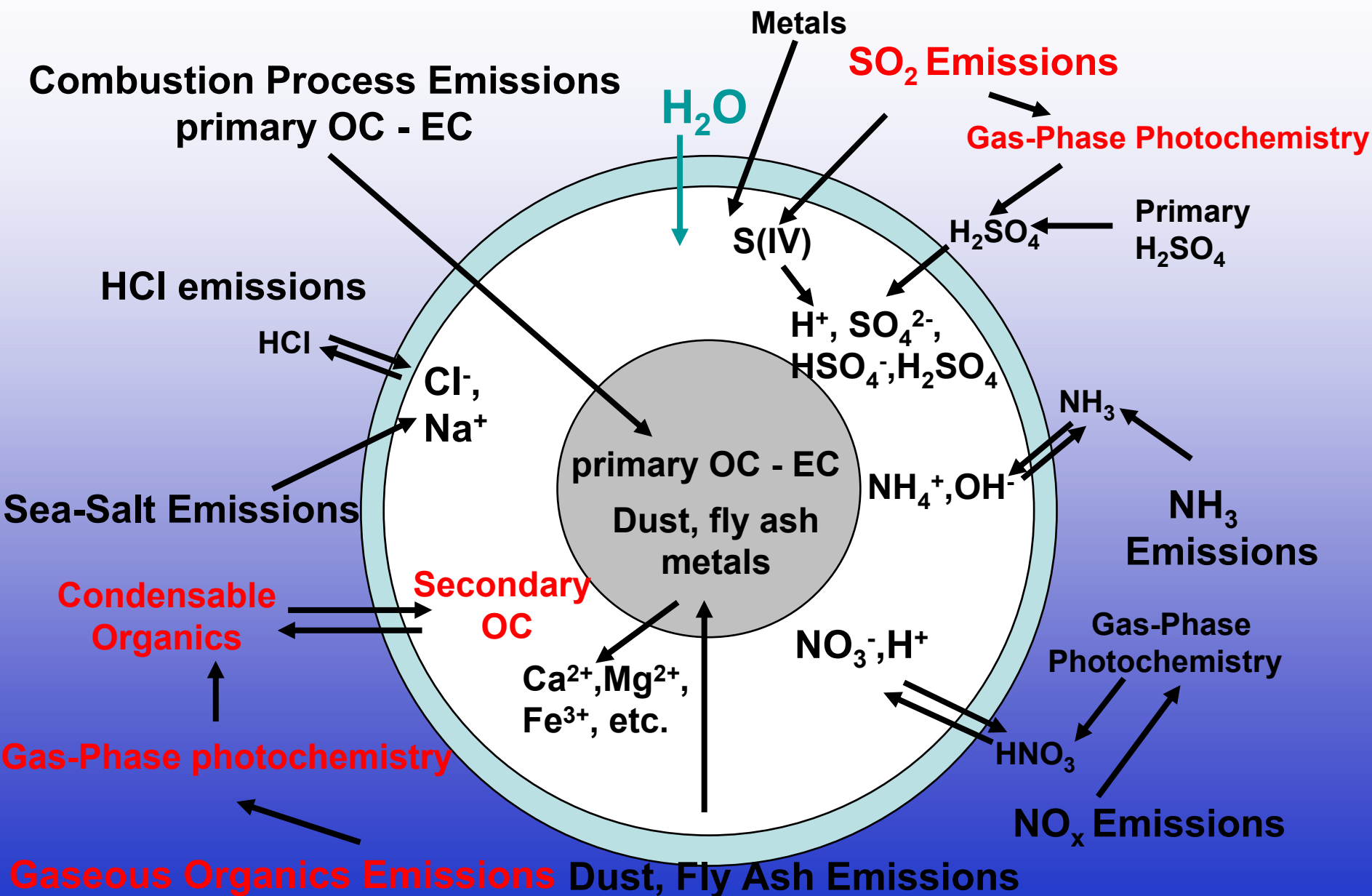


Field campaign in UK, 1997

Repartitioning of the components

- **Solid core of soot and/or insoluble minerals + solid inorganic and organics**
- **Water-soluble fraction** composed of :
 - Inorganic compounds (salts)
 - Hydrophilic organics (polar compounds)
- **Water-insoluble fraction** mainly composed of **hydrophobic organics**
- Uncertainties on repartition : layers ? “Islands” ?

Chemical composition

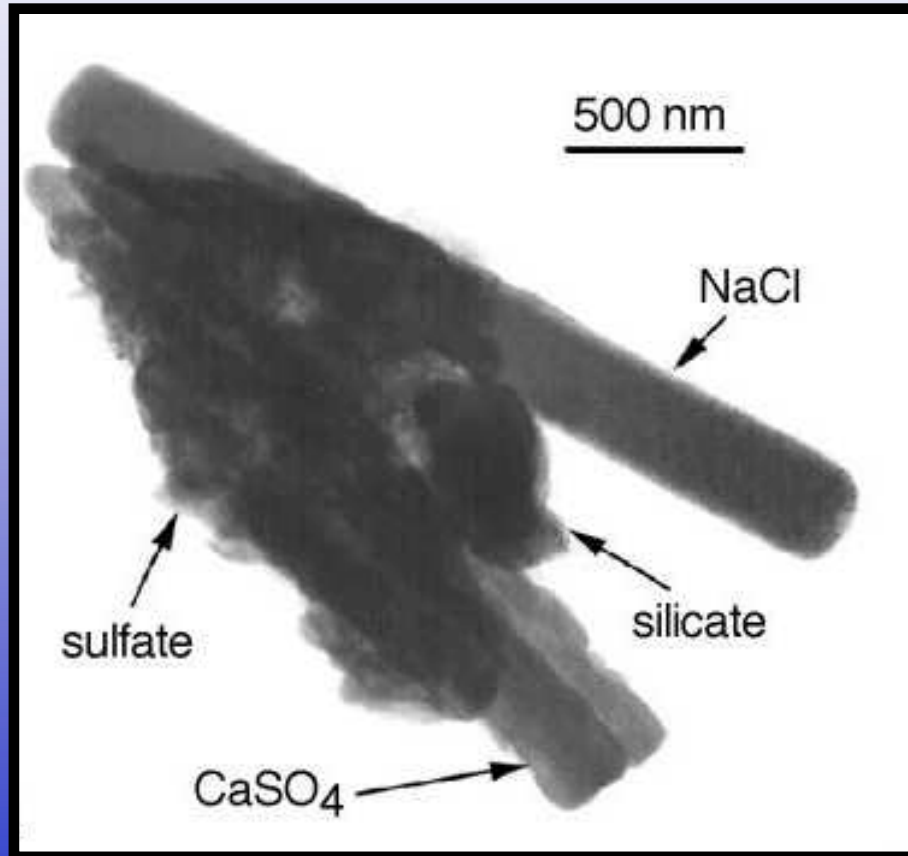


Chemical mixing

- External mixing : particles from different sources remain separated, i.e. not attached to each others
- Internal mixing : the various chemical components are mixed within a single particle. The more aged the air mass is, the more the degree of internal mixing will increase
- In the atmosphere, intermediate state, both internal and external mixing

Chemical mixing

Internal mixture of presumably terrestrial silicate and anhydrite with sea salt



Chemical mixing

External mixture of soot, crustal particles and coal ash

