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Size Distributions of HULIS in Ambient Aerosols and Fresh Biomass Burning Aerosols in South China

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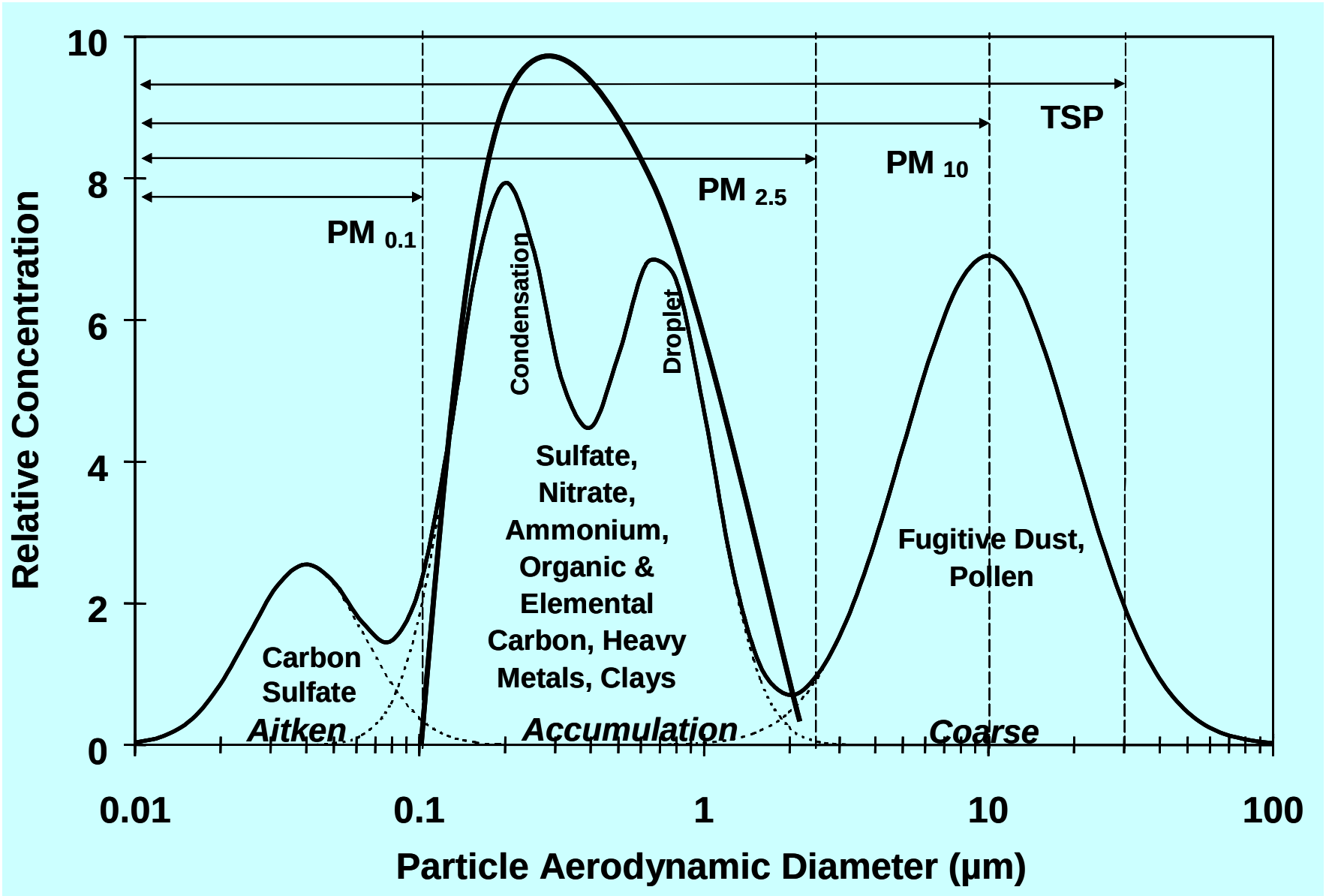
HUmic LIke Substances (HULIS)

HULIS consists of a complex, unresolved mixture of water-extracted organic compounds comprising of polycyclic ring structures with hydrocarbon side chains, and hydroxyl, carboxyl and carbonyl groups.

(Graber and Rudich, 2006)

- Similar to terrestrial and aquatic humic and fulvic acids in UV, FTIR and NMR characters
- **Water-soluble**
- **Of polyacidic nature**
- **Hydrophobic**
- molecular weight: 200 ~ 1000 (depend on method)


10
8
6
4
2
0
Relative Concentration
TSP
PM 10
PM 2.5
PM 0.1
Condensation
Droplet
Sulfate,
Nitrate,
Ammonium,
Organic &
Elemental
Carbon, Heavy
Metals, Clays
Fugitive Dust,
Pollen
Carbon
Sulfate
Aitken
Accumulation
Coarse
0.01
0.1
1
10
100
Particle Aerodynamic Diameter (µm)

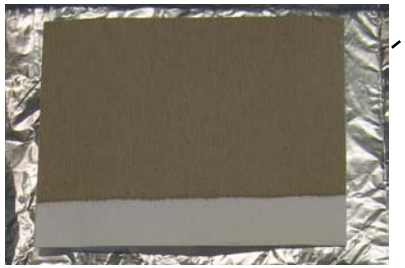
Analytical Methods for HULIS Isolation and Detection Reported in the Literature

Studies	Extraction	Separation	Detection
Zappoli et al., 1999	water extraction	Size exclusion chromatography	UV-Vis
Decesari et al., 2000	water extraction	Ion excahnge chromatography	UV-Vis, TOC, H-NMR
Varga et al., 2001	water extraction	solid-phase extraction cartridge	TOC
Mayol-Bracero et al., 2002	water extraction	Ion excahnge chromatography	TOC
Limbeck et al., 2005	water extraction	SPE+ ion exchange chromatography	TOC
Emmenegger et al., 2007	water extraction	SPE+ Size Exclusion Chromatography	ELSD
Feczko et al., 2007	water extraction	solid-phase extraction	FIA-SAX, TOC
Krivacsy et al., 2008	water extraction	solid-phase extraction	UV-Vis, TOC

Quantity of HULIS is operationally defined by an isolation method.

Isolation: Solid Phase Extraction (SPE)

(Method by Varga et al., 2001, with minor modification)

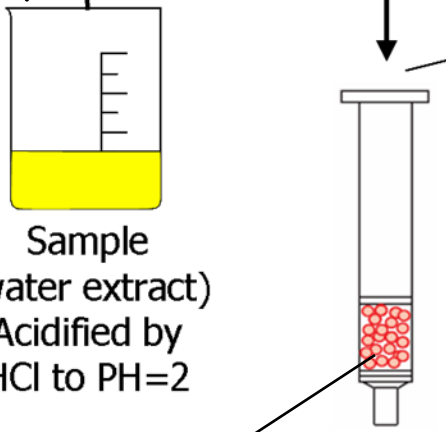


Particles on quartz fiber filter

Purpose:

Remove: inorganic ions &low MW organic acids

Pre-concentrate



Sample (water extract) Acidified by HCl to PH=2

TOC analysis

Rinse with water after sample passed through (collected with effluent together)

Elution with methanol (adjust PH=8.5-9 by NH_4OH)

Eluate

Dryness with N_2

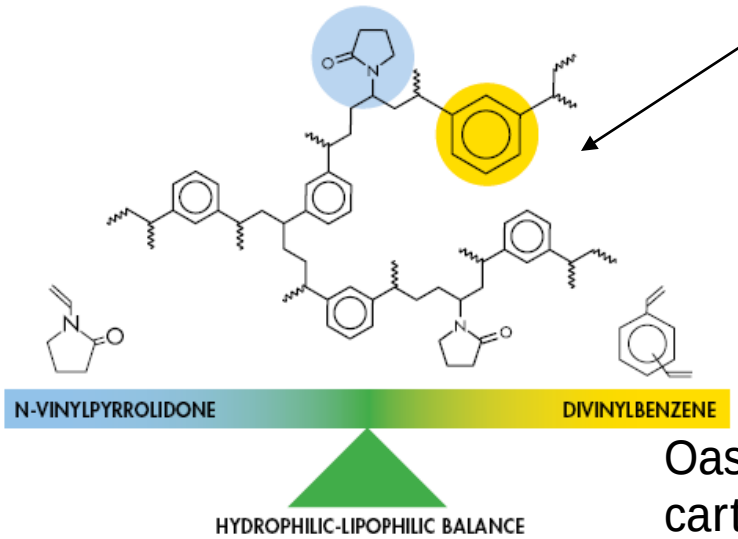
Dissolution in water

ELSD

IC

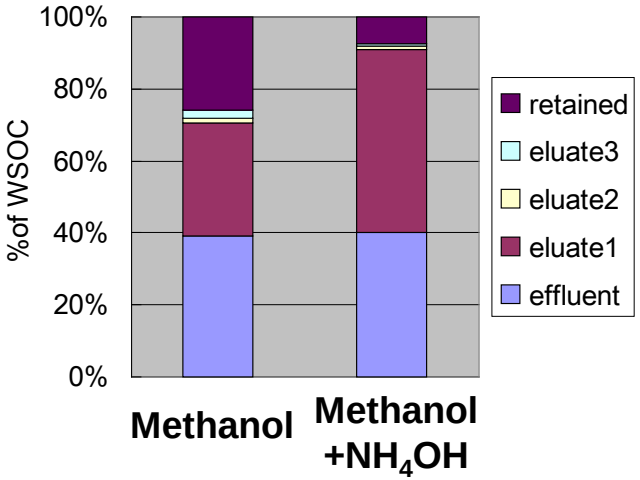
EFFLUENT

TOC analysis

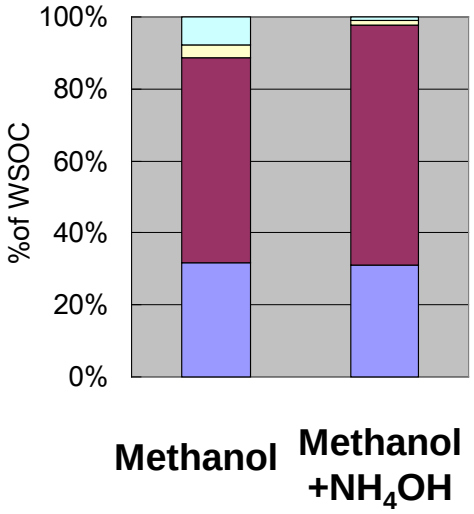


Oasis-HLB SPE cartridge

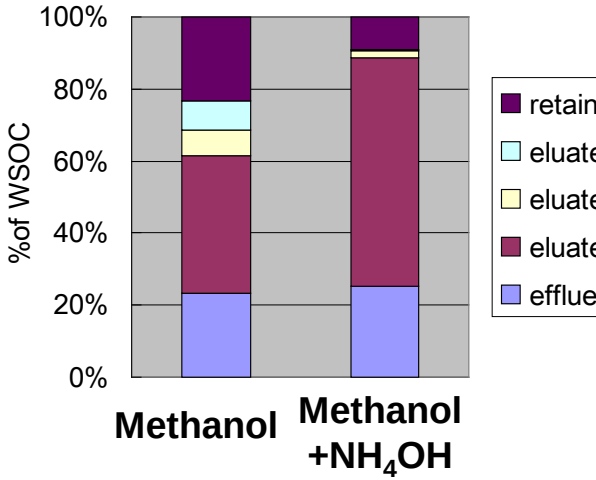
Methanol+NH_4OH elutes more HULIS than methanol alone



Sample #1



Sample #2



Sample #3

Remarks:

Carbon content determined by ECOC analyzer

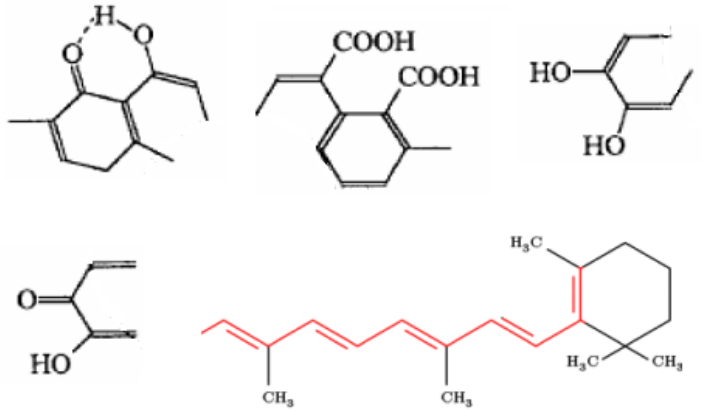
Eluate1: 1.5ml solvent

Eluate2: 1.5ml solvent after eluate1

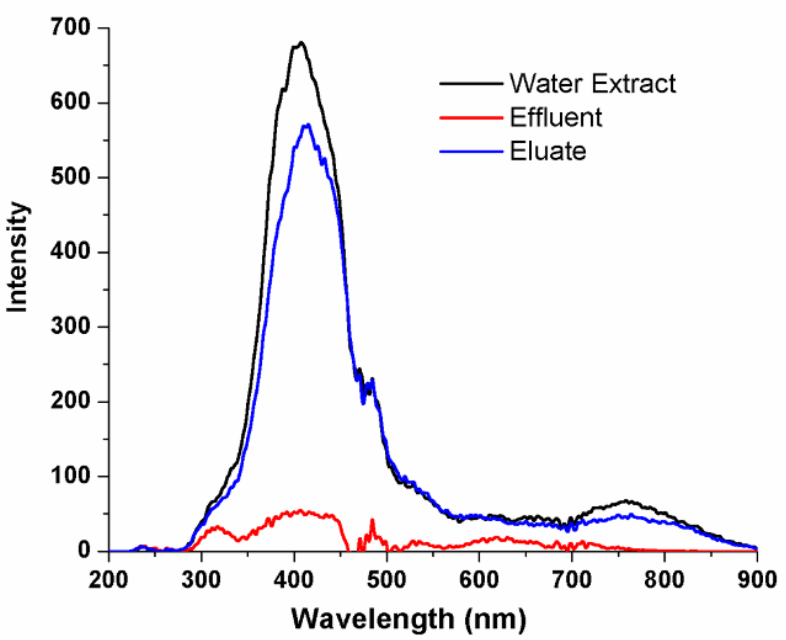
Eluate3: 1.5ml solvent after eluate2

Retained: Retained on SPE cartridge after 3rd elution

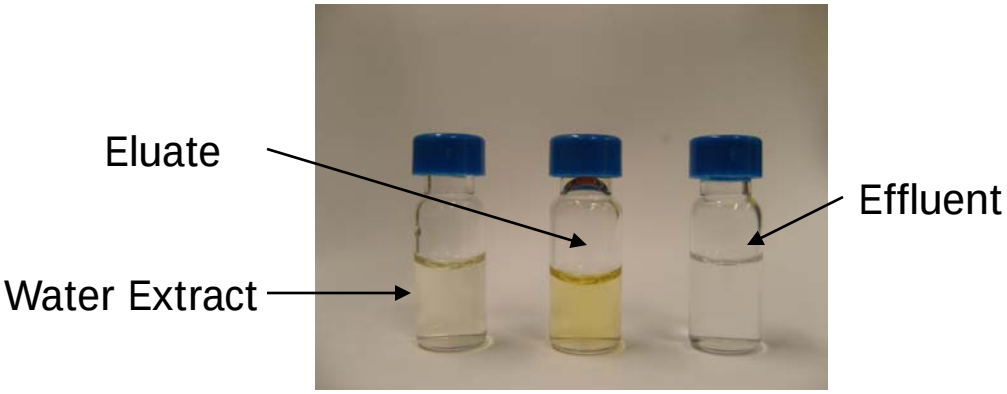
Fluorescence property is retained in the methanol/NH4OH eluate (HULIS fraction)



- presence of poly-conjugated structures



Excitation wavelength 235nm

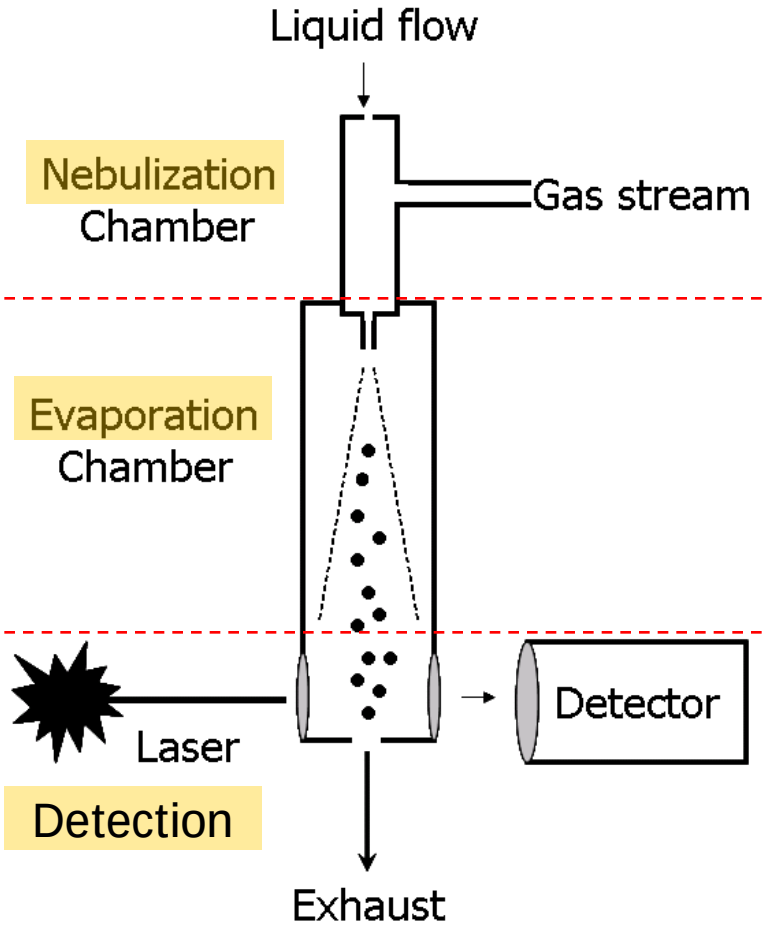


- Over 85% of fluorescence active compounds were collected in the eluate.

ELSD Detection

(Emmenegger et al., EST, 2007)

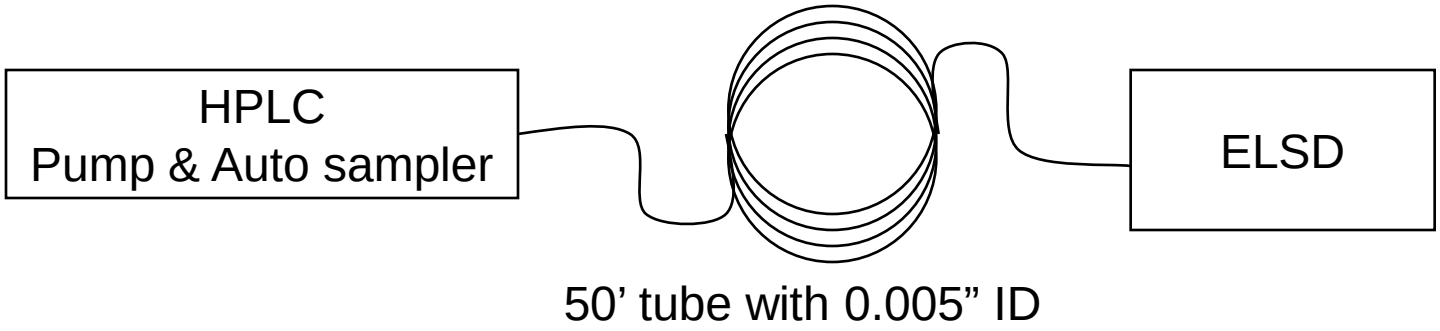
Evaporative Light Scattering Detector



1. **Nebulization:** The liquid passes through a nozzle, mixes with nitrogen gas to form a dispersion of droplets.
2. **Evaporation:** The droplets pass through a heated "drift tube", where the solvent evaporates, leaving a fine mist of dried particles in solvent vapor.
3. **Detection:** The sample particles pass through a cell and scatter light from a laser beam, generating an electrical signal.

Capable of quantifying mass concentrations of non-volatile analytes of unknown chemical structures.

Direct injection to ELSD

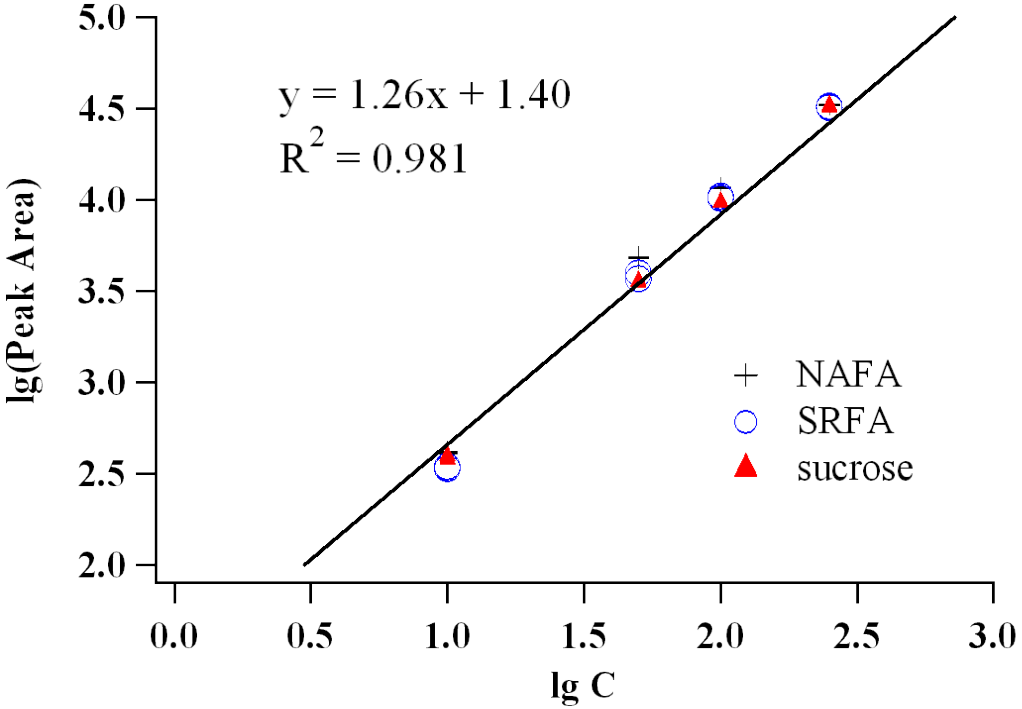


- Mobile phase: 20% ACN & 80% H_2O, FR: 0.6 mL/min
- ELSD nebulizer N_2 FR: 1.5 L/min

  drift tubing temperature: 90ºC

  RT(DT): 0.6-0.7 min

Calibration curve of ELSD



- **ELSD response is based on mass, not on optical or structural characteristics of an analyte.**
- **Widely used in the field of quantifying unknown mixtures lacking appropriate quantification standards**

HULIS can be determined by ELSD with respect to reference Fulvic acid. The detection limit is about 9 ppm (in solution).

Evaporation in ELSD removes LMW acids

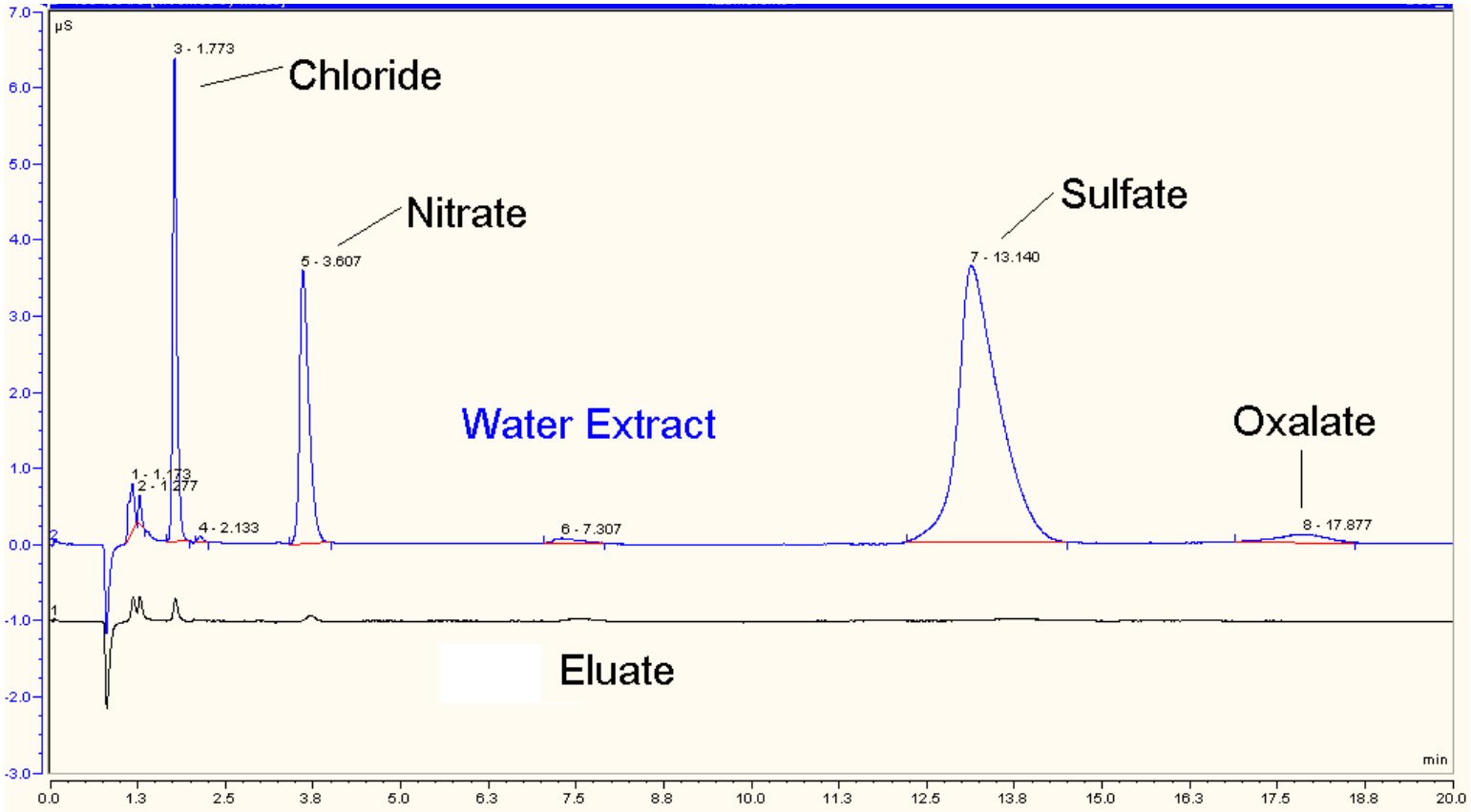
TABLE 1. List of Low Molecular Weight Compounds That Were Separated from HULIS Either during the SPE Step or in the Thermodenuder Part of the ELSD[a]

	separated from HULIS by	
compound	SPE	evaporation in ELSD
C1−C6 monocarboxylic acids		*
oxalic acid	*	
succinic acid		*
malonic ac id	*	
gluatric acid		*
adipic acid		*
D,L-malic acid	*	
4-hydroxybenzoic acid		*
citric acid	*	
D,L-lactic acid		*
Phenol		*
trifluoroacetic acid		*
ammonium nitrate	*	
ammonium sulfate	*	

[a] An asterisk indicates which compound is separated from HULIS during which step.

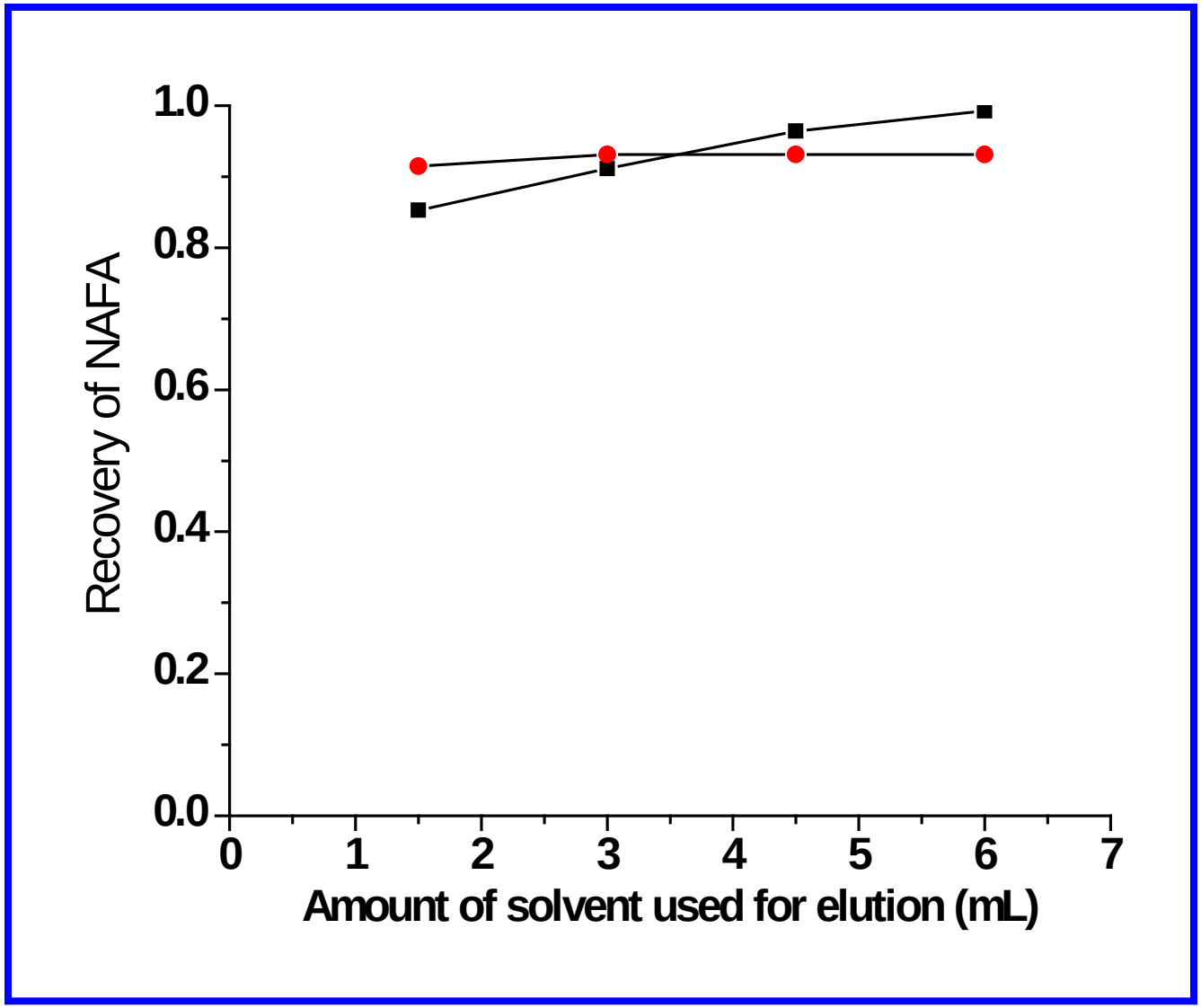
(Emmenegger et al., 2007, EST)

Most of the inorganic ions are removed by SPE



- Cl^-&SO_4^{2-} : >99%
- NO_3^- : >98%

Recovery test using NAFA and SRFA



Preliminary Results

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Ambient sampling

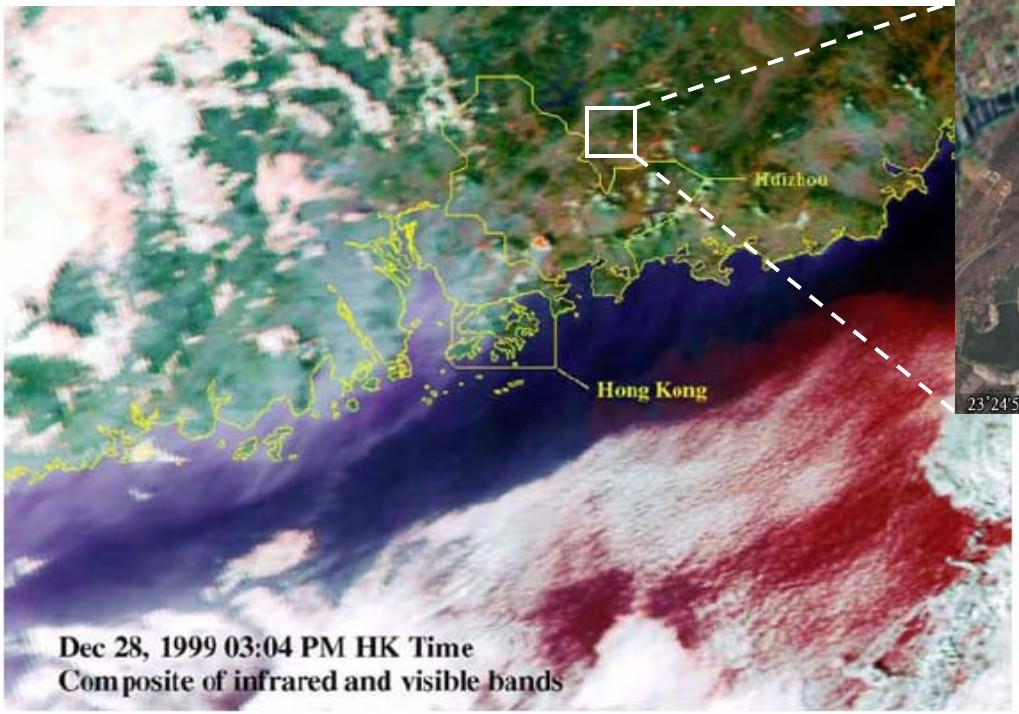


FIGURE 1.Satellite image taken around 1500 LST on 28 December 1999, which shows the movement of the smoke and haze. The red spots over land correspond to the hill fires. (This figure is reproduced from Fung et al., 2005)

114.46˚E, 23.43ºN

～150 km NW to Hong Kong

A small town surrounded by farmland of rice and sugarcane

Biomass burning samples

Samples

- Ambient samples
  - 5 sets of $PM_{2.5}$ high-vol samples collected on quartz fiber filter substrate.
    - (HULIS, ECOC, WSOC, major ions)
  - 5 sets of $PM_{2.5}$ mid-volume samples collected on Teflon and quartz fiber filters.
    - (mass)
  - 5 sets of MOUDI samples (0.056-18 μm)
    - (HULIS, ECOC, WSOC, major ions)
- Biomass burning samples
  - 3 sets of samples from rice straw burning smoke ($PM_{2.5}$ and MOUDI)
  - 3 sets of samples from sugar cane leave burning smoke ($PM_{2.5}$ and MOUDI)

HULIS abundance

Sample type		$PM_{2.5}$ ($\mu g/m^3$)	HULIS ($\mu g/m^3$)	HULIS/WSOM
	1	143.5	18.1	57%
Biomass burning	2	150.3	16.8	43%
Influenced	3	40.2	5.9	67%
Ambient	4	54.6	6.1	61%
	5	136.2	12.1	48%
Mean ± std		105 ± 53	11.8 ± 5.8	55±10%
Sugarcane burning (n=3)		2921±617	221±50	31±2%
Ricestraw burning (n=3)		9537±839	1178±246	28±1%

WSOM=WSOC*2.1 (based on Kiss et al., 2002)

HULIS abundances elsewhere

Type of sample	Method	HULIS ($\mu g/m^3$)	HULIS /WSOM	Reference
Po Valley, Italy, polluted rural site,	Water extracted, SEC, UV-VIS detection	0.6～2.5	19～50%	Zappoli et al. 1999
Amazon, rural site, forest fire affected	Water extracted, IEC, TOC	1.52～27.9	14～29%	Mayol-Bracero et al., 2002
K-puszta, background rural	Water extracted, SPE, TOC	4.4 (winter) 3.2 (summer)	34～65%	Kiss et al., 2002
Six background site in Europe	Water extracted, SPE, FIA-SAX, TOC	0.076～1.77 (yearly mean)	8.1～22%	Feczko et al., 2007
New Zealand, marine urban site	Water extracted, SPE, UV-VIS detection, TOC	0.46～10.34	31～46%	Krivacsy et al., 2008

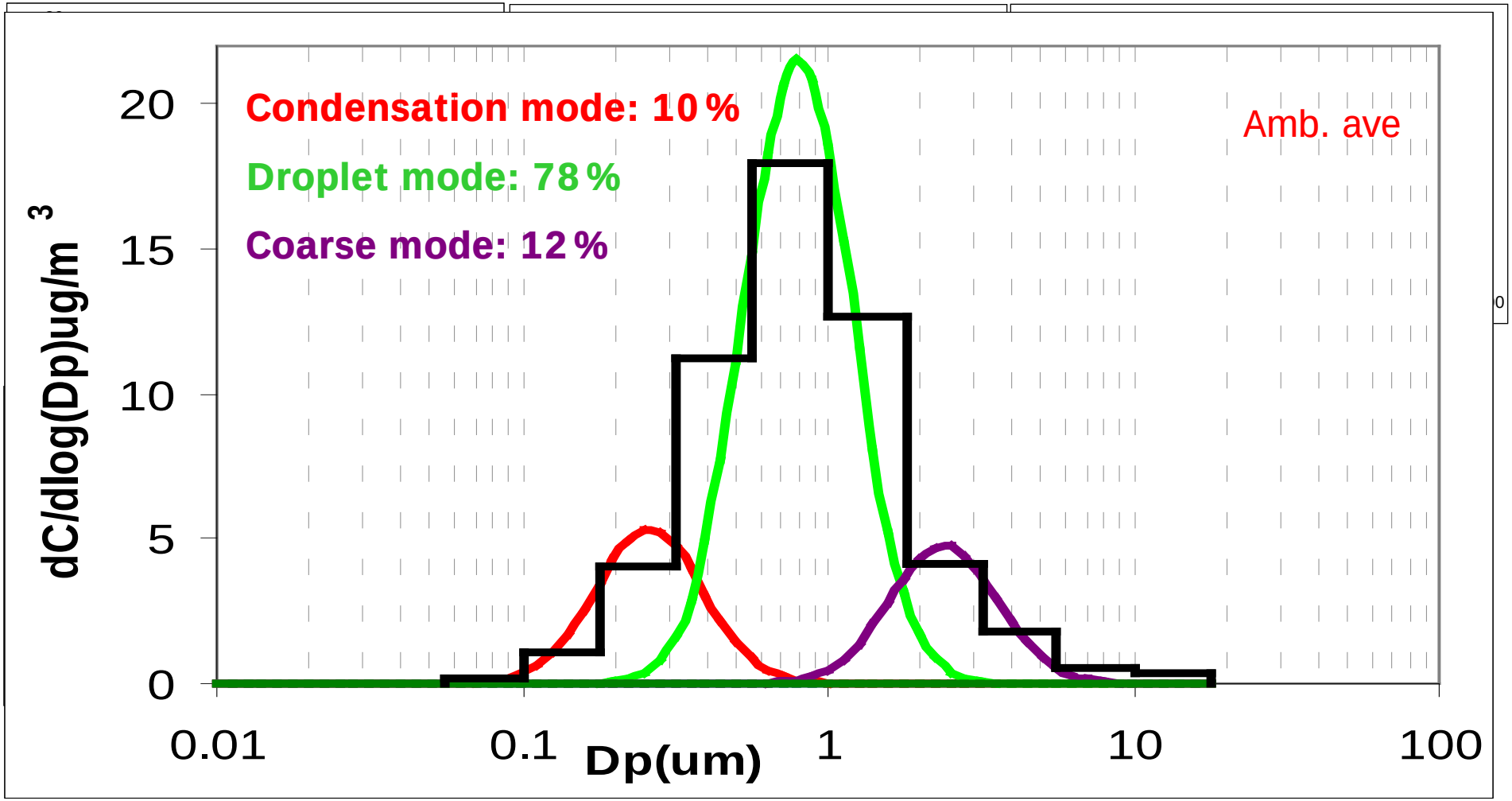
WSOM=WSOC*2.1, HULIS=HULIS-C*1.9 (based on Kiss et al., 2002)

HULIS/K^+ ratio in $PM_{2.5}$: Ambient >> fresh BB aerosols

Sample type		HULIS/K^+	HULIS-C/WSOC	HULIS-C/OC
	1	3.93	63%	30%
Biomass burning	2	4.92	47%	28%
Influenced	3	4.62	74%	32%
Ambient	4	4.09	67%	34%
	5	3.82	53%	24%
Mean ± std		4.3±0.5	61±11%	30±4%
Sugarcane burning (n=3)		0.54±0.11	31±2%	15±2%
Rice straw burning (n=3)		1.0±0.3	34±3%	15±2%

HULIS-C=HULIS/1.9 (based on Kiss et al., 2002)

HULIS ambient size distributions

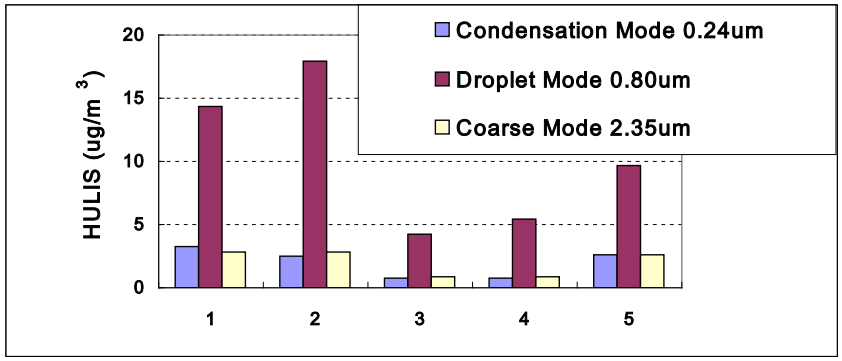


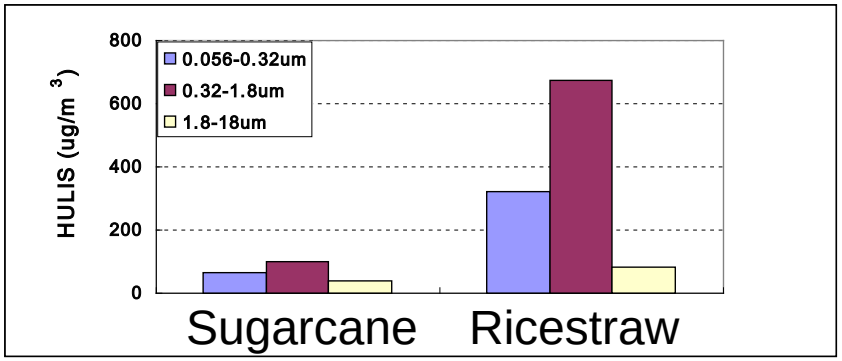
HULIS is dominant in droplet mode particles

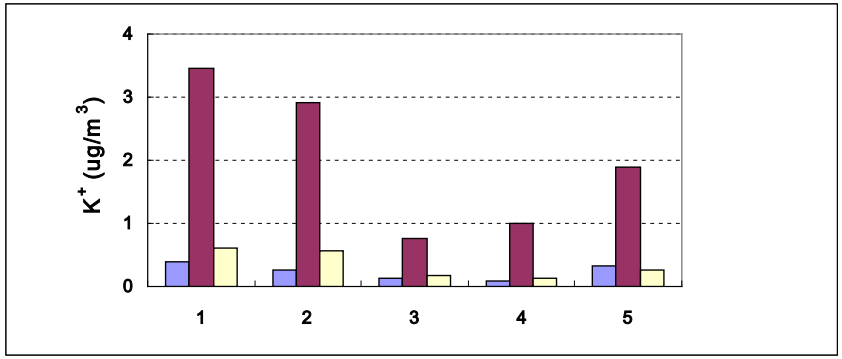
	Droplet HULIS /Total HULIS	Droplet HULIS-C /Droplet TOC	Droplet HULIS /Droplet TWSM
Ambient 01	70%	57%	25%
Ambient02	77%	64%	22%
Ambient03	72%	64%	19%
Ambient04	77%	65%	19%
Ambient05	65%	52%	22%
Ambient mean±std	72±5%	60±7%	22±3%

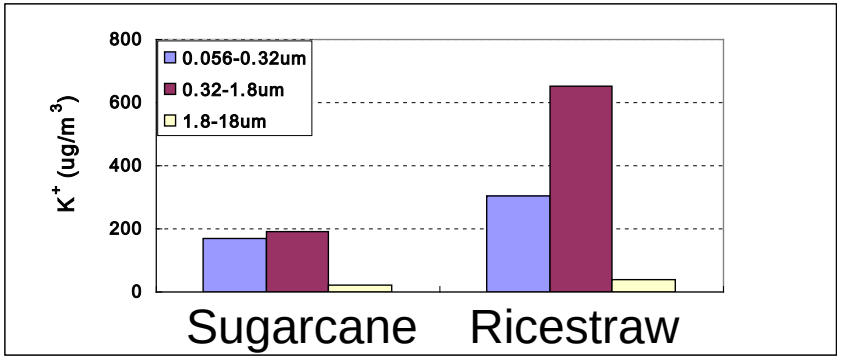
TWSM: total water soluble matters (TOC*2.1+inorganic ions)

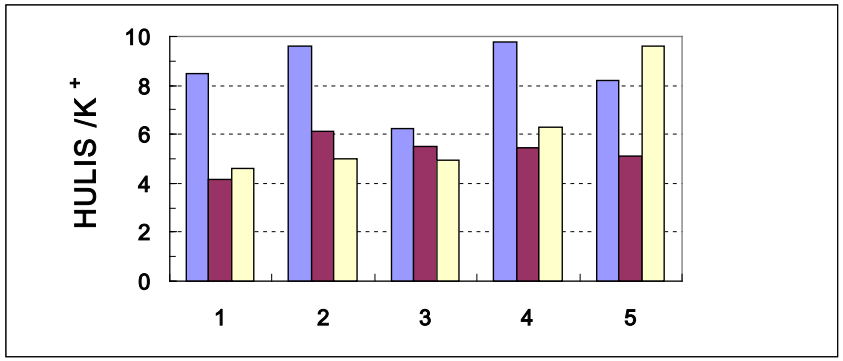
Ambient HULIS/K^+ in individual size modes exceed the corresponding ratios in fresh BB smoke.

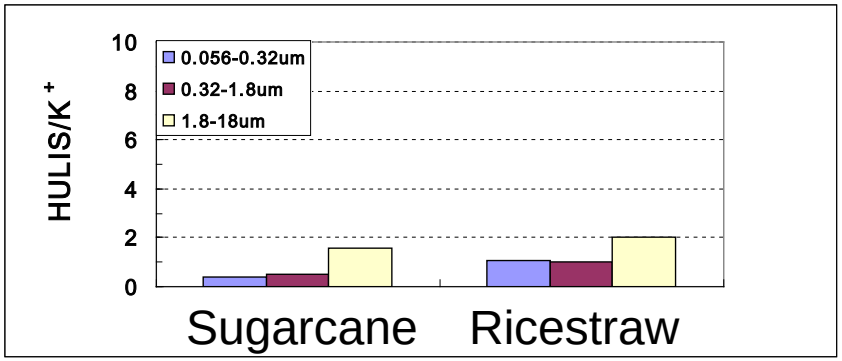












Summary

- HULIS is an abundant component of ambient particles in the PRD region, China.
  - ~55% of water soluble organic matter in $PM_{2.5}$
- Size distribution: the droplet mode HULIS accounts for ~78% of the total HULIS and contributes 60% of WSOC and 22% of water soluble organic matter in this mode, suggesting its important role in the cloud processing of aerosols.
- Biomass burning is a major source of HULIS in the PRD
  - ~30% of water soluble organic matter in fresh biomass burning particles was contributed by HULIS.
- The differences in HULIS/K^+ ratio between ambient and biomass burning samples indicated that there are additional sources of HULIS.
  - Condensation mode: Secondary HULIS from acid-catalyzed particle-phase reaction?
  - Droplet mode: Secondary HULIS formed from in-cloud processing?
  - Coarse mode: Soil-derived HULIS?

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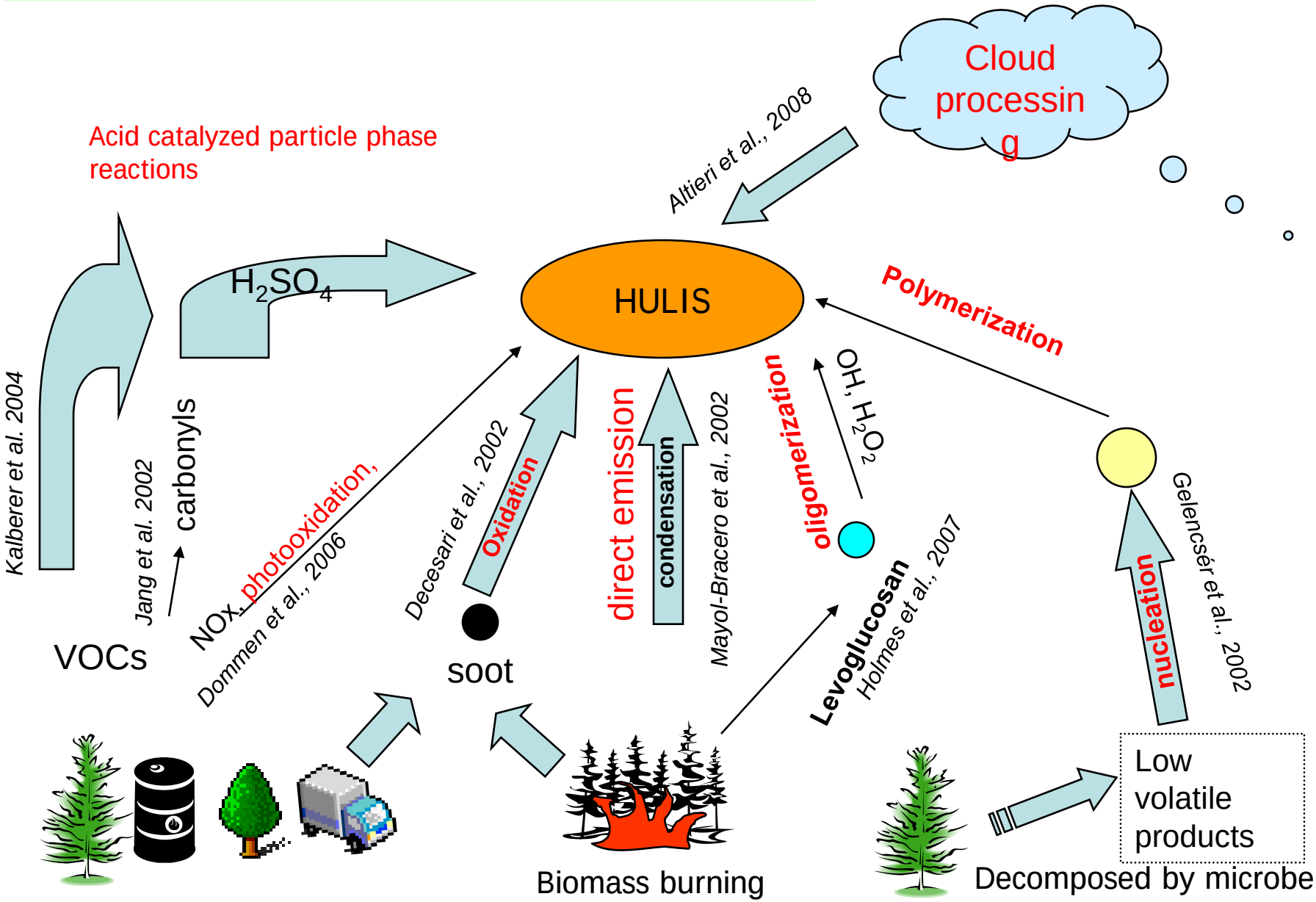
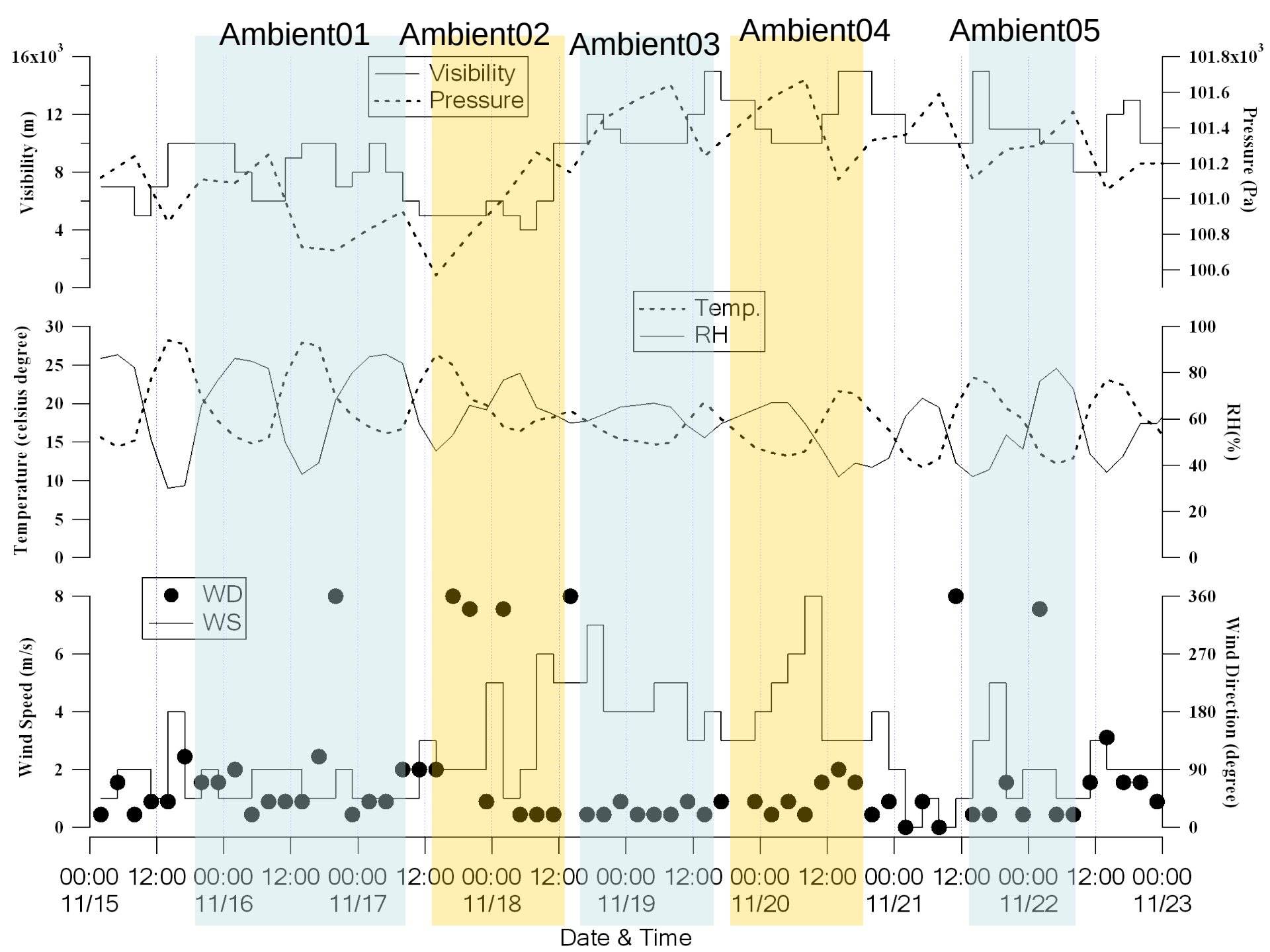
Acknowledgement

- Thank Dr. Lingyan He, Dr. Xiaofeng Huang and Eric Xue’s for helping with sampling.
- Funding support from Hong Kong Research Grants Council.

Suggested origins of HULIS

Modified from Andreas Gelencser presentation, Organic Speciation Workshop




Ambient01
Ambient02
Ambient03
Ambient04
Ambient05
Visibility
Pressure
Temp.
RH
WD
WS
Visibility (m)
Pressure (Pa)
Temperature (celsius degree)
RH(%)
Wind Speed (m/s)
Wind Direction (degree)
16x10^3
101.8x10^3
00:00 11/15
12:00
00:00 11/16
12:00
00:00 11/17
12:00
00:00 11/18
12:00
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Date & Time

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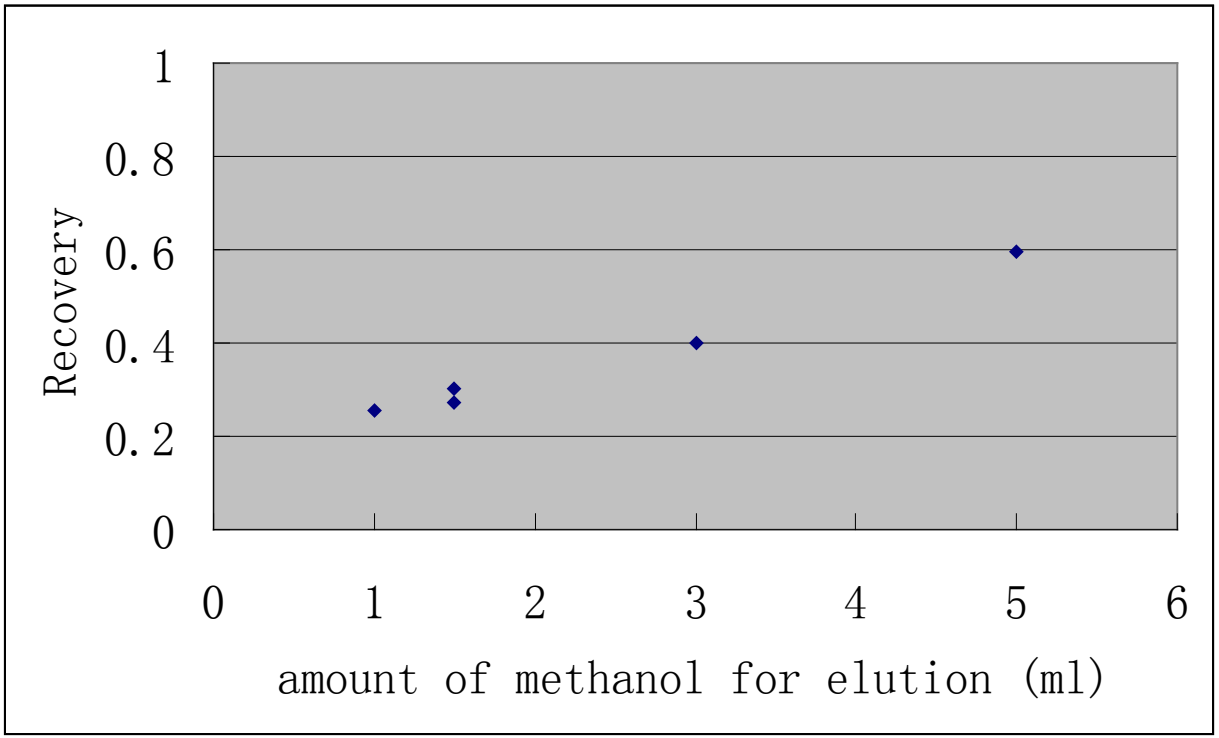
Test sample:
100ppm NAFA+Na_2SO_4 acidified by HCl

- More than 99% Cl^- & SO_4^{2-} are removed.
- But the recovery is poor by using only methanol for elution



Change the solvent to ACN can not help for more elution (16%)

Theory: Retention Factor [k] *vs.* pH for Acids, Bases, and Neutrals