Dry depostion monitoring

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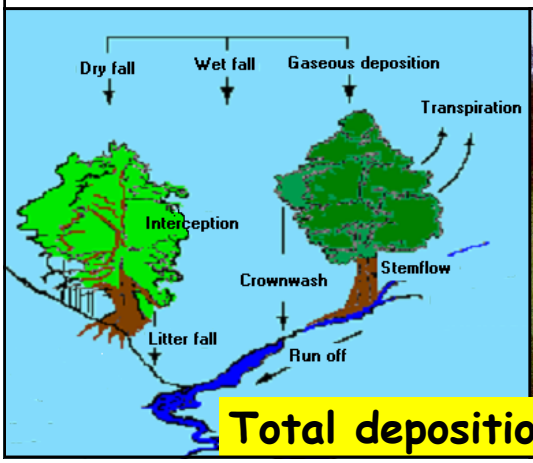
Fundamental items of dry deposition

- Monitoring sites
- Monitoring frequency

Priority of chemical species of dry deposition

Monitoring sites

Should be done at the same site used for wet deposition monitoring



Total deposition = wet + dry

Monitoring frequency

1. Automatic Monitor: hourly

2. Filter Pack Monitor:

Expected

Every Week → 12 months → 1 year

acceptable

Daily → 12 months → 1 year

Biweekly → 12months → 1 year

Priority chemical species

First priority:

SO_2, O_3, NO, NO_2 (Urban)

Particulate mass conc.

Second priority:

NO_2 (rural and remote)

HNO_3, NH_3,

Particulates (SO_4^{2-}, NO_3^-, NH_4^+, and Ca^{2+})

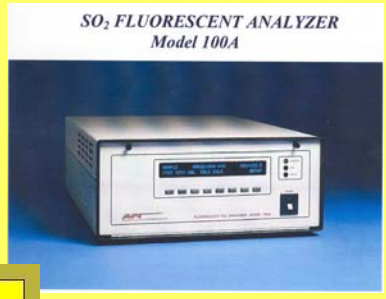
Automatic Monitors

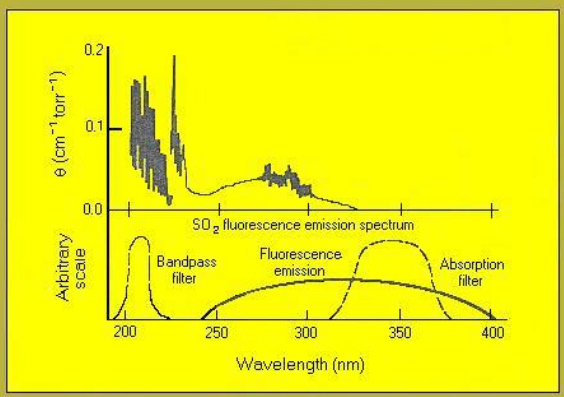
Monitor: SO_2, NO, NO_2(urban), O_3, and PM

Methods:

SO_2	Ultraviolet fluorescent (UVF)
NOx	Chemiluminescence detection (CLD)
O_3	Ultraviolet photometry (UVP)
$PM_{2.5}$	Dichotomous sampler β-ray absorption TOEM

SO_2 Monitor





$SO_2 + h\nu\ 1 \longrightarrow SO_2^*$ (1)

$SO_2^* \longrightarrow SO_2 + h\nu\ 2$ (2)

$SO_2^* \longrightarrow SO + O$ (3)

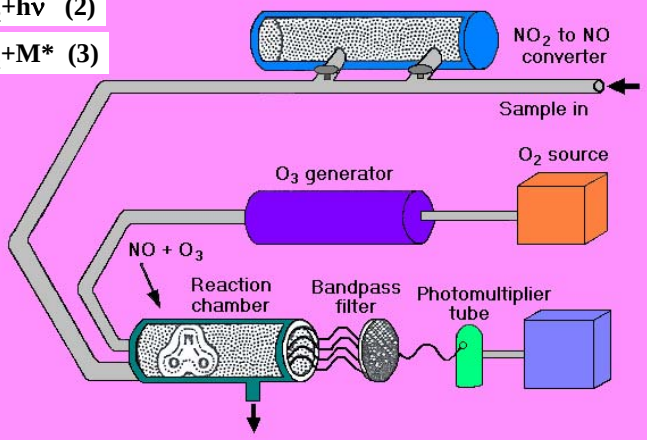
$SO_2^* + M \longrightarrow SO_2 + M^*$ (4)

NO, NO_2 monitor (Chemiluminescence)

$NO + O_3 \longrightarrow NO_2^* + O_2$ (1)

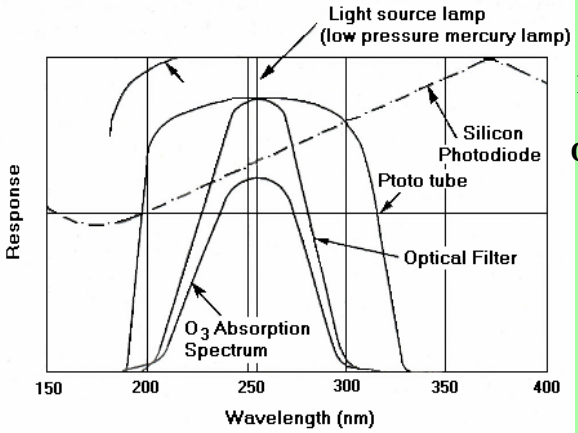
$NO_2^* \longrightarrow NO_2 + h\nu$ (2)

$NO_2^* + M \longrightarrow NO_2 + M^*$ (3)



Ultraviolet Photometric Method for O_3

- Measure absorbing quantity of ultraviolet rays near 254 nm by ozone



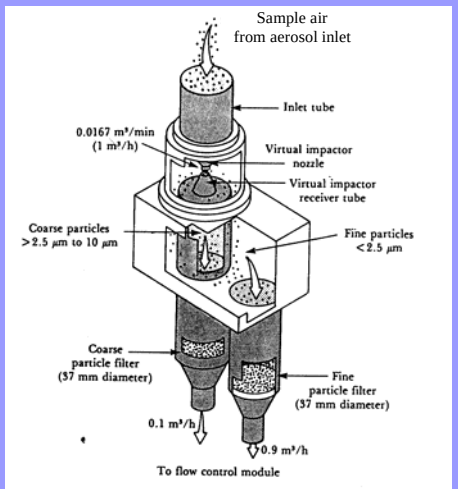
Beer-Lambert Law:

$$O_3(ppm) = \frac{10^6}{kL} \times \frac{760}{P} \times \frac{T}{273} \ln \frac{I_o}{I}$$

k = absorption coefficient
= 124 cm^{-1} atm^{-1}
I = transmitted light quantity
I_o= incident light quantity
L = cell length, cm
T = cell outlet temperature
P = cell outlet pressure

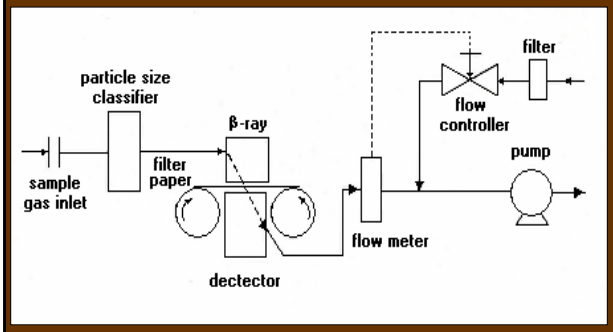
$PM_{2.5}$, PM_{10} Monitor

Dichotomous sampler



β-ray absorption

Absorption rate of β-ray increases in proportion to the mass of the substance when its quality remains constant and the ray at a low energy level irradiated the substance.

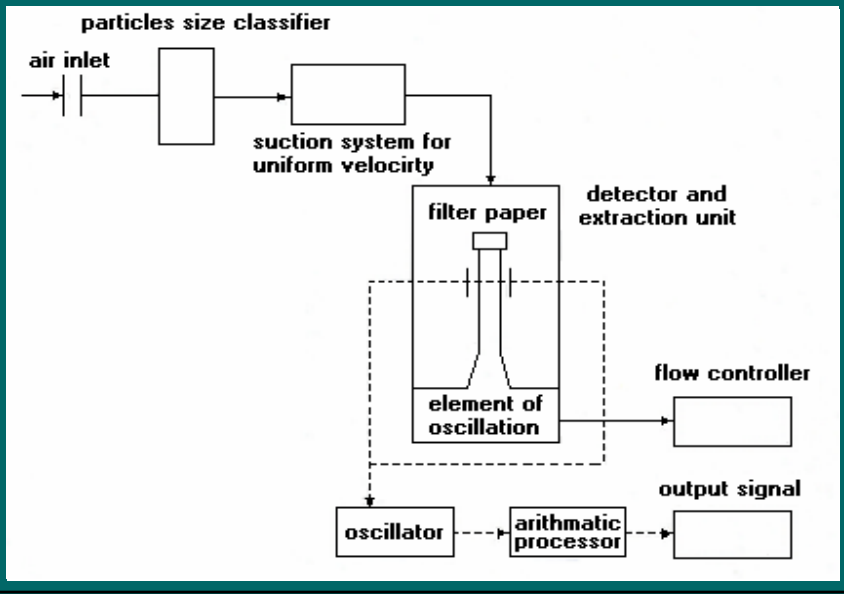


$$I = I_o \exp\left(-\frac{\mu_m}{X_m}\right)$$

$$X_m = \frac{1}{\mu_m} \ln\left(\frac{I_o}{I}\right)$$

I = β-ray intensity transmitted through filter and particulate,
I_o= β-ray intensity transmitted only through filter,
μ_m= mass absorption coefficient (cm^2/g), X_m= mass of particulate matter (g/cm^2)

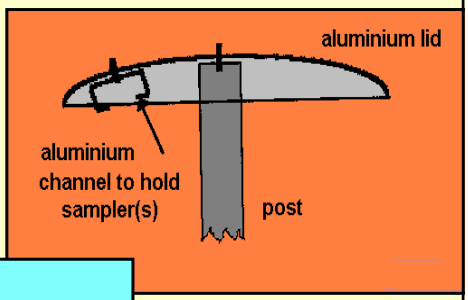
TOEM Method



Passive Sampler

To monitor gases:

SO_2, NO_2, O_3 and NH_3



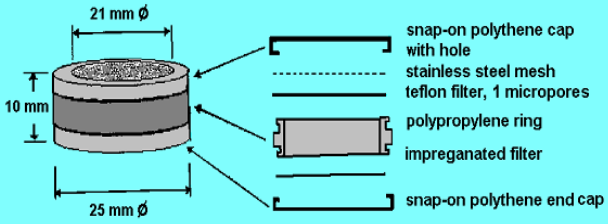


Diagram from Ayers et al, Department of Air Research, CSIRO

Assembly of Filter

Gases	Absorbent	Component analyzed	Analyzer
SO_2	NaOH	Sulphate	IC
NO_2	Ethylene glycol	Nitrite	SP with FIA
HN_3	Citric acid	Amonium	IC

IC - Ion Chromatography

SP with FIA - Spectrophotometry Using flow injection analysis

Fick's Law: $M = D \frac{A}{L} Ct$

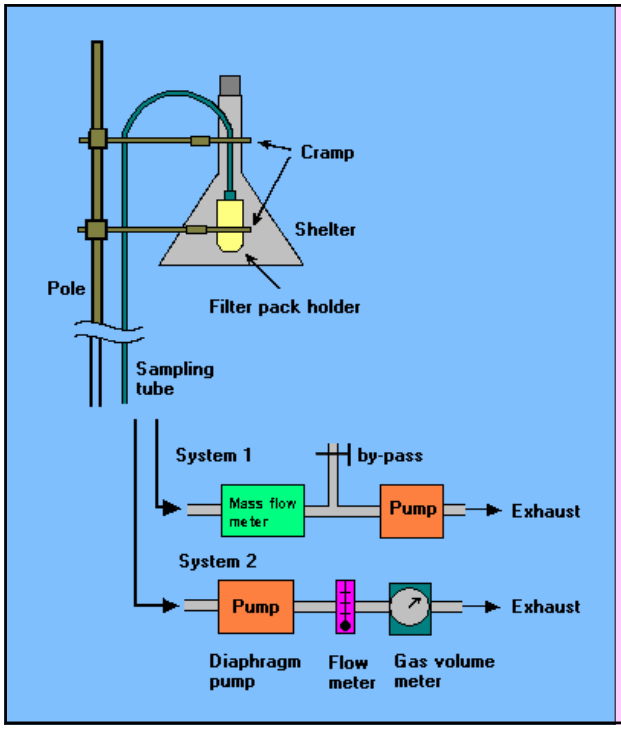
- M = total mass of gas transferred (ng)
- D = diffusion coefficient (m^2/s)
- L = Length of the diffusion path (m)
- A = cross sectional area of diffusion path (m^2)
- C = ambient concentration of contaminant (ng/m^3)
- t = time of exposure to contaminated air (s)
- D = 1.32×10^{-5} m^2/s and A/L = 41.2/m for CSIRO sampler

Filter Pack Method in EANET

To monitor:

Gases- SO_2, HNO_3, HCl, NH_3

Particulate Components– SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+



Sampling height-
3 m above ground

Obstacles nearby
Then- set up higher than 3 m

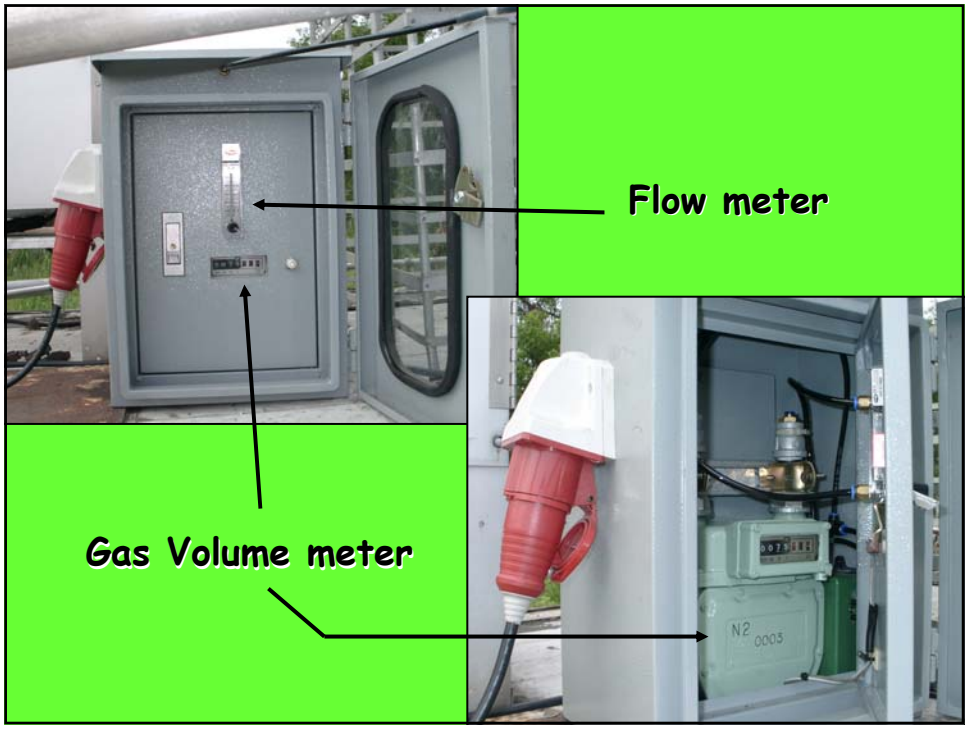
or above the obstacles

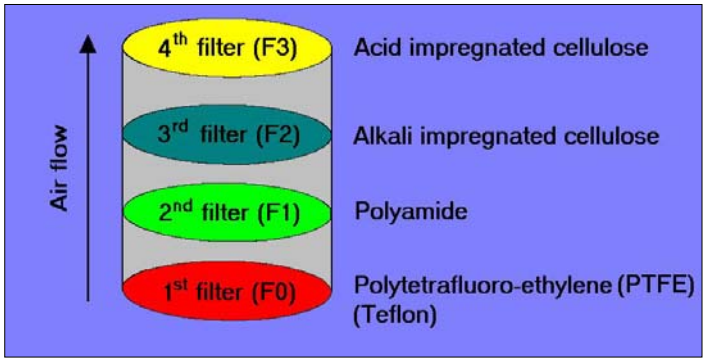
Flow Rate- 1 L/min

If Low conc.-
use 2 L/min

Daily sampling-
use 15 L/min

System 1- for high altitute (mountain)





Stage	Reaction	Collected species
1	Filtration	Aerosol
2	Adsorption	HNO_3 Partial SO_2, HCl
	Neutralization by collected acid gases	Partial NH_3
3	Neutralization by 6%K_2CO_3+2%glycerin in water	SO_2, HCl
4	Neutralization by 5%H_3PO_4+2%glycerine in CH_3OH	NH_3

Preparation of Filter Pack

- Handle filters and extraction solutions in the lab. only under clean condition
- Always use disposable plastic gloves and tweezers when handling filters
- Always seal up the filters, especially impregnated one to avoid the contamination

NILU filter holder (4-stage open face)

Mounting a filter on a stage

Tightening a stage by And Exclusive torque

Sealed filter case

Sealed filter holder

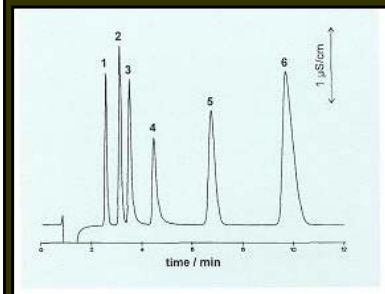
Extraction and Chemical Analysis

- Extraction - every month
- Chemical analysis - every month
- Chemical analysis - carried out as soon as possible after the extractions
- The extraction samples – shaking on a shaker or ultrasonic bath for 20 min
- Extraction and Chemical analysis of blank filter – carried out at the same time

Analyzed species and solvent for each stage

Stage	Species	Solvent
1	SO_4^{2-}, NO_3^-, Cl^-, Na^+, K^+, Ca^{2+}, NH_4^+,	Deionized water
2	SO_4^{2-}, NO_3^-, Cl^-, NH_4^+	Deionized water
3	SO_4^{2-}, Cl^-	0.05% H_2O_2
4	NH_4^+	Deionized water

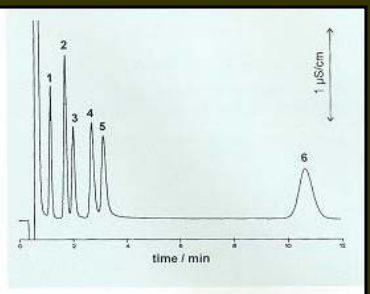
Analyzer: Ion chromatography (IC)



6.1010.000 IC Cation Column Metrosep Cation 1-2

Eluent	4 mmol/L tartaric acid; 1 mmol/L pyridine-2,6-dicarbonic acid
Full Scale	5 µS/cm
Flow	1.0 mL/min
Loop	10 µL
Sample	Standard in eluent

1	1 ppm Lithium	4	10 ppm Potassium
2	5 ppm Sodium	5	10 ppm Calcium
3	5 ppm Ammonium	6	10 ppm Magnesium



6.1005.000 IC Anion Column PRP-X100

Eluent	2 mmol/L phthalic acid; 8% acetone; pH=5.0 (NaOH)
Full Scale	4 µS/cm
Flow	2.0 mL/min
Loop	100 µL
Sample	Standard in water

1	5 ppm Fluoride	4	10 ppm Bromide
2	5 ppm Chloride	5	10 ppm Nitrate
3	5 ppm Nitrite	6	10 ppm Sulphate

Ion Chromatography Report

Treatment of Blank

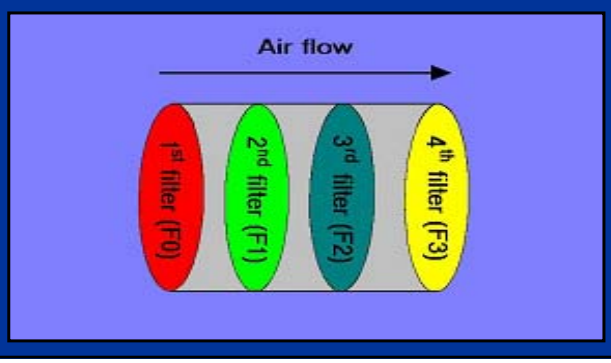
- Determine a blank value as median of 5 analytical results of blank filters

3
5
11 → Median value
12
20

- Chemical analysis of samples and blanks should be done each month
- When blank value > sample value
  → non-detected (N.D.)
- If samples are obviously contaminated
  → unrecorded data
- Samplings are stopped accidentally→sample rejected

Artifacts of filter pack

Increase of temperature during sampling period causes particulate collected on filter, ie. NH_4NO_3, NH_4Cl and NaCl to volatilize to gases, ie. NH_3, HNO_3, and HCl, and recollected on following filters.



Artifact of filter pack method

Artifacts of HNO_3

$NH_4NO_3(P) \rightarrow NH_3(G) + NHO_3(G)$

$NH_4NO_3(P) + H_2SO_4(P) \rightarrow NH_4SO_4(P) + HNO_3(G)$

$NaNO_3(P) + H_2SO_4(P) \rightarrow NaHSO_4(P) + HNO_3(G)$

Artifacts of NH_3

$NH_4NO_3(P) \rightarrow NH_3(G) + NHO_3(G)$

$NH_4Cl(P) \rightarrow NH_3(G) + HCl(G)$

$H_2SO_4(P) + NH_3(G) \rightarrow NH_4HSO_4(P)$

$NH_4HSO_4(P) + NH_3(G) \rightarrow (NH_4)_2SO_4(P)$

Artifacts of HCl

$NaCl(P) + HNO_3(G) \rightarrow HCl(G) + NaNO_3(P)$

$2NaCl(P) + H_2SO_4 \rightarrow 2HCl(G) + Na_2SO_4(P)$

$NH_4Cl(P) \rightarrow HCl(G) + NH_3(G)$

Calculation of Results

$$C_{Air} = \alpha(\text{net } C_{Sol})\left(\frac{V_{Sol}}{V_{Air}}\right)$$

$$\alpha = \frac{10^3}{M}; \qquad \text{net } C_{Sol} = C_{Sol,\,Sample} - C_{Sol,\,Blank}$$

C_{Air} : concentration in the air (nmol/m^3)
net C_{Sol} : net concentration in the solution (mg/L)
V_{Sol} : volume of the solution (ml)
V_{Air} : volume of the sampling air corrected at 20 °C, 1 atm (m^3)
M : molecular weight

Determination of Concentrations

Species	M	Equation
Aerosol		$C_{Air} = \alpha(\text{net } C_{Sol,\,F_0})\left(\frac{V_{Sol}}{V_{Air}}\right)$
SO_4^{2-}	96.06	
NO_3^-	62.01	
Cl^-	35.45	
Na^+	22.99	
K^+,	39.10	
Mg^{2+}	24.31	
Ca^{2+}	40.08	
NH_4^+	18.01	
SO_2	96.06 (SO_4^{2-})	$C_{Air} = \alpha(\text{net } C_{Sol,F_1} + \text{net } C_{Sol,F_2})(V_{Sol}/V_{Air})$
HNO_3	62.01 (NO_3^-)	$C_{Air} = \alpha(\text{net } C_{Sol,F_1})(V_{Sol}/V_{Air})$
HCl	35.45 (Cl^-)	$C_{Air} = \alpha(\text{net } C_{Sol,F_1} + \text{net } C_{Sol,F_2})(V_{Sol}/V_{Air})$
NH_3	18.04 (NH_4^+)	$C_{Air} = \alpha(\text{net } C_{Sol,F_1} + \text{net } C_{Sol,F3})(V_{Sol}/V_{Air})$

Form (Dry) January 2003 — Calculation of air concentration (Filter Pack)

Site name : Chiangmai — Site Classification : Rural

Name of Laboratory : KMUTT — Name of reporter : Sugrit Buddhirakkul

Sample no.		start		End		Ave. temperature		Air volume	correction
Jan-03		Date	Time	Date	Time	C		m3	m3
		30/12/2002	9:00	6/1/2003	9:00	20.9		10.08	10.22
particle		SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
F0(mg/l)	Sample	0.362	0.272	0.861	0.141	0.318	0.151	0.074	0.476
	Blank	0.212	0.131	0.154	0.046	0.153	0.064	0.061	0.241
	Net	0.150	0.141	0.707	0.095	0.165	0.087	0.013	0.235
Air conc. (nmol/m^3)		3.064	4.449	39.032	10.349	14.038	5.870	1.060	11.496
gas		SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
F1(mg/l)	Sample	0.423	0.415	1.450	0.089				
	Blank	0.231	0.311	0.626	0.031				
	Net	0.192	0.104	0.824	0.058				
F2(mg/l)	Sample	1.428		0.41					
	Blank	0.062		0.053					
	Net	1.367		0.357					
F3(mg/l)	Sample				2.643				
	Blank				0.052				
	Net				2.591				
Air conc. (nmol/m^3)		SO_2	HNO_3	HCl	NH_3				
		31.754	3.281	65.178	287.844				

$C_{Air} = \alpha(\text{net } C_{Sol,F_0})\left(\frac{V_{Sol}}{V_{Air}}\right)$

$C_{Air} = \alpha(\text{net } C_{Sol,F_1} + \text{net } C_{Sol,F3})(V_{Sol}/V_{Air})$

M = 18

Data Report

Form (Dry) — **Results of air concentration analysis (Filter Pack)**

Site name : Chiangmai — **Site Classification : Rural**

Name of Laboratory : KMUTT — **Name of reporter : Sugrit Buddhirakkul**

Unit : nmol/m^3

Sample	Sampling period				Gas				Particle							
no.	Start		End		SO_2	HNO_3	HCl	NH_3	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
	Date	Time	Date	Time												
015	18/12/2000	9.55	25/12/2000	10.00	65.103	18.856	15.355	5.887	18.475	0.475	0.028	52.860	2.902	2.166	0.982	0.196
019	23/1/2001	9.00	6/2/2001	12.30	9.567	21.841	14.403	298.441	15.080	12.888	8.077	41.730	11.246	27.965	5.535	18.124
034	24/2/2001	9.20	3/3/2001	10.00	20.435	43.361	55.821	351.094	47.715	17.325	2.405	45.296	8.679	57.594	5.334	32.833
048	19/3/2001	9.30	26/3/2001	9.30	5.515	4.6	28.8	102.6	0.053	1.068	0.482	32.666	2.628	19.630	0.000	18.832
059	29/4/2001	8.00	6/5/2001	7.55	3.747	13.419	5.859	220.510	14.667	2.455	1.454	40.983	5.030	7.262	13.033	10.540
073	7/6/2001	9.10	14/6/2001	9.15	5.059	1.247	0.000	138.925	0.361	0.390	0.000	11.861	0.000	0.000	0.000	4.354
083	29/6/2001	9.26	6/7/2001	9.30	8.801	3.024	32.591	75.407	3.9	2.585	1.7	7.067	5.7	2.487	1.6	6.987
092	8/8/2001	9.00	15/8/2001	9.00	60.639	13.172	54.226	261.667	26.632	18.720	11.252	61.334	18.772	10.340	2.931	20.492
108	14/9/2001	9.00	21/9/2001	9.00	13.627	4.678	71.461	223.529	3.788	5.708	6.669	17.080	2.411	1.871	0.271	3.950