Traceability Issue in $PM_{2.5}$ and PM_{10}

Shankar G. Aggarwal, Ph.D.

CSIR-National Physical Laboratory, New Delhi-110 012, India

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(aggarwalsg@nplindia.org)

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REVIEW PAPER

Traceability Issue in $PM_{2.5}$ and PM_{10} Measurements

S. G. Aggarwal[1]*, S. Kumar[1], P. Mandal[2], B. Sarangi[1], K. Singh[1], J. Pokhariyal[1], S. K. Mishra[1], S. Agarwal[2], D. Sinha[3], S. Singh[1], C. Sharma[1] and P. K. Gupta[1]

[1]CSIR-National Physical Laboratory, New Delhi 110012, India

[2]Zonal Laboratory, CSIR-National Environmental Engineering Research Institute, New Delhi 110028, India

[3]Government Nagarjun Post Graduate Science College, Raipur 492010, India

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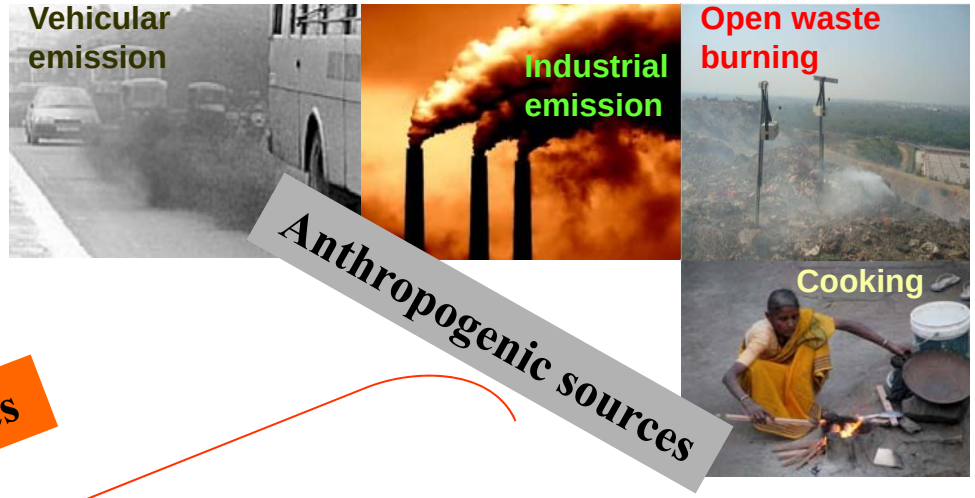
Abstract…

Abstract: Nowadays particle size and mass concentration measurements are the important parameter of the ambient air quality standards of several countries. The regulatory limits of mass concentration of particulate matter (PM) for the size classes of $PM_{2.5}$ and PM_{10}, i.e., particle sizes of less than or equal to 2.5 and 10 µm in aerodynamic diameter, respectively in air are defined on yearly and hourly time-weighted-average basis. However, these limits are different in different regulations of the countries. Both of the parameters relate with the human health, climate and other issues, therefore accurate and precise measurement of these parameters are very important. Despite this, so far not much work has progressed in national metrology institutes (NMIs) worldwide on calibration and traceability issue of PM measurements. In this paper in context of PM measurement traceability, we present systematically the (1) air quality regulation in different countries, (2) reference methods for size and mass measurements, (3) variation/error and limitations of PM measurements based on the current results in this study and previously published results, (4) current status of PM size and mass calibration facility, (5) expected uncertainty in PM measurements, (6) add-on uncertainty in other parameters of national ambient air quality standards due to PM measurements, (7) where does traceability of PM issue stand against other parameters of air quality standards and its impact on health and climate, (8) NMIs working on this issue, (9) status at Bureau International des Poids et Mesures (BIPM), France and (10) conclusion. The aim of this paper is to better understand the importance of international system of units (SI) traceability issue in PM measurements, so wherever and whenever it is measured, should be acceptable everywhere, and data should be comparable for improving air quality and thus the quality of life. Funding agencies should be aware of this issue, and accept the results from the principle investigators and team only when their results have the traceability link to SI. NMIs should make program to involve industries in gas and aerosol metrology work to fulfill the requirement of calibration and standards. The regulatory authorities/ministry should work together with NMIs to improve the data quality of ambient measurements. This will greatly help to better make the policies and decisions on the related impacts. These were also the ultimate goals of "one-day pre-AdMet workshop" organized at National Physical Laboratory, New Delhi, India on February 20th, 2013.

Focus…

1. Air quality regulation in different countries,
2. Reference methods for size and mass measurements,
3. Variation/error and limitations of PM measurements based on the current results in this study and previously published results,
4. Current status of PM size and mass calibration facility,
5. Expected uncertainty in PM measurements,
6. Add-on uncertainty in other parameters of national ambient air quality standards due to PM measurements,
7. Where does traceability of PM issue stand against other parameters of air quality standards and its impact on health and climate,
8. NMIs working on this issue,
9. Status at Bureau International des Poids et Mesures (BIPM), France,
10. Conclusion

Atmospheric aerosols…

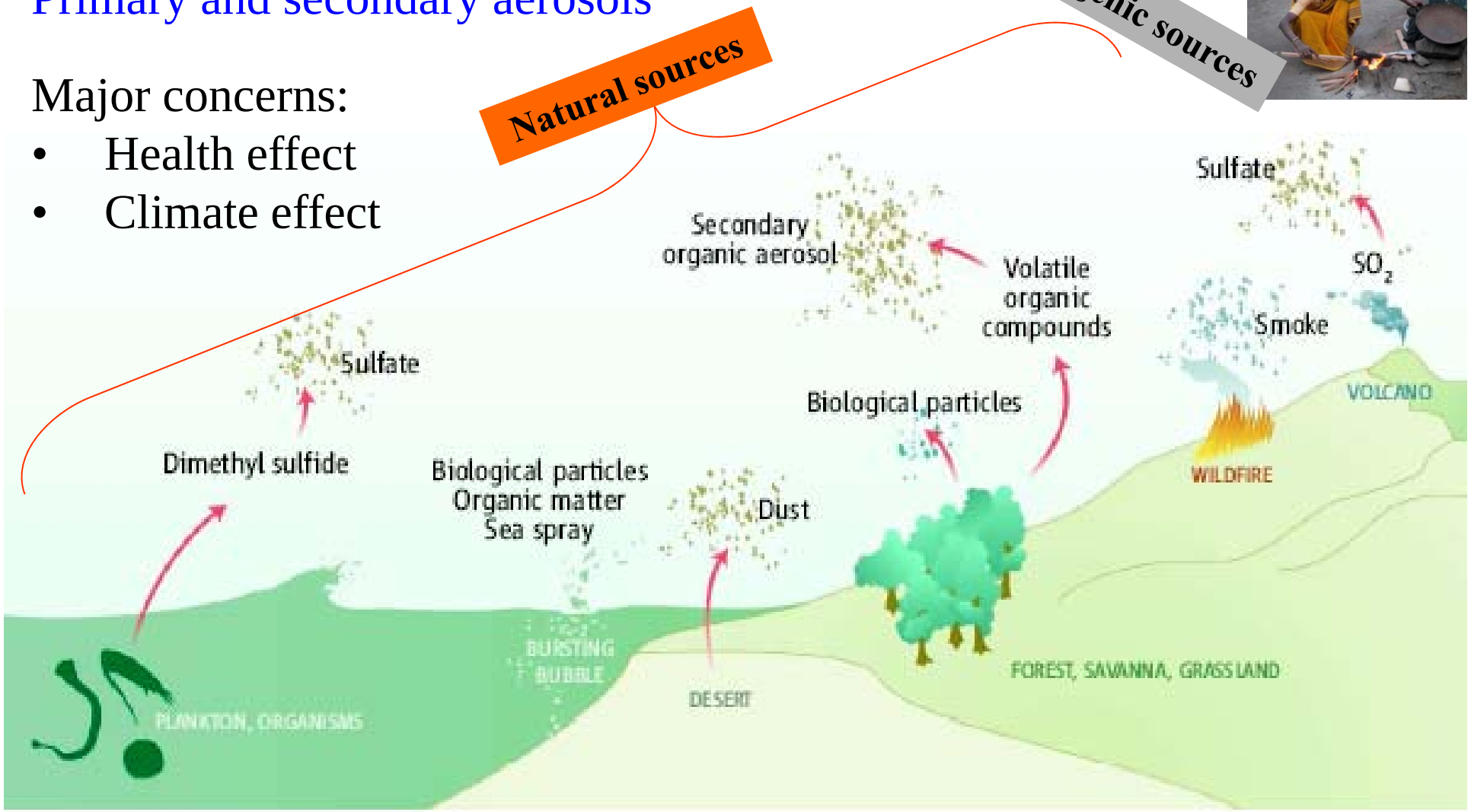


Size: Few nanometers to >100 μm

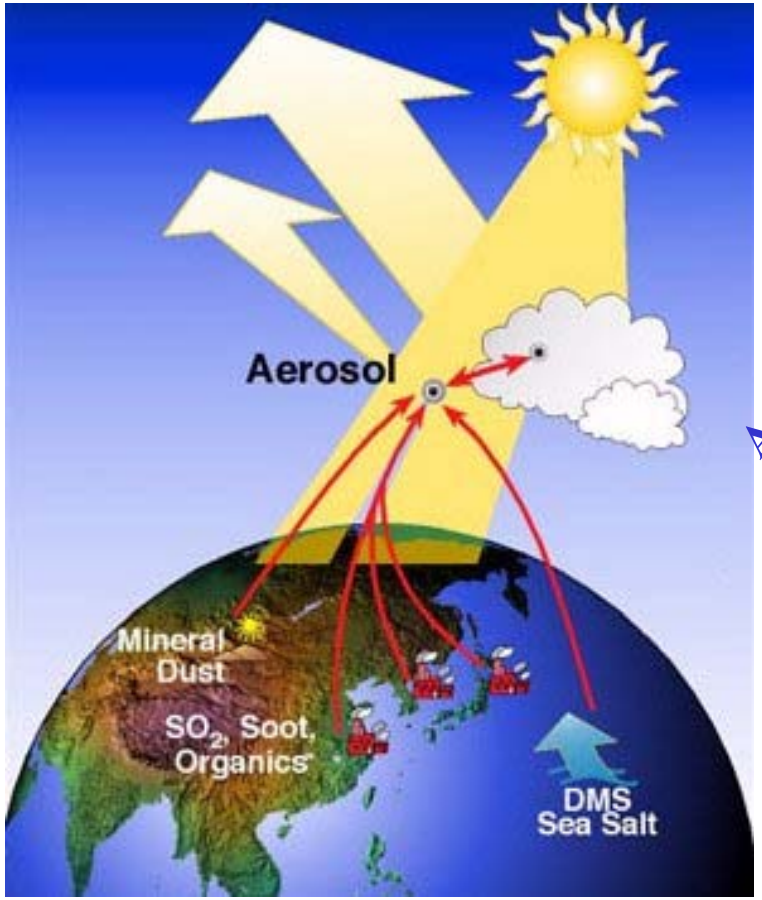
Primary and secondary aerosols

Major concerns:

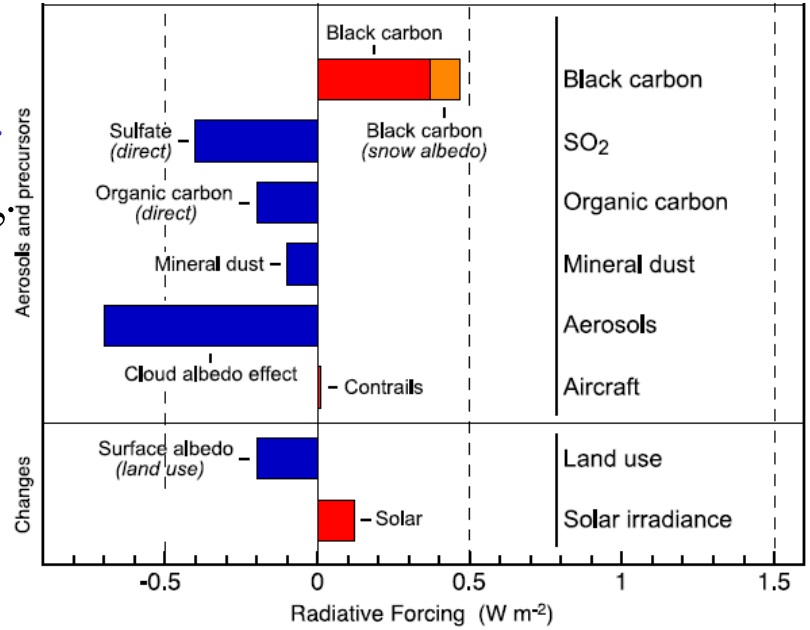
- Health effect
- Climate effect



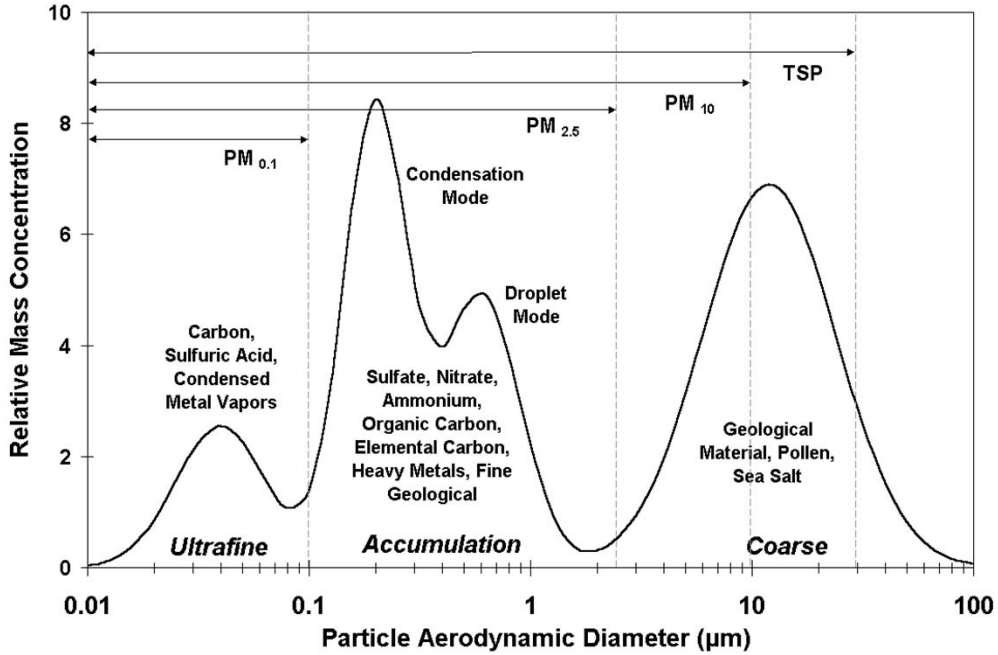
Aerosol effects: Climate effects…



Aerosol radiative forcing…
(Direct and indirect effects: cooling or warming!)



Atmospheric Particle Mass and Size Distribution



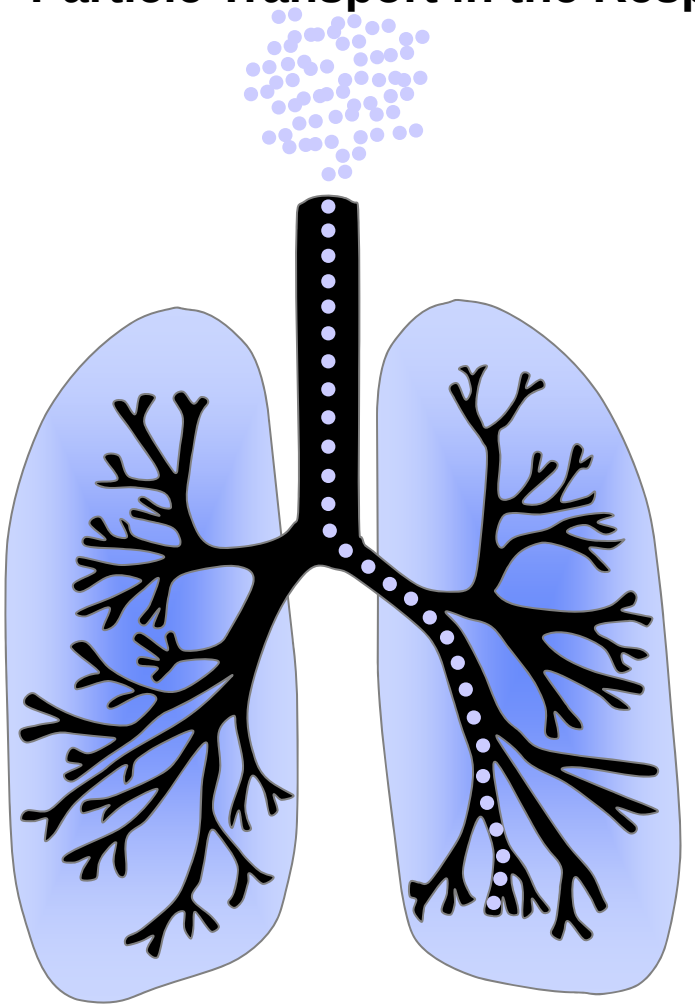
Aerosol characterization

Physical — Optical — Chemical

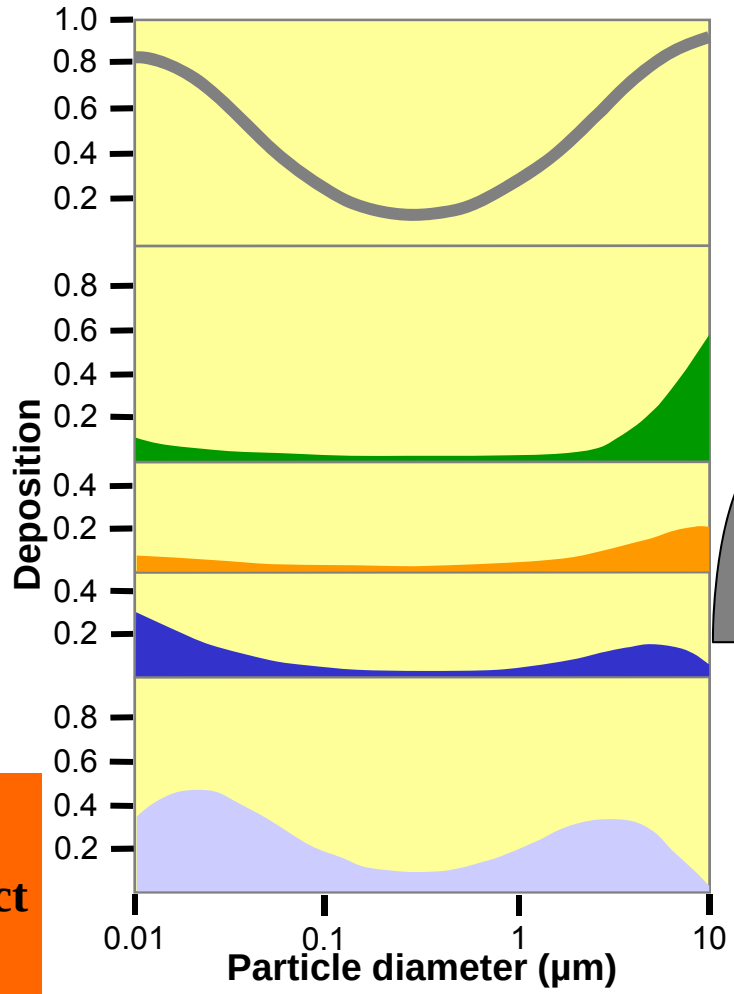
Physical	Optical	Chemical
Size, Shape CCN Hygroscopicity	Scattering Absorption	At bulk level At molecular level

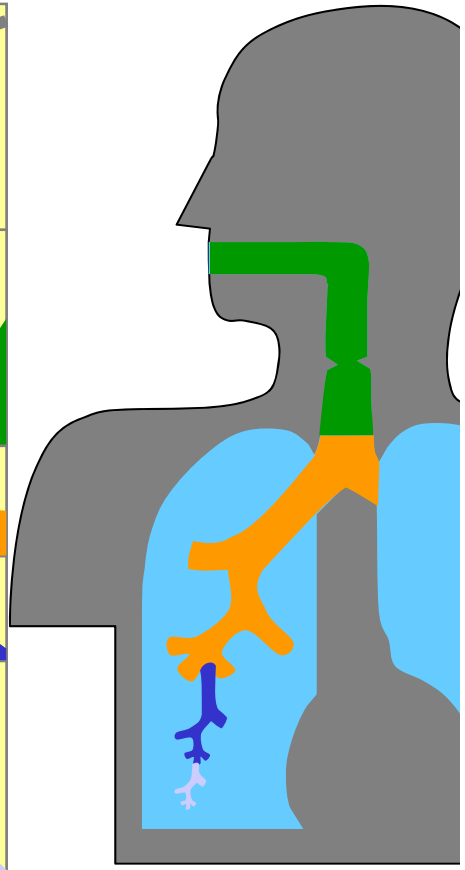
Health effects…

Particle Transport in the Respiratory Tract



Particle densitiy: 1 g cm^{-3}
Respiratory flow rate: 300 cm^{3} s^{-1}
Breathing cycle period : 5 s





- **Particle characteristics**
- **Geometry of the respiratory tract**
- **Fluid dynamics**

Table 1 Ambient air quality standards (AAQS) of different countries

Countries	Criteria pollutants										
	Averaging Time	PM_{10} ($\mu g\ m^{-3}$)	$PM_{2.5}$ ($\mu g\ m^{-3}$)	Pb ($\mu g\ m^{-3}$)	As ($\mu g\ m^{-3}$)	Ni ($\mu g\ m^{-3}$)	BaP ($\mu g\ m^{-3}$)	O_3 (ppm)	NO_2 (ppm)	SO_2 (ppm)	CO (ppn
Australia 2003[a]	Annual	–	25	0.5	–	–	–	–	0.03	0.02	–
	24-h	50	8	–	–	–	–	–	–	0.08	–
	8-h	–	–	–	–	–	–	–	–	–	9.0
	4-h	–	–	–	–	–	–	0.08	–	–	–
	1-h	–	–	–	–	–	–	0.10	0.12	0.20	–
China 2012[b]	Annual	70	35	0.5	–	–	0.001	–	0.021	0.022	–
	24-h	150	75	–	–		0.0025	–	0.04	0.056	3.4
	8-h	–	–	–	–	–	–	0.08	–	–	–
	4-h	–	–	–	–	–	–	–	–	–	–
	1-h		–	–	–	–	–	0.1	0.1	0.19	8.6
EU 2012[c]	Annual	40	25	0.5	0.006	0.02	0.001	–	0.021	–	–
	24-h	50	–	–	–	–	–	–	–	0.047	–
	8-h	–	–	–	–	–	–	0.06	–	–	8.6
	4-h	–	–	–	–	–	–	–	–	–	–
	1-h	–	–	–	–	–	–	–	0.10	0.13	–
India 2009[d]	Annual	60	40	0.5	0.006	0.02	0.001	–	0.02	0.02	–
	24-h	100	60	1	–	–	–	–	0.04	0.03	–
	8-h	–	–	–	–	–	–	0.05	–	–	1.7
	4-h	–	–	–	–	–	–	–	–	–	
	1-h	–	–	–	–	–	–	0.09	–	–	3.4
Japan 2009[e]	Annual		15								
	24-h		35						0.04–0.06	0.04	10
	8-h										20
	4-h										
	1-h									0.1	

NATIONAL AMBIENT AIR QUALITY STANDARDS
CENTRAL POLLUTION CONTROL BOARD
NOTIFICATION

New Delhi, the 18th November, 2009

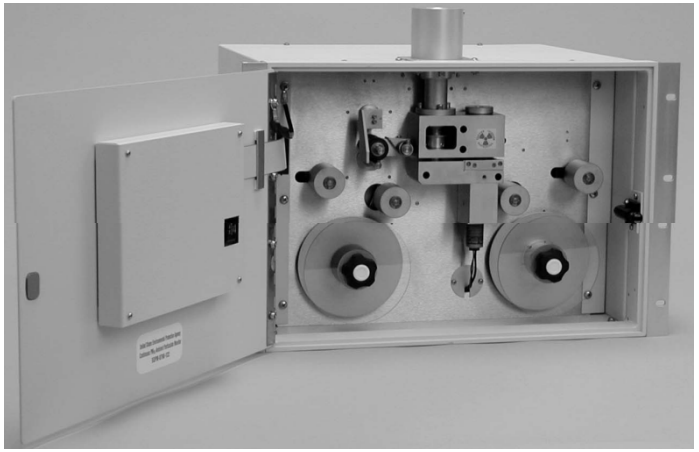
S. No.	Pollutant	Time Weighted Average	Concentration in Ambient Air		
			Industrial, Residential, Rural and Other Area	Ecologically Sensitive Area (notified by Central Government)	Methods of Measurement
(1)	(2)	(3)	(4)	(5)	(6)
1	Sulphur Dioxide (SO_2), µg/m^3	Annual* 24 hours**	50 80	20 80	- Improved West and Gaeke -Ultraviolet fluorescence
2	Nitrogen Dioxide (NO_2), µg/m^3	Annual* 24 hours**	40 80	30 80	- Modified Jacob & Hochheiser (Na-Arsenite) - Chemiluminescence
3	Particulate Matter (size less than 10µm) or PM_{10} µg/m^3	Annual* 24 hours**	60 100	60 100	- Gravimetric - TOEM - Beta attenuation
4	Particulate Matter (size less than 2.5µm) or $PM_{2.5}$ µg/m^3	Annual* 24 hours**	40 60	40 60	- Gravimetric - TOEM - Beta attenuation
5	Ozone (O_3) µg/m^3	8 hours** 1 hour**	100 180	100 180	- UV photometric - Chemilminescence - Chemical Method
6	Lead (Pb) µg/m^3	Annual* 24 hours**	0.50 1.0	0.50 1.0	- AAS /ICP method after sampling on EPM 2000 or equivalent filter paper - ED-XRF using Teflon filter
7	Carbon Monoxide (CO) mg/m^3	8 hours** 1 hour**	02 04	02 04	- Non Dispersive Infra Red (NDIR) spectroscopy
8	Ammonia (NH_3) µg/m^3	Annual* 24 hours**	100 400	100 400	-Chemiluminescence -Indophenol blue method
9	Benzene (C_6H_6) µg/m^3	Annual*	05	05	- Gas chromatography based continuous analyzer - Adsorption and Desorption followed by GC analysis
10	Benzo(a)Pyrene (BaP) - particulate phase only, ng/m^3	Annual*	01	01	- Solvent extraction followed by HPLC/GC analysis
11	Arsenic (As), ng/m^3	Annual*	06	06	- AAS /ICP method after sampling on EPM 2000 or equivalent filter paper
12	Nickel (Ni), ng/m^3	Annual*	20	20	- AAS /ICP method after sampling on EPM 2000 or equivalent filter paper

http://cpcb.nic.in/National_Ambient_Air_Quality_Standards.php

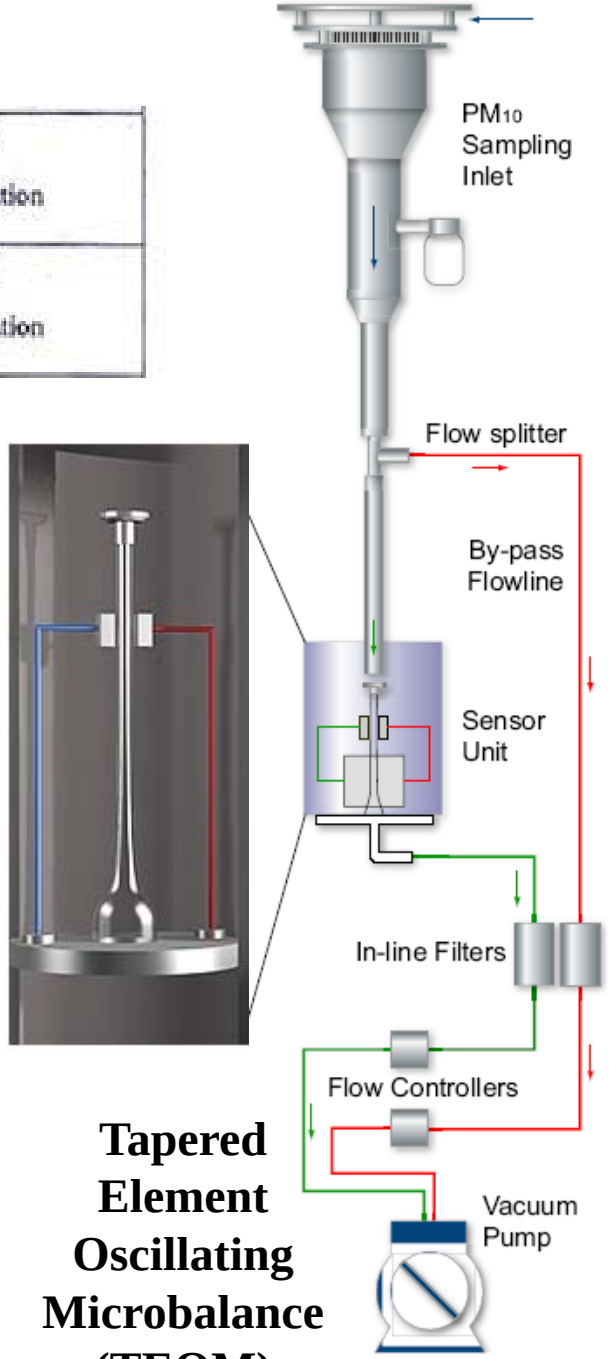
NAAQS: Particle mass measurement:

3	Particulate Matter (size less than 10µm) or PM_{10} µg/m^3	Annual*	60	60	- Gravimetric - TOEM
		24 hours**	100	100	- Beta attenuation
4	Particulate Matter (size less than 2.5µm) or $PM_{2.5}$ µg/m^3	Annual*	40	40	- Gravimetric - TOEM
		24 hours**	60	60	- Beta attenuation

PM10/PM2.5 sampler



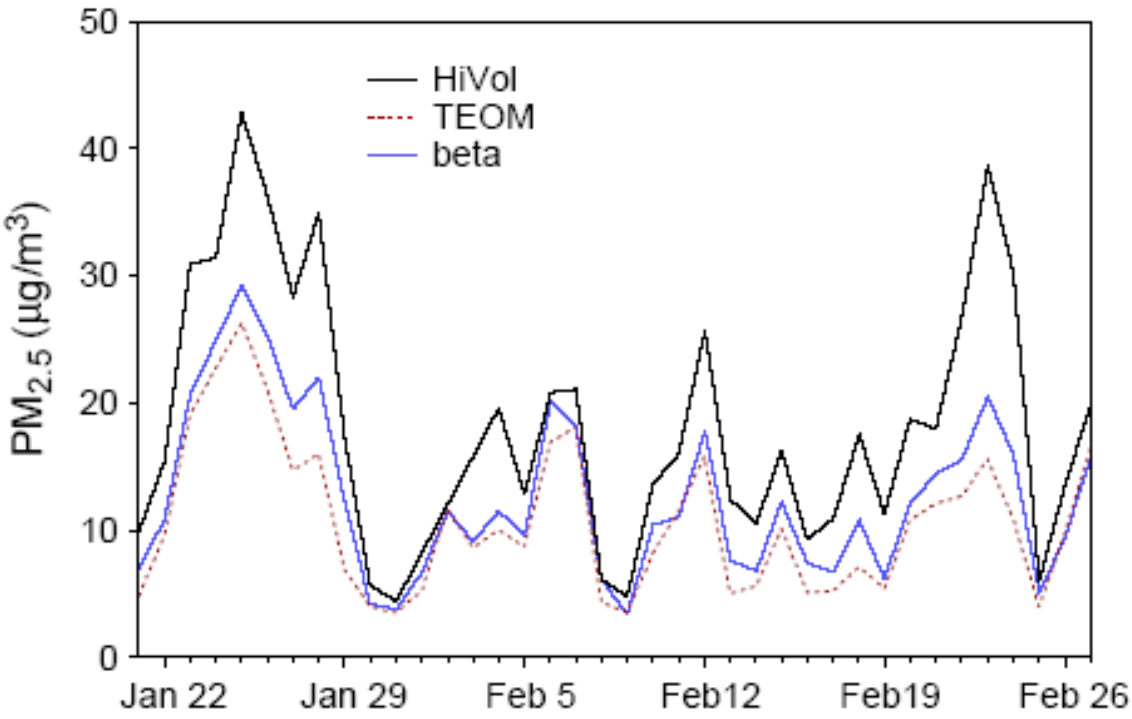
Beta Attenuation



Tapered Element Oscillating Microbalance (TEOM)

Comparison between all three techniques: $PM_{2.5}$ mass measurements

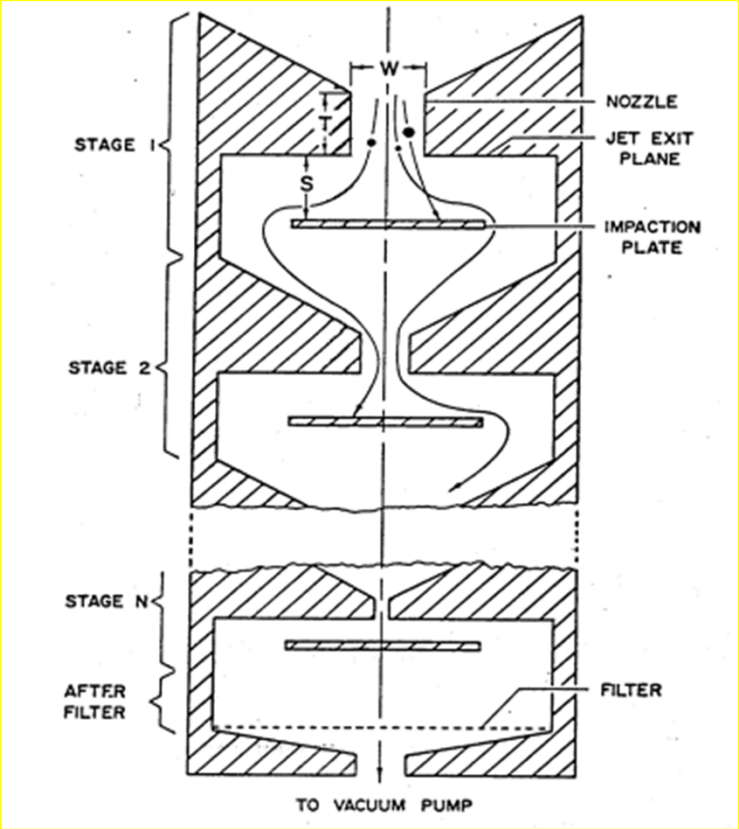
More than 30 % differences in mass measurement were reported in these three techniques.

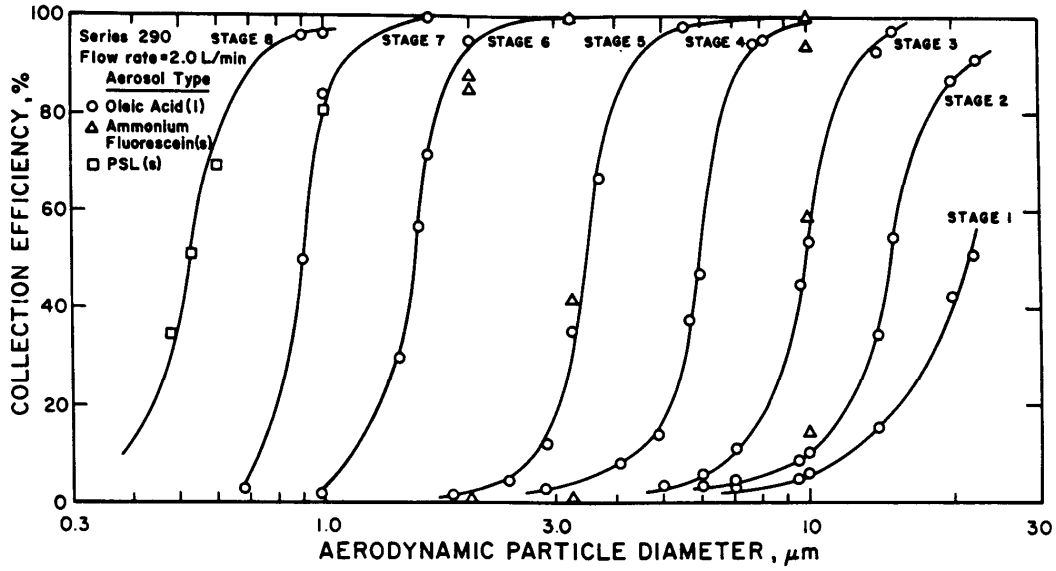


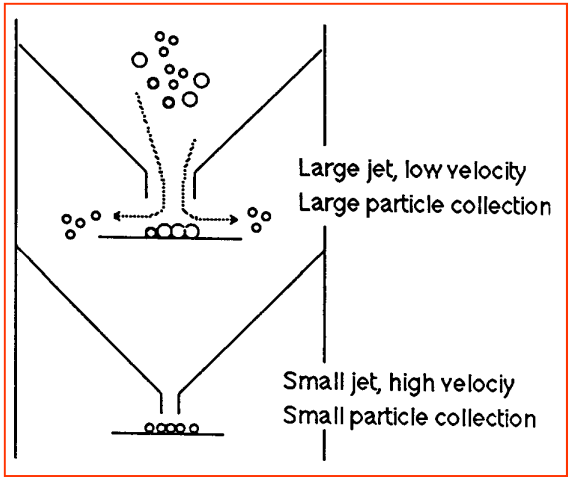
These differences are regarded because of:

1. **difference in measurement principles, i.e. different calibration methods those may not always be traceable to SI.**
2. **for segregation of PM2.5 (or PM10), an impactor or a cyclone is used at the inlet of the air flow to the sampler/s (filter/s). Hence calibration of these impactor and cyclone as well as precise control (calibration) of drawn air flow through the sampler are the major issues (cutoff size calibration).**

Impactor theory







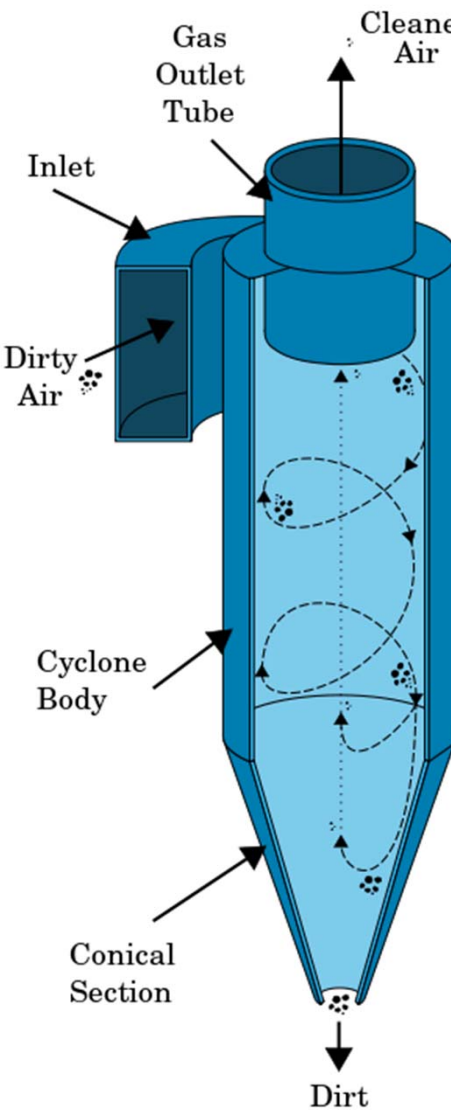
Impactor theory combines the parameters for size segregation of particles called Stokes number:

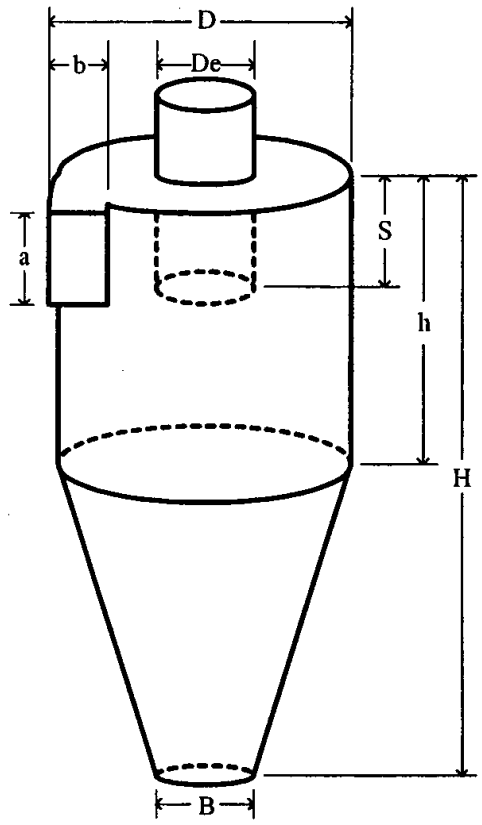
$$d_{50} = \left(\frac{9 \mu W Stk_{50}}{\rho_p V_o C} \right)^{1/2}$$

$$St = \frac{\rho \, d_p^{\,2} \, C \, V}{9 \, \mu \, W}$$

where: ρ = particle density
d_p = particle Stokes diameter
C = Cunningham slip factor, as defined in Equation 2
V = mean velocity in the jet
μ = air viscosity
W = jet diameter or width

Cyclone theory





Cutoff diameter derived by Lapple (1950):

$$Dp_{50} = 3\sqrt{\frac{\mu b}{2\pi\rho_p U_i C N_t}}$$

where U_i is the gas velocity at the inlet; μ is the air dynamic viscosity; ρ_p is the particle density; C is the slip correction factor of the particle corresponding to Dp_{50}. The number of turns N_t can be calculated as $N_t = tU_i/\pi D$ and the residence time t is equal to the volume of the cyclone divided by the volumetric flow rate, Q.

$$Dp_{50} = \frac{3}{U_{t\max}}\sqrt{\frac{\mu Q}{\pi\rho_p C(H-S)}}$$

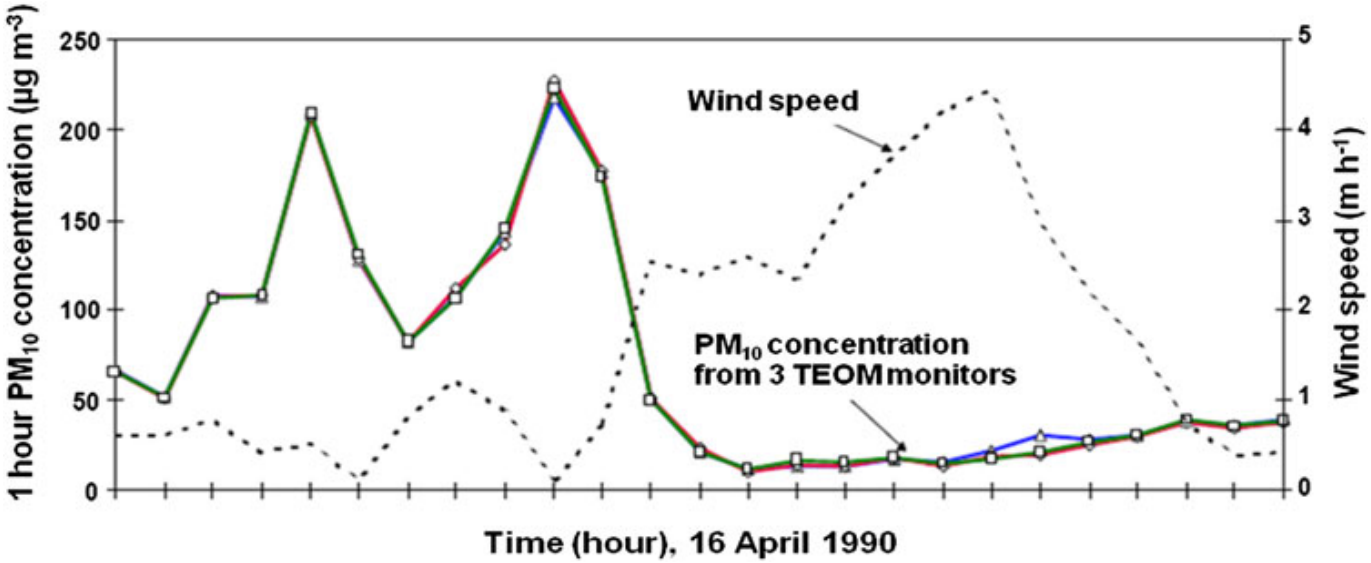
Iozia and Leith (1989):

$$Dp_{50} = \frac{3}{U_{t\max}}\sqrt{\frac{\mu Q}{\pi\chi_c\rho_p}}$$

$$U_{t\max} = 6.1\times U_i\times\left(\frac{ab}{D^2}\right)^{0.61}\times\left(\frac{De}{D}\right)^{-0.74}\times\left(\frac{H}{D}\right)^{-0.33}$$

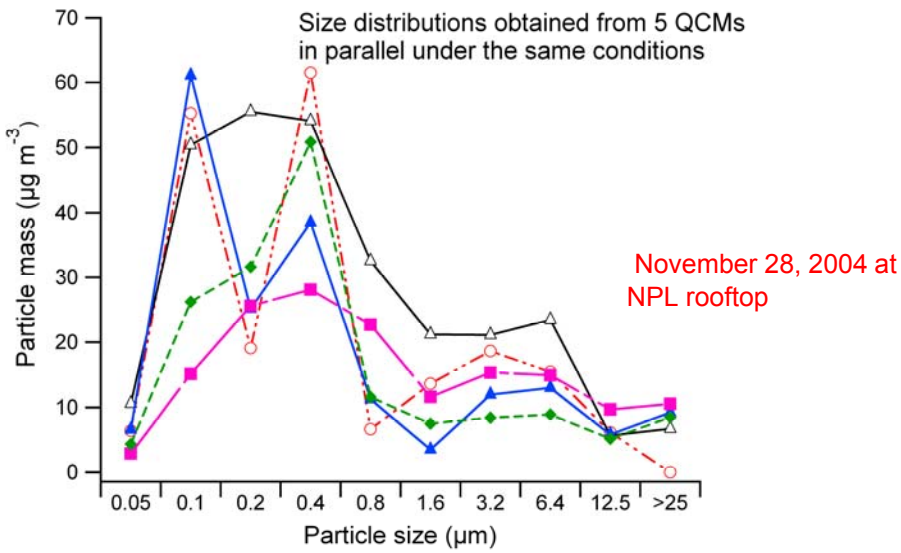
and χ_c is the length of the central core.

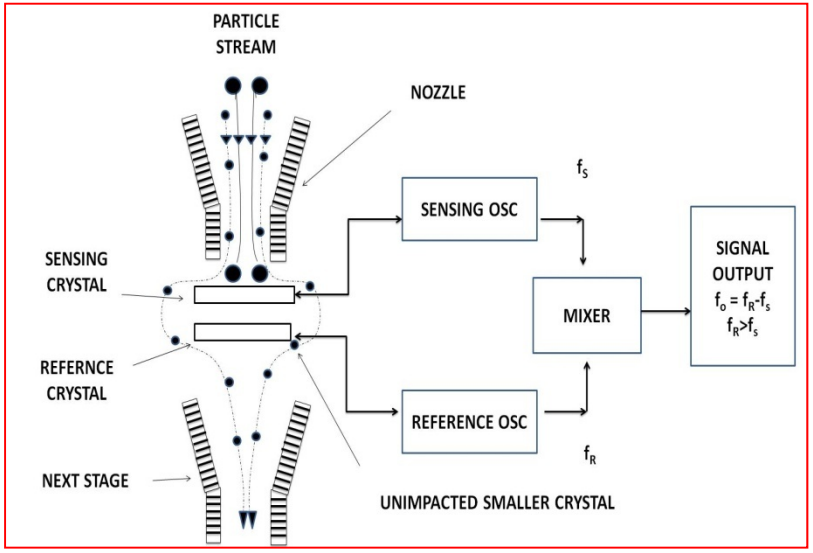
PM10 mass measurement results by three TEOM samplers (from a manufacturer).



Size/mass calibration is needed…

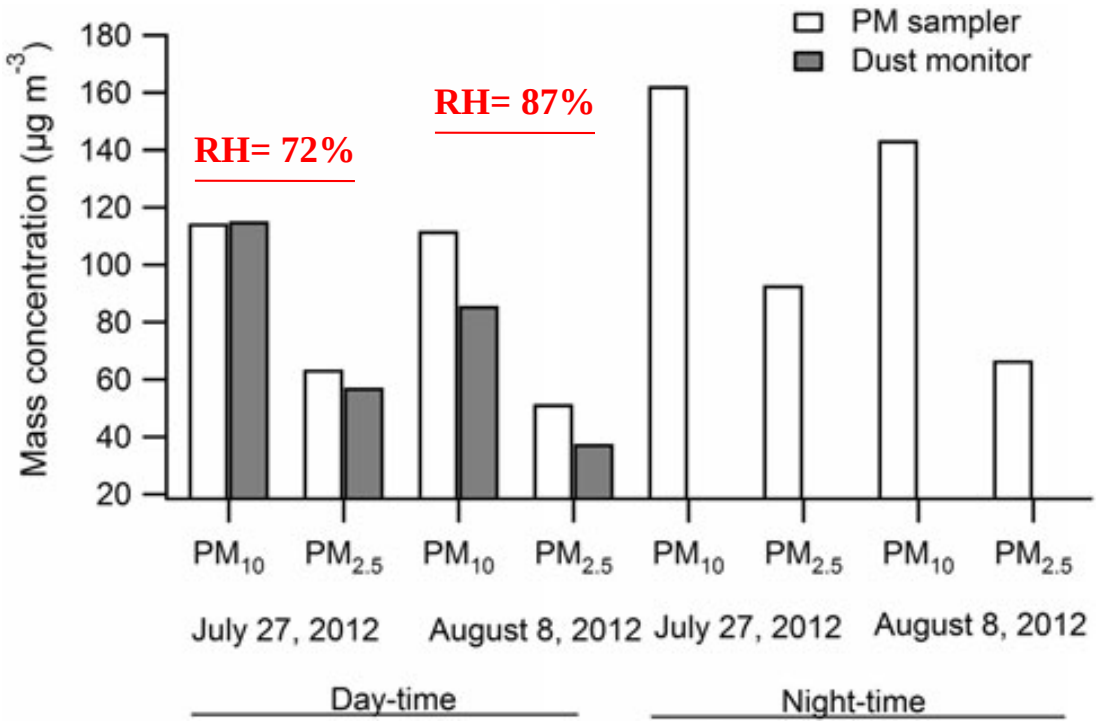
Comparison results of aerosol mass distribution measured using QCMs from different groups





Comparison of PM2.5 and PM10 mass

PM sampler (gravimetric technique) Vs.
Dust monitor system (particle counting by scattering based technique)



Comparison between all three techniques: possible causes of bias

- **Techniques vs. environmental conditions**
- **Evaporation/volatilization losses, diffusion losses, charge effect**
- **Flow calibration vs. cutoff size calibration**
- **Balance calibration/sensitivity, Beta absorption calibration, frequency calibration (mass-frequency relationship)**

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An International Journal for Scientific Research into the Environment and its Relationship with Man

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The effect of environmental conditions and electrical charge on the weighing accuracy of different filter materials

Chuen-Jinn Tsai[a,*], Chung-Tso Chang[a], Bow-Huei Shih[a], Shankar G. Aggarwal[a], Shou-Nan Li[b], Hung Min Chein[b], Tung-Sheng Shih[c]

Where does traceability of PM issue stand against other parameters of air quality standards and its impact on health and climate

Cyclone/Impactor
- **Air flow: Yes**
- **Cutoff size: No**

Gravimetric measurement: Yes
(large uncertainty due to: water content, evaporation loss,/volatilization, charge effect)

Beta Attenuation measurement: not clear
(large uncertainty due to: water content, compositional changes, evaporation loss,/volatilization)

TOEM measurement: not clear
(large uncertainty due to: environmental condition changes, evaporation loss,/volatilization)

Add-on uncertainty in other parameters of national ambient air quality standards due to PM measurements

NAAQS: Chemical Analysis

- **Metals: As, Ni, Pb**

  (Using ICP-MS)

- **PAHs**

  (Using GC-MS)

Metal determination:

As, Ni, Pb

NATIONAL AMBIENT AIR QUALITY STANDARDS

S. No.	Pollutant	Time Weighted Average	Concentration in Ambient Air		
			Industrial, Residential, Rural and Other Area	Ecologically Sensitive Area (notified by Central Government)	Methods of Measurement
(1)	(2)	(3)	(4)	(5)	(6)
6	Lead (Pb) $\mu g/m^3$	Annual* 24 hours**	0.50 1.0	0.50 1.0	- AAS /ICP method after sampling on EPM 2000 or equivalent filter paper - ED-XRF using Teflon filter
11	Arsenic (As), ng/m^3	Annual*	06	06	- AAS /ICP method after sampling on EPM 2000 or equivalent filter paper
12	Nickel (Ni), ng/m^3	Annual*	20	20	- AAS /ICP method after sampling on EPM 2000 or equivalent filter paper

Analysis: Microwave digestion followed by ICP-MS analysis

Chemical Analysis: Metals

$PM_{2.5}/PM_{10}$ sampling
Quartz filter: Baked, conditioned and weighed

↓

Filter conditioning and weighing
Storing: -20 °C in glass bottle

↓

Take a filter cut in plastic/ Teflon vessel

↓

Add HNO_3+H_2O_2/+HF
(5 ml, 3 ml, 1 ml)

↓

Perform microwave/open digestion

↓

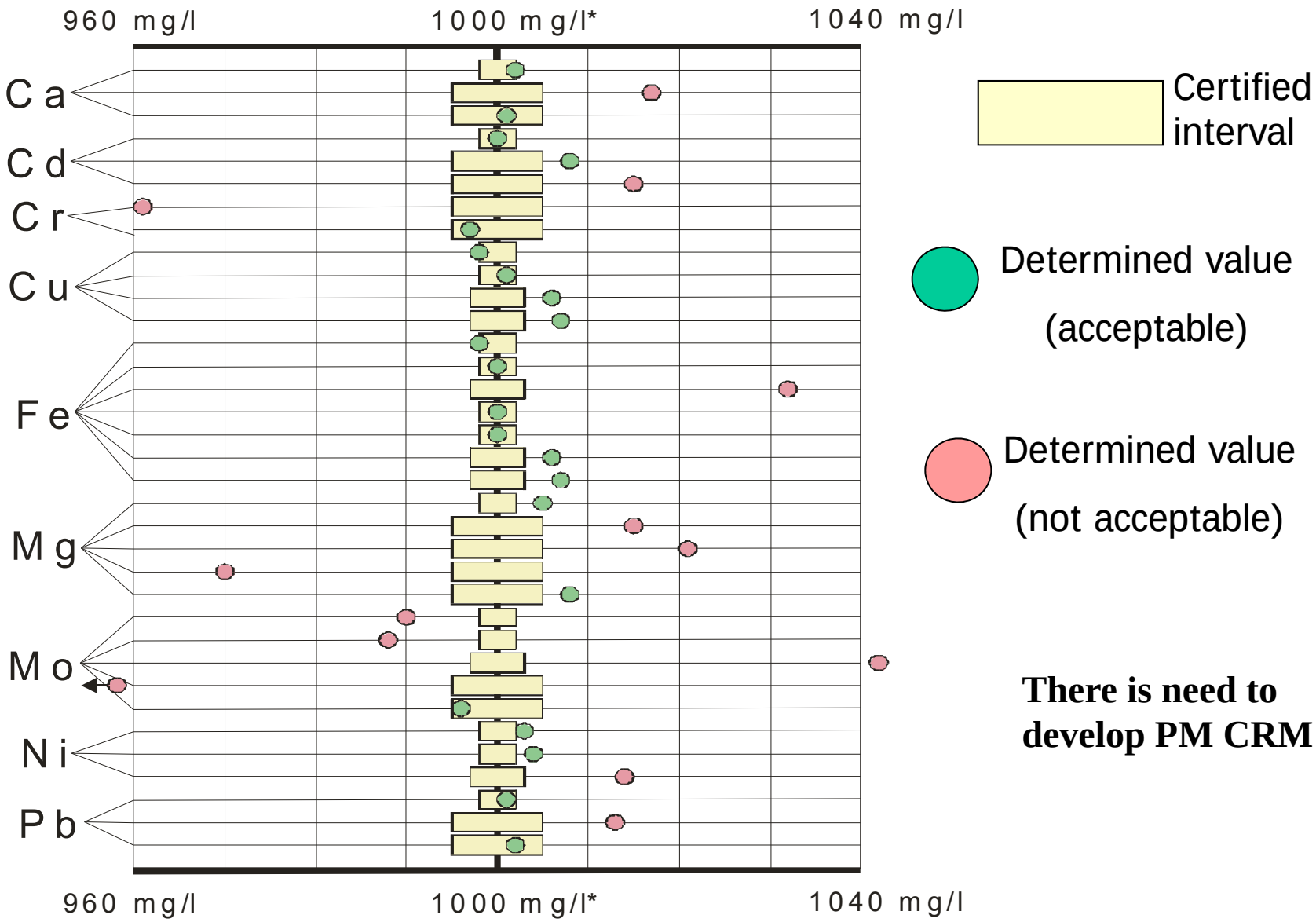
Transfer the extract in a plastic beaker by washing (~50 ml)

↓

Transfer the extract by filtering into a pre-weighed plastic bottle, and weight the sample solution finally

- ❑Why Quartz, pre-baked
- ❑Why -20 °C in glass bottle
- ❑Why not HCl
- ❑Why HF
- ❑Microwave/open digestion
- ❑Use ultrapure (sub-boiled) acids
- ❑Use elemental fee Milli-Q water
- ❑Final solution → why gravimetric preparation
- ❑Use SI traceable calibration solutions

Reality: Accuracy of different commercial calibration solutions (according to the measurements done by NMIs)



There is need to develop PM CRM

More defined standards are needed!

11	Arsenic (As), ng/m³	Annual*	06	06	• AAS /ICP method after sampling on EPM 2000 or equivalent filter paper

Uncertainty budget for the arsenic determination in aerosol samples using ICP-HRMS

SC = Sensitivity coefficient, DOF= Degrees of freedom

Source of uncertainty	Distribution, Type A or B	Relative standard uncertainty											SC	DOF
		HVS-118	HVS-119	HVS-120	HVS-121	HVS-122	IND-232	IND-233	IND-234	IND-235	IND-236	HS-52		
Calibration solution	Normal, Type B	0.003											1	∞
Instrumental calibration (linearity)	Normal, Type A	0.029											1	2
Repeatability	Normal, Type A	0.005	0.005	0.021	0.015	0.001	0.005	0.008	0.002	0.007	0.003	0.000	1	2
Air volume	Rectangular, Type B	0.029											1	∞
Sample digestion	Rectangular, Type A	0.032											1	2
(ng/m³)														
Combined uncertainty		0.963	0.481	0.350	0.808	0.429	0.690	0.939	1.738	0.773	0.548	0.374		
As concentration		18.44	9.201	6.252	14.93	8.237	13.21	17.83	33.41	14.74	10.52	7.193		
Expanded uncertainty (*k=2*)		1.926	0.961	0.699	1.617	0.857	1.379	1.878	3.477	1.545	1.096	0.748		

Kumar, Aggarwal et al., 2014

Current status of aerosol metrology: Traceability issue in PM measurements

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About the conference

The 7th Asian Aerosol Conference (AAC 2011) of Asian Aerosol Research Assembly (AARA) begins on Wednesday, 17 August 2011 and consists of a series of plenary, regular and poster sessions. It is with great pleasure that the conference organizers invite you to attend the conference, to present your work, discuss new discoveries and problems, exchange views, and develop plans for the future of aerosol science and technology. This will benefit the specialists , increase public awareness and knowledge. The conference will explore applications to important societal issues involving the climate, environment, health, energy, materials, and other facets of our life.

Major topics will include:

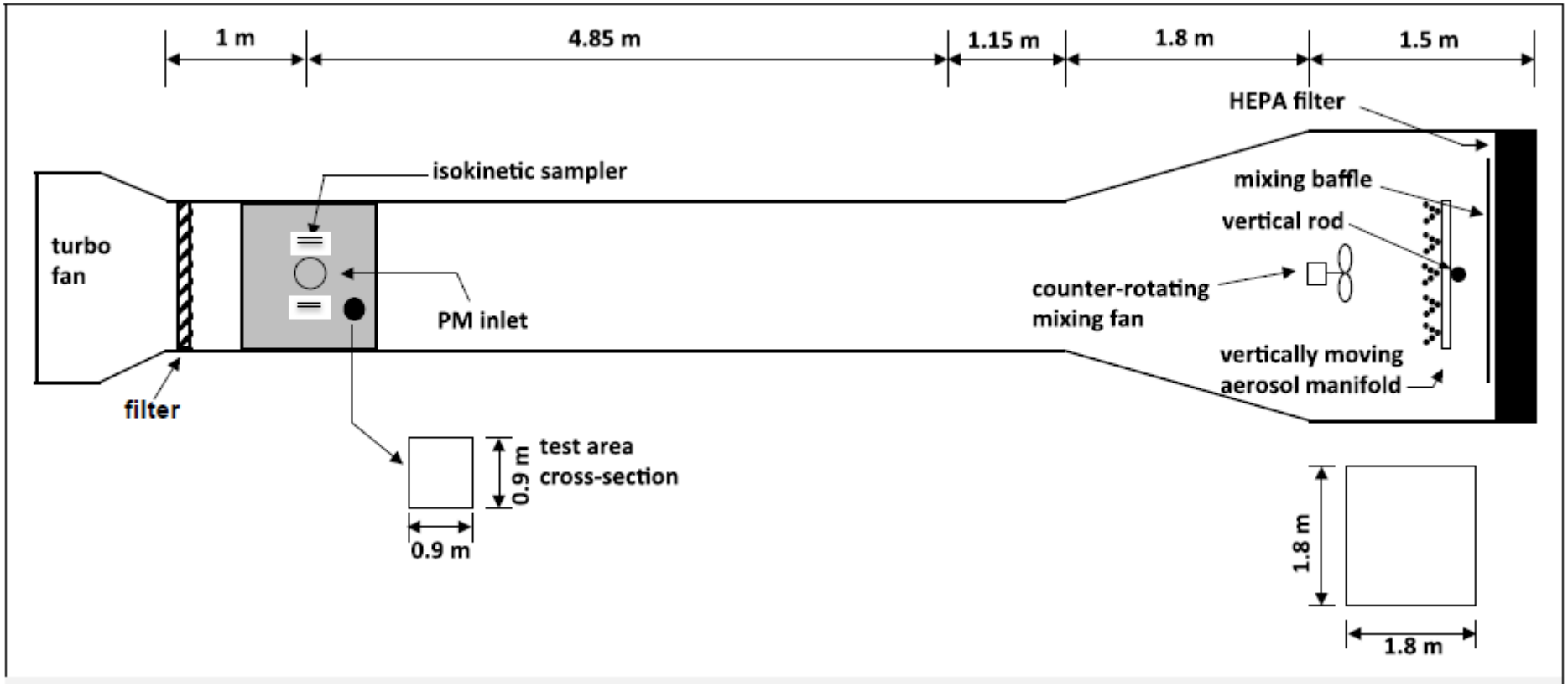
- Fundamentals of aerosol physics and chemistry
- Aerosol instrumentation
- Aerosol and climate change
- ~~Aerosol remote sensing~~ techniques
- Aerosol metrology
- Asian haze and dust storm
- Atmospheric brown clouds
- Bio-aerosols, biodefense, inactivation of bioagents
- Indoor pollution control
- Health and environment related aerosols
- Nanoparticle and nanoaerosol technology
- Radioactive and nuclear aerosols
- Urban air pollution and source apportionment
- Other aerosol related topics

- About the Conference
- Conference Committee
- General Information
- Abstract Submission
- Registration
- Exhibition Information
- Conference Hotel
- Tours&Spechial Events
- About Xi'an

Development of aerosol wind tunnel and its application for evaluating the performance of ambient PM_{10} inlets

Sangil Lee [1], Miae Yu [1], Hun H. Kim [2]

[1] *Center for Gas Analysis, Korea Research Institute of Standards and Science, Daejeon, Republic of Korea*
[2] *Center for Analytical Measurement Service, Korea Research Institute of Standards and Science, Daejeon, Republic of Korea*



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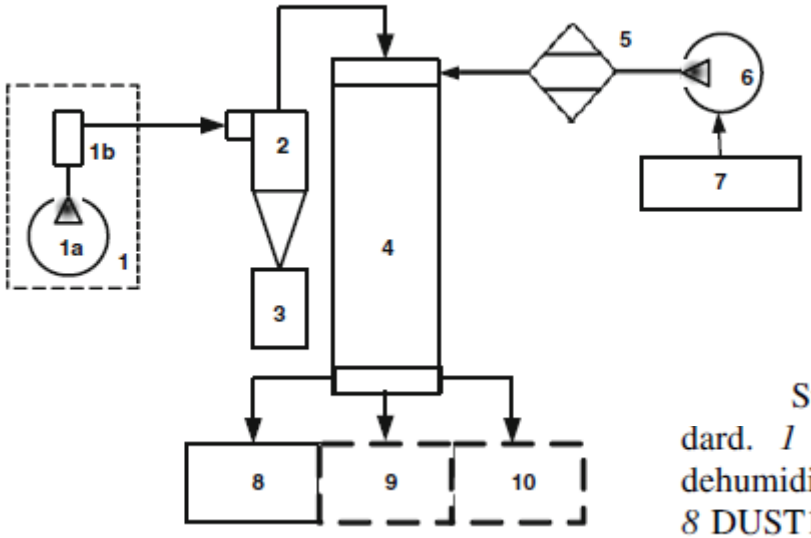
REVIEW PAPER

Progress in Development of Russian National Measurement Standards in the Field of Mass Concentration Measurement of Suspended Particles

Y. A. Kustikov* and B. I. Popov

Scientific Research Laboratory of the State Standards in the Field of Disperse Medium Parameters Measurements, D.I. Mendeleyev Institute for Metrology, Moskovsky pr. 19, 190005 St. Petersburg, Russia



Structure chart of the transportable (mobile) working standard. *1* Generator, *1a* compressor, *1b* nebulizer, *2* cyclone, *3* dehumidifier, *4* column mixer, *5* dryer, *6* air blower, *7* power unit, *8* DUST1-E, *9* instrument under verification

@NPLI

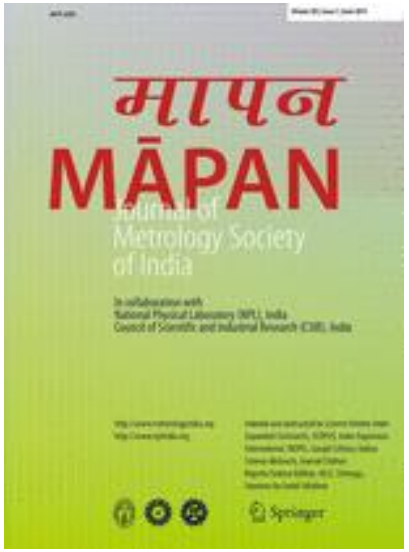
--Workshop

MiC workshop on "Gas and aerosol metrology", as pre-Admet-13 international conference, was organized during Feb.20, 2013 at NPL, New Delhi

About 80 delegates, including 6 invited speakers from other countries

Special issue on this workshop

http://link.springer.com/journal/12647/28/3/page/1

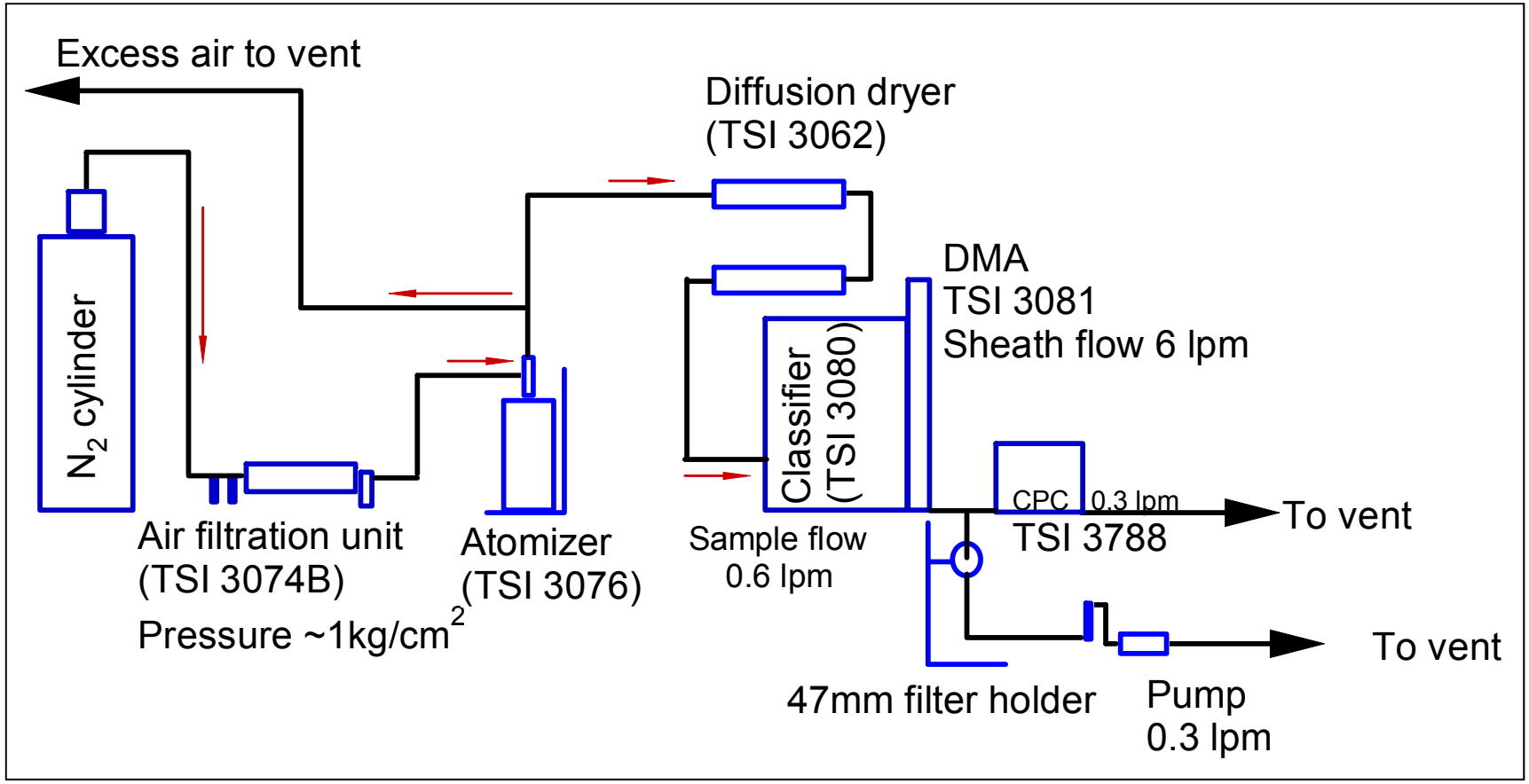


Our setup for counter's calibration check…

We used scanning mobility particle sizer (SMPS) consists of a DMA (TSI 3081) and CPC (TSI 3788)

Our approach… (CPC derived volume vs. filter based volume)

This approach is based on the comparison of particle volumes derived from scanning mobility particle sizer (SMPS) with corresponding particle volume, which are collected on filter and determined by mass (gravimetric method).



Dried ammonium sulfate particles were introduced to SMPS and particles of size range 14 - 615 nm were segregated by DMA and number concentration was measured by CPC.

Conclusion... (1)

- Less work has been done so far for PM measurement traceability dissemination, especially for its size and mass related calibration.

- The inlets (size cutoff) of most of the commercially available PM samplers are not traceable to SI.

- Few NMIs are now taking initiatives for setting up the calibration facility of PM2.5 and PM10 impactors.

- Awareness programs on PM measurement and traceability issue should be organized more often.

Conclusion... (2)

Industries and manufacturers should participate in "traceability to SI through NMI program in ambient measurements" to improve the data quality which have significant impact on several issues, e.g. health, climate, societal, economy and other developments.

NMIs should make program to involve industries in gas and aerosol metrology work to fulfill the requirement of calibration and standards.

The regulatory authorities/ministry should work together with NMIs to improve the data quality of ambient measurements.

This will greatly help to better make the policies and decisions on the related impacts.

Thank you….!


March 20, 2013 06:33 AM
Temperature 18º C
Humidity 89%


March 21, 2013 06:32AM
Temperature 18º C
Humidity 83%