#### AMBIENT AIR QUALITY MONITORING TECHNIQUES AND QUALITY ASSURANCE



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#### Sources of Air Pollution Natural • Forest Fire • Volcanoes • Dust storms Man made • Domestic • Industrial • Vehicular • Non point source

Classification of	f Air Pollutants
Primary Pollutants (emitted in to the atmosphere directly from identifiable sources	Secondary Pollutants (Those formed as a result of reactions among two or more pollutants
Suspended Particulate Mattter Sulphur dioxide Nitrogen dioxide Hydrocarbons Carbon monoxide Metals	Ozone Formaldehyde Peroxy Acetyl Nitrate (PAN)

Typical Sources	of some Air Pollutants
Air Pollutants	Major Sources
Sulphur Dioxide (SO <sub>2</sub> )	Fuel combustion, power station, industrial processes, chemical processes, diesel
Nitrogen Oxide (NO <sub>x</sub> )	Transport (road, rail, passenger and ommercial), fuel combustion, power station, industrial boilers, chemical
Particulate Matter (SPM, RSPM-PM <sub>10</sub> , RSPM-PM <sub>25</sub> )	Hocesses, waste incinerators, sherters fuel combustion, power station, construction activities, industrial processes, diesel vehicle exhaust, re suspended road dust, domestic
Carbon Monoxide (CO)	Transport, combustion, industrial processes,
Ozone (O3)	Secondary pollutants formed during

of some Air Pollutants
Transport, oil based fuel combustion
waste incinerator, vaporization of fuel Petrol combustion products, petrol filling
stations, chemical process Fuel combustion, industrial emission
Transport, solvents (especially used in
Fuel combustion, chemical process, transport motal production and finishing
operation, product manufacture
particles Fuel combustion, metal production

# -Site selection for rural and remote sites

- Selection of sampling sites is a critical factor in monitoring.
- Sampling sites should be located in areas suitable for the purpose.
- They should properly represent the area in question.

#### -Criteria for Monitoring Sites

-Land use in the vicinity of the sites is likely to remain in almost the same condition for several decades.
-The samples should represent the area in question.
-Consideration of the topographic features and

meteorological conditions should be taken into account.

#### Minimum Distance to Emission Sources

-Regions within 50 km of large pollution sources should be excluded as remote sites.
-Regions within 20 kmof large pollution sources should be excluded as rural sites.
-Regions within 500 m of main roads should be excluded as remote and rural sites.

#### Local criteria

- An open, flat, grassy area far enough from trees, hills and other obstructions. No objects should be within a few meters of the collector, and no object should shade the collector.
- The top of an obstruction as viewed from the collector should be less than 30 degrees above the horizon.
- Regions within 100 m of emission sources (waste disposal sites, incinerators, parking lots, open storage of agricultural products, domestic heating) should be excluded.

#### **Site selection**

- Intake points of automatic instruments should be 5 to 10 meters from the ground if no obstructions are located around the sites.
- They should be around 3 meters higher than the height of the buildings if buildings or other obstructions are located around the sites, or the intake points are on the buildings.

#### Microscale Considerations for Site Selection

- Obstructions to local wind flow (avoid nearby buildings, walls or forests)
- Logistical factors such as site access, site security, availability of utilities
- Consistency with monitoring objectives

#### **Measurement parameters**

• The first priority parameters for air concentration monitoring are NO<sub>2</sub> (urban), SO<sub>2</sub>, O<sub>3</sub>, and NO, and particle mass concentration. For particle mass concentration, it is recommended to start with a 10  $\mu$ m cut-off.

#### Measurement instruments and monitoring interval

- For routine monitoring of the air concentration, automatic instruments are commercially or conventionally available for SO<sub>2</sub> (such as ultraviolet fluorescent (UVF) method), NO (such as chemiluminescence detection (CLD) method), O<sub>3</sub> (such as ultraviolet photometric method and CLD method) and PM10 (such as ß-ray absorption method and TEOM method) to obtain one-hour averaged values.
- Chemical/Gravimetric method

#### Ambient Air Monitoring Methods and Equipment

- Selection will be determined by the Aim of the Survey
- If only average concentration values of pollutants in low and <u>"smoothly" polluted</u> areas are required, then non sophisticated but trustworthy equipment is recommended.
- If **retracking** to emitting source and / or assessment of impact is intended, then sophisticated, **high temporal resolution** equipment might be necessary.

# MONITORING METHODS

- Detector Tubes
- Passive / Diffusive Sampling
- Wet Chemical
- Continuous Monitoring
  - Point sampling
  - Open Path

# **DETECTOR TUBE**

- **ADVANTAGE**
- Quantitative
- Provides instant value

# **Passive Sampling**

#### ADVANTAGES

- Provides average values for a certain period of time usually between one week and one month
- Method requires no power supply for the sampling
- Method recognized as low cost of sampling as compared to other techniques
- Ideal for survey applications either in remote areas or assessment of personal exposure
- Samples can be collected from any part of the country and shipped to laboratory for analysis

# PASSIVE SAMPLING

#### DISADVANTAGE

- Peaks not available
- Co-relation with meteorological parameters not possible



Sampling and measurement Techniques of air pollutants (Wet Chemical Methods)					
Parameter Technique Instrument					
SPM/RSPM Gravimetric		HVS/RDS			
\$O <sub>2</sub>	Colorimetric	Spectrophotometer			
NO <sub>2</sub>	Colorimetric	Spectrophotometer			
Ozone	Ozone Colorimetric Spectrophotometer				
Metals	Spectroscopy	AAS			
РАН	Chromatography	Gas Chromatograph			
втх	Chromatography	Gas Chromatograph			

#### **State-of-the-Art "Wet" Chemical**

#### Advantages

- low costs
- simple equipment
- · normal laboratories' performances sufficient
- accepted as basic reference methods
- internal calibration possible
- automatic integration of sampling period
- any chemically reactive component detectable
- small power required

#### State-of-the-Art "Wet" Chemical

#### Disadvantages

- simplicity of equipment may lead to "easy handling"
- calibration of sampling system absorption solutions and analytical procedures are necessary, "Ring Test" required
- 'normal' laboratory performance must yield maximum accuracy
- integration results in loss of short-time-event-tracing
- higher risk of "non-reliability" by contamination
- universality is also the crux as to interferences





# Measurement of VOCs in Ambient air using Canister sampling method

#### Canister :

- It is made of stainless steel and is electro polished from inside.
- It is commercially available.





## Need for Automatic Monitoring System

- Continuous Information Flow
- Warning at critical period
- Accuracy and precision of information
- Minimise Human Error

## **Continuous Instruments**

- A Glimpse on Physics Behind
- NDIR Absorption : carbon monoxide
- UV / VIS / IR Absorption : ozone, hydrocarbons
- UV Fluorescence : Sulphur dioxide
- Chemiluminescence : nitrogen oxides, ozone
- FID : hydrocarbons
- Beta ray absorption, light scattering, TOEM : SPM
- Particle size analysers : impactors, particle counters etc.
- GC FID, PID : Benzene, Toluene, Xylene

#### **Continuous Instruments**

#### Advantages

- low response times less than 1 min
- high selectivity
- high temporal resolution in non-stop coverage
- good stability under normal conditions
- intermittent calibrations and zero checks automatically or manually triggered

#### **Continuous Instruments**

#### Disadvantages

- high costs in investment and maintenance
- all, as to "high tech" application in field (non-Laboratory-conditions)
- <u>calibration</u> methods, systems and units required; science of their own; "Ring Tests" absolutely necessary
- highly qualified personnel required for service, calibration checks, data acquisition etc.
- integration requires computerization
- ambient conditions, e.g. dust, shocks, condensation may cause serious problems



# Conclusion

**Powerful**, but **expensive** and **requiring endeavour and endurance** besides enthusiasm

# **OPEN PATH**

#### ADVANTAGE

- Many parameters with same instrument
- Average concentration for the path length
- Less moving parts

#### DISADVANTAGE

- Effect of environmental conditions
- Calibration not easy









# Certified materials and certified samples (Traceability)

- In order to assure the reliability of measurements, the certified solution and certified materials that were certified for traceability should be used.
- Standard weights for analytical balance
- Absorbance and wavelength filters for spectrophotometer
- Chemical standards

#### Importance of QA/QC activities

- Considering the significance of possible future problems regarding acid deposition, it becomes increasingly important to obtain accurate and precise data on acid deposition.
- However, informed decisions cannot be made on the basis of unreliable data, and therefore certain levels of data quality should be assured.
- A monitoring system without adequate QA/QC runs the risk of not being able to control the quality of data, and not being able to assure accuracy and precision.
- QA/QC has thus become essential part of all measurement systems because it requires especially high international comparability of data.

#### Objectives of QA/QC program

• The objectives of this QA/QC program are to obtain reliable data which can be comparable with other networks by ensuring data accuracy, precision, representativeness and completeness in monitoring.

#### Coverage of QA/QC programs

- QA/QC programs should cover the whole process of monitoring activities, starting from sampling activities to the end, reporting.
- All the related organizations need to implement QA/QC activities.

#### Definition of QA/QC

- Quality control (QC): the routine use of procedures designed to achieve and maintain a specified level of quality for a measurement system
- Quality Assurance (QA): a set of coordinated actions such as plans, specifications, and policies used to assure that a measurement program can be quantifiable and produce data of known quality
- QA is quality control for QC.



#### **Requirements for calibration of HVS**

Roots meter Top Loading Orifice Kit Soap bubble apparatus/meter

# Why to Calibrate

- Calibration of HVS is necessary to establish traceability of field measurement to a primary standard via flow rate transfer standard
- The most common flow rate transfer standard used for calibration of flow of HVS is orifice method
- As air pollutants concentration is expressed as mass per unit volume of air, the accuracy of flow measurement is very important

#### When to Calibrate

- Single point Calibration Once in a month
- ➤ Multi point Calibration
  - When sampler is first installed
  - Every six months
  - After major repair work
  - When a one point calibration check deviates by more than ±7% from the calibration curve

# What to Calibrate

- Flowmeter / Manometer
- Rotameter















# **On-Going QA/QC Activities**

- Daily automatic calibration checks
- Manual calibrations every 2 weeks
- Linearity checks
- Flow rate checks
- Visual check of met sensors
- Daily checklist

# Quality Assurance

#### **Quality Assurance for AQM Networks**

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- Systems audits
  - Operating procedures
  - Calibration proceduresMaintenance procedures
- Performance audits
- Flow rate checks
  - Reference standards for continuous monitors and met equipment
- "Blind" standards for off-site laboratories
- Data quality review
- Develop corrective action plans

# Data Management

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# Data Management for Networks

- Data acquisition
- Data reduction
- Data validation
- Data analysis

# **Data Acquisition**

- Automatic data polling
- Review for outliers
- Preset software alarms w/telephone notification
- Daily data polling
- Loading into permanent database (e.g., Oracle)

#### **Data Handling**

Data Reduction = Manipulation of raw data to create intermediate products such as averages, minimum values, maximum values, and standard deviations

Data Validation = Systematic review of measurement data for outlier identification, error detection, reasonableness, or exceedance of acceptance criteria. Data validation identifies suspect data whereas QC activities prevent bad data from being collected.

 
 Data Analysis
 = Interpretation of data to identify data trends, understand underlying causes of pollution events, relate concentration to meteorological conditions, etc.

# Data ValidationLevel I-Validity checks of raw<br/>monitoring dataLevel II-Independent evaluation of<br/>resultsLevel III-Review to identify data<br/>outliers and anomalies

#### Acceptance Criteria

- Routine check and review procedures
- Tests for internal consistency
- Tests of consistency of data with previous data sets
- Tests of consistency with data collected under similar conditions

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#### Reporting of Monitoring Data

- Total number of samples
- Percent data capture
- Mean, median, minimum, and maximum values
- Detection limits (DL's)
- · Frequency above and below DL's
- Number of exceedances
- Upwind versus downwind

#### **Measured data**

- The units to be used for SO<sub>2</sub>, NO/NO<sub>2</sub> and O<sub>3</sub> should be ppb, and that for PM should be µg/m<sup>3</sup>.
- For automatic instruments, SO<sub>2</sub>, NO/NO<sub>2</sub> and O<sub>3</sub> should be expressed one digit under decimal, and PM should be expressed by integral numbers (e.g., 15.3 ppb for SO<sub>2</sub> and 52  $\mu$ g/m<sup>3</sup> for PM).

#### Reporting of Meteorological Data

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- Hourly averages for all parameters
- Summary wind roses
- Percent data capture
- Summary of atmospheric stability
- Mean value and range for each parameter



Concentration in Ambient Air Method of Measurement					Method of Measurement	
Pollutant	Average	Area	and other Areas	Sensitive Area		
Sulphur Dioxide (SQ)	Annual Average*	80 μg/m <sup>3</sup>	60 uz/m <sup>3</sup>	15 με/m <sup>3</sup>	1. Improved West and Gaeke Method	
	24 Hours Average**	120 μg/m <sup>2</sup>	80 µg/m <sup>-</sup>	30 μg/m <sup>3</sup>	2. Ultraviolet Fluorescence	
Oxides of Nitrogen	Annual Average*	80 μg/m <sup>3</sup>	60 µg/m <sup>3</sup>	15 μg/m <sup>3</sup>	1. Jacob & Hochheiser modified (NaOH-NaAsO 2) Metho	
as NO 2	24 Hours Average**	120 μg/m <sup>3</sup>	80 µg/m <sup>3</sup>	30 μg/m <sup>3</sup>	2. Gas Phase Chemiluminiscence	
Suspended Particulate	Annual Average*	360 μg/m <sup>3</sup>	140 μg/m <sup>3</sup>	70 μg/m <sup>3</sup>	High Volume Sampling (Average flow rate not less than $1.1  m^3 / minute)$	
Matter (SPM)	24 Hours Average**	500 μg/m <sup>3</sup>	200 μg/m <sup>3</sup>	100μg/m <sup>3</sup>		
Respirable Particulate Matter (Size less than 10µm) (RPM)	Annual Average* 24 Hours Average**	120 μg/m <sup>3</sup> 150 μg/m <sup>3</sup>	60 μg/m <sup>3</sup> 100 μg/m <sup>3</sup>	50 μg/m <sup>3</sup> 75 μg/m <sup>3</sup>	Respirable Particulate Matter Sampler	
Lead (Pb)	Annual Average*	1.0 μg/m <sup>3</sup>	0.75 μg/m <sup>3</sup>	0.50 µg/m <sup>3</sup>	AAS Method after sampling using EPM 2000	
	24 Hour Average**	1.5 μg/m <sup>3</sup>	1.0 μg/m <sup>3</sup>	0.75 µg/m <sup>3</sup>	Or equivalent filter paper	
Carbon Monoxide	8 Hours Average**	5.0 mg/m <sup>3</sup>	2.0 mg/m <sup>3</sup>	1.0 mg/m <sup>3</sup>	Non dispersive Infrared Spectroscopy	
(CO)	1 Hour Average	10.0 mg/m <sup>3</sup>	4.0 mg/m <sup>3</sup>	2.0 mg/m <sup>3</sup>		
Ammonia (NH 3)	nmonia (NH ?) Annual Average* 100 µg/m <sup>3</sup> 24 Hour Averare** 400 µg/m <sup>3</sup>					
* Annual Arithmetic meainterval. ** 24 hourly/8 hourly valuesceed but not on two consorts NOTE <ol> <li>National Ambient Air (of safety, to protect the 2. Whenever and wherever category, it would be or investigations.</li> <li>The State Government</li> </ol>	n of minimum 104 mea es should be met 98% o ecutive days. Quality Standard : The k public health, vegetatio r two consecutive value onsidered adequate reas / State Board shall noti	surements in a ye of the time in a ye evels of air qualit in and property. is exceed the limit on to institute rep fy the sensitive a	ear twice a week 24 ho ear. However, 2% of t y necessary with an au it specified above for gular/continuous mon and other areas in the t	urly at uniform he time, it may lequate margin he respective toring and further espective states		

#### Remarks

• Without quality control procedures in place, laboratories cannot hope to remain incontrol, and without quality assurance procedures in place, they cannot ensure that they are in-control.

#### OBJECTIVES OF INTERLABORATORY COMPARISON

•To determine performance of individual laboratories

•Identify problems in laboratories and initiate remedial action related to individual staff performance or calibration of instruments

•Establish the effectiveness and comparability of new test methods and similarly to monitor established methods

•Identify inter-laboratory differences

•Provide additional confidence to laboratory clients

#### Inter-laboratory Comparison conducted by CPCB

•	At a time 15 lal	poratories can participate
•	Parameters -	Sulphur dioxide
		Nitrogen dioxide
		Ozone
		Carbon monoxide
•	All participar	nts are required to work with their own set of
	instrument	s, chemicals and analysers.
•	Duration -	5 Working days - 8 Working days

#### **EVALUATION OF RESULTS**

- Values assigned by pilot laboratory (CPCB) with a set range of tolerance ± 15%)
  - Values assigned by CPCB are based on calibration of automatic analysers employing Static Injection of pure gas (100%)
- Z Scores (Robust)

Re	Results of Inter-laboratory comparison conducted in December 2001								
Participant Code	Method	Refer Nitro	rence Conce ogen dioxide (	ntration µg/m³)	Refer	ence Concen hur dioxide (	tration μg/m³)		
		28	79	115	16	39	100		
1	Chemical	33*	73	176*	14	40	98		
2	Chemical	32	94*	134*	17	41	100		
3	Chemical	30	108*	114	15	33*	96		
4	Chemical	30	85	88*	17	12*	41*		
5	Chemical	34*	107*	128	13*	44	104		
6	Chemical	31	90	125	17	42	101		
7	Chemical	30	93*	111	16	46*	100		
8	Chemical	41*	87	124	14	45	105		

Percentage (%) of Labs 33 exceeding +/-(15%) SRT		40	27	13	21	7	
lo. of Labs 15%) SRT	exceeding +/-	5	6	4	2	3	1
Average Concentration 3		32	88	123	15	39	95
15	Analyser	30	77	114	13*	40	103
14	Analyser				16	43	94
13	Analyser	29	75	112	17	39	96
12	Chemical	32	79	119	17	43	107
11	Chemical	31	72	112	16	37	90
10	Chemical	34*	94*	156*	15		90
9	Chemical	33*	105*	112	14	44	101

Reference Concentration 103 ug/m3										
arithmetic stand, stand, deviation										
No.	Board	Impinger	1	1		mean	dev.	dev.	to setpoint	to setpoint
			µg/m <sup>3</sup>	µg/m <sup>3</sup>	µg/m <sup>3</sup>	µq/m <sup>3</sup>	µg/m <sup>3</sup>	%	abs.	rel. (%)
1	Andhra Pradesh PCB	midget type	121.1	117.9	119.1	119	2	1	15.9	15
2	Gujrat PCB	midget type	(8,3)	(29)	107.4	107			4.0	4
3	Haryana PCB	midget type	98.4	113.6	127.8	113	15	13	9.9	10
4	Madhya Pradesh PCB	midget type	151.3	92.4		122	42	34	18.4	18
5	Punjab PCB	midget type	107.3	187.6	160.9	152	41	27	48.5	47
6	Tamil Nadu PCB	midget type	114.4	108.6	108.6	111	3	3	7.1	7
7	West Bengal PCB	midget type	127.4	131.8	109.8	123	12	9	19.6	19
8	CPCB I	midget type	95.8	90.2	95.8	94	3	3	-9.5	-9
9	CPCB II (Saltzman)	fritted type	110.4	108.4	114.2	111	3	3	7.6	7
10	HLUG (Saltzman)	fritted type	(137,8)	99.8	95.8	98	3	3	-5.6	-5



			diox	ide,1	4.03.	2000	,			
		Refere	nce d	concei	ntratio	on 63 i	ug/n	13		
						arithmetic	stand.	stand.	deviation	deviation
No.	Board	Impinger	1			mean	dev.	dev.	to setpoint	to setpoir
			µg/m³	µg/m³	µg/m³	µg/m <sup>3</sup>	µg/m <sup>3</sup>	%	abs.	rel. (%
1	Andhra Pradesh PCB	midget type	52.1	52.1	52.1	52	0	0	-10.9	-17
2	Gujrat PCB	midget type	44.8	67.1	47.7	53	12	23	-9.8	-16
3	Haryana PCB	midget type	61.3	61.3	56.9	60	3	4	-3.2	-5
4	Madhya Pradesh PCB	midget type	69.4	47.5	65.7	61	12	19	-2.1	-3
5	Punjab PCB	midget type								
6	Tamil Nadu PCB	midget type	56.8	60.6	53.0	57	4	7	-6.2	-10
7	West Bengal PCB	midget type	59.3	59.3	59.3	59	0	0	-3.7	-6
8	CPCB I	midget type	53.0	56.7	60.5	57	4	7	-6.3	-10
9	CPCB II	Muencke type	60.3	62.8	62.8	62	1	2	-1.0	-2
10	HLUG	Muencke type	57.3	57.3	56.1	57	1	1	-6.1	-10

Rounds of	SULP		Qualitana	NITRO	GENDIOXIDE	Qualitara
Testing	Concn.	Participated		Concn.	Labs	
1 -	(µg/m3) 24 (28)	10	6	(µg/m3) 15 (21)	Participated	5
Mar 2000)	63 (58)	10	2	75 (82)	10	3
Mar. 2000)	97 (95)	10	3	103 (115)	10	4
	139 (131)	10	Nil	181(190)	10	2
2	26 (26)	12	1	15 (21)	12	8
Feb. 2001	42 (41)	12	Nil	30 (33)	12	4
	65 (75)	12	2	73 (86)	12	6
	93 (98)	12	2	114 119)	12	Nil
3	26 (25)	10	1	19 (19)	10	6
Mar. 2001)	42 (39)	10	1	24 (30)	10	5
	65 (62)	10	1	71 (74)	10	4
	93 (92)	10	2	117 108)	10	2
4	16(15)	15	2	28 (32)	14	5
Dec. 2001	39 (39)	15	3	79 (88)	14	6
	100 (95)	15	1	115 (123)	14	4





ASSESSMENT CRITERIA BASED ON Z SCORE					
$Zi \pounds 2 =$	Results are Satisfactory				
±2 <zi <±3="&lt;/td"><td>Results are Questionable</td></zi>	Results are Questionable				
$\pm 3 \pounds Zi =$	Results Unsatisfactory				

#### EVALUATION BASED ON Z SCORE

(Between Laboratory Z Score of sulphur dioxide)

Participant Code	Reference Concentration (ug/m3)			
	97	24	63	139
	0.27	1.69	1.68	
	1.35	1.18	1.35	1.19
	-	0.33	1.01	).89
	0.36	8.67	1.35	3.89
	0.72	0.5		.29
	3.33**	1.18	.67	.89
	0.63	0.33		.15
	0.09		1.69	2.2*
<del>0</del>	1.8	0.67		0.75

#### CONCLUSIONS

Most of the State Pollution Control Boards have participated in the inter-laboratory comparison for sulphur dioxide and nitrogen dioxide measurements by wet chemical methods

Overall, the results indicate relative consistency in measurements at higher concentration ranges as compared to lower concentrations.

#### **FUTURE PLANS**

To conduct inter-laboratory comparison study for other parameters e.g., Ozone, Carbon monoxide

To conduct interlaboratory comparison by sending standard gas mixtures in canisters or cylinders to different state pollution control boards, public sector undertakings.

# THANK YOU !