Air pollution Measurements and Emission Estimates

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Types of measurements

There are two types of air measurements:

1) Ambient measurement, Ambient Monitoring (concentration of pollutants in the air the public breathes)

2) Source measurement, source testing

Both are required in the ambient Air Quality standard philosophy.

Concentration must be measured to determine whether that air is really safe to breath

This means that air quality should meet the NAAQS.
To achieve that: Control and Monitoring of Air pollutants should be implemented.

To control pollutant concentrations:

The time, the place, and the amount of emissions, should be regulated.

The emission rates of various sources of air pollutants (i.e. factories, power plants, automobiles) must be regulated and measured.
Why measurements are needed?

1) Legal Requirements

2) Evaluation of air pollution control devices

Note: The control devices should be bought with guarantees. The buyer will usually not pay for the control devices until tests demonstrate that the device meets these performance guarantees in actual plant operation.
• The principal requirement of a sampling system is to obtain a sample that is representative of the atmosphere at a particular place and time and that can be evaluated as a mass or volume concentration.

• The sampling system should not alter the chemical or physical characteristics of the sample in an undesirable manner.
The major components of most sampling systems are:

1) An inlet manifold
2) An Air mover
3) A collection medium
4) Flow measurement device
(1) The inlet manifold transports the material from the ambient atmosphere to the collection medium or analytical device in an unaltered condition, all inlet of ambient air must be rainproof.

(2) The air mover provides the force to create a vacuum or lower pressure at the end of the sampling system (pumps).
(3) The collecting medium, may be solid or liquid sorbent for dissolving gases, a filter surface for collecting particles, or a chamber to contain an aliquot of air for analysis.

(4) The flow device measures the volume of air associated with the sampling system.
FIGURE 4.1
The components of any ambient-monitoring or source-sampling device. If the detector functions in real time (not cumulative), then the gas meter is not needed, but some kind of signal integrator or recorder is.
A Representative sample

In Air measurements there are two important problems

1) To obtain a suitable representative sample

2) The determination of the concentration of the pollutant of interest in it correctly.

The representative ambient air sample has been the topic of legal and technical controversy.
1. The air inside the parking structure normally contains much more CO than the NAQQS allows for ambient air. If the sample was taken from inside such a parking structure, the result will show great violation of NAQQS.

2. If the sample is taken directly across the street from such a structure, in most cases the concentration will be an order of magnitude less than inside the structure.
3. A block away, the concentration will be even less.

4. On the side walk directly adjacent to the structure, the concentration may be twice as high as on the opposite side of the street.
FIGURE 4.2
Illustration of some of the problems of choosing a sampler site to measure ambient CO in a city.
•Which of these locations is suitable for obtaining a sample of ambient air?

•Generally the ambient air sampler should be located at the place to which the public has free access where the pollutant concentration is highest.

•This means that all indoor spaces and plant sites which the public has no access are excluded.
Where can we put an ambient air monitor?

In Place:
1- Has the power
2- Shelter from rain and snow
3- Constant temp. environment
4- Easy access from monitoring personnel
5- Protection from vandalism
6- If possible free rent place
• The traditional place has been the roof of county health building or of the county courthouse.

• Unfortunately the concentration of the auto-related pollutants measured there is often much lower than at street levels at the busiest intersection downtown.
There are EPA guidelines for the proper placement of intake for air samples that are meant to represent ambient air. For example: CO measurements must be made at street level, downtown.

In Fig. 4.2 the air pollution control agency could meet this requirement by renting an office on the second floor of a downtown building and hanging its sampling probe out of the window, about 10 feet above the sidewalk.
In source testing: The representative sample problem is equally difficult.

- If the gas flow in large industrial smokestack is steady, well mixed across the diameter of the stack then the sample taken can be representative any time and at any place. But most of such stacks have variation in velocities and concentrations from point to point, and from time to time. Therefore, many separate measurements must be made and averaged.
FIGURE 4.3
Measured velocities and particle mass flow rates (velocity x concentration) in a complex duct. The values shown are the ratio of the observed value to the average value for the whole duct. For example, near the bend, where the velocity is shown as 1.2, the measured velocity was $1.2 \times 39 \text{ ft/s} = 47 \text{ ft/s} = 14.3 \text{ m/s}$ [2].
Example 4.1. In a source test, the stack was divided into four sectors, each of which had the same cross-sectional area. The following velocities and pollutant concentrations were measured in these sectors:

<table>
<thead>
<tr>
<th>Sector number</th>
<th>Velocity $V$, m/s</th>
<th>Concentration $c$, mg/m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>500</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
<td>600</td>
</tr>
<tr>
<td>3</td>
<td>14</td>
<td>650</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>675</td>
</tr>
</tbody>
</table>

What is the average concentration in the gas flowing in this stack?

The average concentration is

$$c_{\text{avg}} = \frac{\text{Total mass}}{\text{Total volume}} = \frac{\sum V A c}{\sum V A} = \left[ \frac{\sum V c}{\sum V} \right]_{\text{for equal areas}}$$

$$= \frac{10 \times 500 + 12 \times 600 + 14 \times 650 + 15 \times 675}{10 + 12 + 14 + 15} = 616 \text{ mg/m}^3$$
Even 36 feet farther downstream, the velocity and concentration data do not indicate that the flow become uniform, although nonuniformity is much less than it was close to the bend.

Presumably, if one went far enough downstream in this duct, one would find that the flow velocities and particle concentrations had become uniform. If one could do that, He should.

But more typical sampling situation is shown in figure 4.4. In such ducts, one cannot find a place “far downstream from any change of direction or other flow disturbance”.
In newer plants, designers sometimes considered the problems of obtaining a uniform gas flow and have provided access and a suitable location for the source sampler to place the required instruments.
FIGURE 4.4
The long straight duct and the comfortable place to stand and rest one's instruments, with rain cover power supplied, are not the norm for source testing [3]. (Reproduced with permission of Academic the University of Minnesota.)
4.2 Getting the representative sample to the detector

Many sampling instruments have some kind of devices on the inlet to exclude unwanted materials. e.g.:

- Insects sucked into a particulate sampler nozzle lead to erroneously (incorrectly) high readings.
- Air often contains large dust particles, which are of little health concern, that weigh more than all of the fine particles in the same air sample, which are of serious health concern.

- Before 1987, the sampler inlet was designed to exclude all particles larger than 50 micron. The quantity sampled was called Total Suspended particulate (TSP).

- The 1987 modification changed the inlet to exclude all particles larger than 10 micron, the quantity sampled is called PM$_{10}$ (particulate matter 10 micron or smaller).

- The 1997 modification changed the inlet again to exclude all particles larger than 2.5 micron.
• In sampling devices, gases may condense in the sampling device, or react with the solids they encounter there.

• Many combustion stack gases have a high water content and will condense on the walls of unheated sampling probe. In such cases, probes are normally heated to prevent this.

• Acid gases like SO$_2$ will react with alkaline solids on a filter, thus increasing the weight of solids on the filter.
• If a grab sample taken in the field is brought to the lab for analysis, the sample container must not react with or modify its content in transit. Even apparently inert materials like glass react with some air pollutants.
4.3 Concentration Determination

- After representative sample has been obtained, the concentration of the pollutant in it must be determined.
- Some pollutants, can be measured easily by real time instruments.
- Most of these operate optically, due to absorbance and transmittance at a particulate wavelength. i.e. Spectrophotometric methods.
The problem of interferences

• The problem of interferences in air pollutants measurements is not trivial.

• Even in the spectrophotometric methods, some interferences gases can be absorbed at the same wavelength.

For example: Measuring SO₂ gas in N₂ gas is easy. One passes the gas through a dilute solution of NaOH, in which the reaction is

\[ \text{SO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \]

the change in NaOH concentration is measured by simple acid base titration.
However, if the problem is to measure SO$_2$ in air, CO$_2$ in the air will also react and cause interference by the reaction:

$$\text{CO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$$

• If CO$_2$ concentration in air in this case is steady and known, a correction could be made in principle (but not in practice).
• But in the other cases, the concentration of the interfering components may not be known.

• The US EPA adopted a new method for measuring NO₂ and had to withdraw it when it became clear that the method was not adequately protected from such interferences.
4.4 Averaging

If we are measuring ambient air quality with real-time instruments, we generally want to know the average concentration over some period of time so that we can compare it with the applicable ambient standards, which all have some measuring period.

Average concentration = \( c_{\text{avg}} = \frac{1}{\Delta t} \int c \, dt \)

\( c \) = the instantaneous concentration

\( t \) = the time of measurement
Most of real-time instruments present their results as an electronic signal that can be easily averaged by built-in electronics for any suitably chosen averaging time.

The older instruments for gases as well as the current instruments for particulates are not real-time instruments, but rather are averaging instruments.
For example:

In EPA method for PM$_{2.5}$ sampling, it consists of:

- Special inlet that exclude particles >2.5 micron
- A filter
- A fan
- A flow measuring device
- Suitable housing

A pre-weighed filter is placed in the filter holder, and air is sucked through it for 24 hours at a measured rate.

Average concentration $= c_{avg} = \frac{\text{Increase in filter weight}}{\text{Air flow rate} \times \Delta \text{time}}$
Example 4.2. A PM$_{2.5}$ sampler ran for 24 hours at an average flow rate of 16.7 L/min. The tare weight of the fresh filter was 0.1400 g, and the gross weight of the filter, dried to the same humidity as the fresh filter, was 0.1405 g. What was the average PM$_{2.5}$ concentration in the air drawn through the sampler?

$$c_{\text{avg}} = \frac{(0.1405 - 0.1400) \text{ g}}{16.7 \text{ L/min} \times 24 \text{ h}} \times \frac{\text{h}}{60 \text{ min}} \times \frac{1000 \text{ L}}{\text{m}^3} = 2.08 \times 10^{-5} \frac{\text{g}}{\text{m}^3} = 20.8 \frac{\mu\text{g}}{\text{m}^3}$$

This answer would normally be reported as 21 $\mu$g/m$^3$. 

Notes on example 4.2

- The sample size is small

- The average value 21 μg/m³ is 84% of the annual avg. NAAQS.

- Measured change in filter weight is only 0.5 mg. Therefore, high quality weighing and sample humidity control is needed.

- If the weighings are only reliable to ±100 μg, then our confidence in the difference of the two measurements is ±200 μg, and our confidence in the ambient concentration is only about ±40%.
If the weighing uncertainty were ±10 μg, then our uncertainty in the concentration would be ±4 percent.

The example also shows that the resulting measurement is the average over the past 24 hours. This type of instrument is not nearly as suitable for determining hourly variations or trends as are the real-time instruments.
• Efforts to develop a suitable real-time instrument for PM2.5 have so far not been completely successful, mostly because of this small sample size problem.

• Note that the 16.7 L/min flow rate for PM$_{2.5}$ samplers is close to the average human breathing rate, so that the sample weight increase, 500 $\mu$g, is close to the mass of fine particles breathed in per day by an average person when the PM$_{2.5}$ concentration is 20.8 $\mu$g $/m^3$.)
Older measuring schemes for gas pollutants operated somewhat like the following:

1- passing a measured volume of gas through a bubbler that contained a solution that reacted specifically (no interferences!) with the gas to be measured and then titrating the solution to determine the concentration of the pollutant in the gas or measuring the color of the solution.
Many source sampling devices use the cumulative measuring schemes.

For example:

The EPA recommended sampling train for measuring the concentration of SO$_2$ gas in a stack. The pitot tube is used to measure the gas velocity in the stack. The sample of gas is pulled by the pump through the sampling probe. A needle valve and rotameter are used to ensure the flow rate of gas is in the right range, and into a dry gas meter.
FIGURE 4.5
U.S. EPA “Method 6” sampling train for SO$_2$. Glass wool excludes particulate matter from the rest of the sampling train. The midget bubbler contains an aqueous isopropanol solution, which removes SO$_3$ but not SO$_2$, its contents are discarded after the sampling is completed. The first two midget impingers contain an aqueous solution of hydrogen peroxide; the third impinger is empty and traps carryover liquid from the second. At the end of the test, the contents of the three midget impingers, plus the water used to rinse them, are combined and titrated with barium perchlorate, using a thorin indicator. The silica gel drying tube protects the pump, rotameter, and dry gas meter from moisture carried over from the impingers [4].
4.5 Standard Analytical Methods

EPA has standard methods for various pollutants. (often these are different for ambient monitoring than for source sampling.)

These methods define the pollutant. i.e.

In ambient air SO₂ is defined as the material which is detected by the SO₂ method shown in *EPA STANDARD METHODS FOR MAJOR AIR POLLUTANTS IN AMBIENT AIR* (the West-Gaeke method).

However, in powerplant stack SO₂ is defined as that material that is detected by “Method 6” (Fig. 4.5) which is chemically quite different from the West-Gaeke method.
Test methods for major air pollutants in ambient air

Reference methods

Equivalent methods

TSP, PM$_{10}$, PM$_{2.5}$

✓ 3 standard methods,
✓ An inlet designed to exclude particles larger than a certain size.
✓ Collecting on a filter for 24 hours
✓ Averaging the results (weight difference)
SO$_2$: West-Gaeke Method

• Known volume of air bubbled through a solution of sodium tetrachloro mercurate (TCM), which form a complex with SO$_2$.

• After several reactions, solution treated with pararosaniline (magenta dye, C$_{19}$H$_{18}$N$_3$Cl), to form intensely colored pararosaniline methyl sulfonic acid.

• The concentration is determined in a colorimeter, at wavelength 548 nm.
Ozone  *(chemiluminescence by ethylene)*

• The air is mixed with ethylene, which reacts with ozone in a light-emitting reaction (chemiluminescent reaction).

• The light is measured with a photomultiplier tube.

**Note:** Chemiluminescence is the emission of light with limited emission of heat, as the result of a chemical reaction.
• It is measured by non-dispersive infrared (NDIR) absorption.

• Non-dispersive means that the IR is not dispersed by a prism or grating into specific wavelengths; rather, filters are used to obtain a wavelength band at which CO strongly absorbs.

Note:

• This method is sensitive for water vapor interferences.
Hydrocarbons (Non-methane)

• Gas is passed through a flame ionization detector (FID), where HCs burn in a hydrogen flame.

• HCs cause more ionization than H₂ and this ionization is detected electronically.

• Part of the sample is diverted to a gas chromatograph, where CH₄ is separated from other gases and then quantified. CH₄ concentration is subtracted from the total hydrocarbon value from the FID.

Note:

• HC determination is important even it is not NAAQS, for ozone control program.
• NO₂ is converted to NO which is then reacted with O₃

• The light from this chemiluminescence reaction is measured.

• Ambient air contains NO (often more than NO₂), so a parallel sample is run without conversion of the NO₂ to NO. The resulting NO reading is subtracted from the combined NO and NO₂ to give the NO₂ value.

• The instrument normally reports both NO₂ and NO concentrations.
A TSP filter is extracted with HNO₃ and HCL to dissolve the lead.

Atomic absorption spectroscopy (AAS) used to determine the amount of lead in the extract.

**AAS:** is a spectro-analytical procedure for the qualitative and quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state.
Determination pollutant flow rate

The mass flow rate of pollutant is the product of the concentration in the gas and the molar or mass flow rate of the gas.

Example 4.3

The sampling train shown in Fig. 4.5 indicates that the concentration of $\text{SO}_2$ in a stack is 600 ppm. The Pitot tube and manometer in the same figure indicate that the flow velocity is 40 ft/s. The stack diameter is 5 ft. The stack gas temperature and pressure are 450° F and 1 atm. What is the $\text{SO}_2$ flow rate?
The molar flow rate of the gas is

Molar gas flow rate = \( V A \rho \)

\[
= 40 \text{ ft/s} \times \frac{\pi}{4} (5 \text{ ft})^2 \times 2.59 \times 10^{-3} \frac{\text{lbmol}}{\text{std ft}^3} \times \frac{528^\circ\text{R}}{910^\circ\text{R}}
\]

\[
= 1.18 \frac{\text{lbmol}}{\text{s}} = 536 \frac{\text{mol}}{\text{s}}
\]

The molar flow rate of \( \text{SO}_2 \) is

\[
1.18 \text{ lbmol/s} \times 600 \times 10^{-6} = 7.08 \times 10^{-4} \text{ lbmol/s} = 0.32 \text{ mol/s}
\]

Multiplying by the molecular weight of \( \text{SO}_2 \), we have

\[
7.08 \times 10^{-4} \times 64 = 4.53 \times 10^{-2} \text{ lb/s} = 163 \text{ lb/h} = 20.6 \text{ g/s} = 74.1 \text{ kg/h}
\]
Isokinetic Sampling

- In stack sampling for particulates, one must maintain isokinetic (constant) flow into the sampling probe.

![Diagram showing isokinetic sampling](image)
Emission Factors

• Emission testing is expensive

• For simple, well-defined sources (power plant stack), it can be tedious but it is not difficult.

• For poorly defined sources (e.g., dust from unpaved roads or Co from forest fires), reliable test results are difficult to get.

• Furthermore, Testing only possible after the facility is in Place.
Often we want to know what the emissions from a new facility will be before it is built.

To meet these needs, the EPA has produced a very useful set of emission factor documents.

These are commonly referred to by their original publication number, AP-42.

These are summaries of the results of past emission tests, organized to make them easy to apply.
## TABLE 4.2
Emission factors for bituminous and subbituminous coal combustion without control equipment

<table>
<thead>
<tr>
<th>Furnace type</th>
<th>All particles</th>
<th>PM(_{10})</th>
<th>SO(_x)</th>
<th>NO(_x)</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC, wall-fired, dry bottom</td>
<td>10A</td>
<td>2.3A</td>
<td>38S</td>
<td>21.7</td>
<td>0.5</td>
</tr>
<tr>
<td>PC, wall-fired, wet bottom</td>
<td>7A</td>
<td>2.6A</td>
<td>38S</td>
<td>34</td>
<td>0.5</td>
</tr>
<tr>
<td>PC, tangential fired, dry bottom</td>
<td>10A</td>
<td>2.3A</td>
<td>38S</td>
<td>14.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Cyclone</td>
<td>2A</td>
<td>0.26A</td>
<td>38S</td>
<td>33.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Spreader stoker</td>
<td>66</td>
<td>13.2</td>
<td>38S</td>
<td>13.7</td>
<td>5</td>
</tr>
<tr>
<td>Hand-fired</td>
<td>15</td>
<td>6.2</td>
<td>31S</td>
<td>9.1</td>
<td>275</td>
</tr>
</tbody>
</table>

Source: Tables 1.1-3 and 1.1-4 of EPA Emission Factors Book [7]. Section 1.1 of that document (Bituminous and Subbituminous Coal Combustion) is 46 pages long and has 19 tables, 6 figures, and 77 literature citations.

aTo obtain emission factors in kg/MT, divide table values by 2.

bThe various furnace types are described in [7] and in combustion books. PC means pulverized coal.

cThe letter A on some particulate and PM\(_{10}\) values indicates that the weight percentage of ash in the coal should be multiplied by the value given. Example: If the factor is 10A and the ash content is 8%, the particulate emissions before the control equipment would be 10 \times 8 or 80 lb of particulate per ton of coal.

dS = the sulfur content, which plays the same role as A in the preceding footnote.

eSO\(_x\) is expressed as SO\(_2\). It includes SO\(_2\), SO\(_3\), and gaseous sulfates.

fNO\(_x\) is expressed as NO\(_2\). It includes NO and NO\(_2\).
Example 4.4.

Table 4.2 shows part of two tables from one section of the EPA emission factors library. It shows the estimated emissions from the combustion of bituminous coal if no control devices are used. These are the emissions *going into* the control devices. Comparing them to the permitted emissions *coming out of the* plant (Table 3.1), one can estimate the degree of control required.

Using this table, estimate the emissions from a 500-MW power plant at full load, burning a typical Pittsburgh seam coal (see inside the back cover and Appendix C). The thermal efficiency is 35 percent. The power plant's boiler is assumed to be of the PC, wall-fired, dry bottom type.
\[
\text{Coal consumption rate} = \frac{\text{Power output}}{\text{Efficiency} \times \text{coal heating value}}
\]

\[
= \frac{500 \text{ MW}}{0.35 \times 13,600 \text{ Btu/lb}} \times \frac{3413 \text{ Btu}}{\text{kWh}} \times \frac{1000 \text{ kW}}{\text{MW}}
\]

\[
= 3.585 \times 10^5 \frac{\text{lb}}{\text{h}} = 179 \frac{\text{ton}}{\text{h}} = 163 \frac{\text{tonne}}{\text{h}}
\]

The particulate emission rate is

\[
\text{Particulate emission rate} = \left( \text{emission factor} \right) \left( \text{coal flow rate} \right) = 10A \frac{\text{lb}}{\text{ton}} \left( \text{coal flow rate} \right)
\]

\[
= (10 \times 8.7) \frac{\text{lb}}{\text{ton}} \times 179 \frac{\text{ton}}{\text{h}} = 1.56 \times 10^4 \frac{\text{lb}}{\text{h}}
\]

\[
= 7.8 \frac{\text{ton}}{\text{h}} = 7.1 \frac{\text{tonne}}{\text{h}}
\]

For carbon monoxide we can see that the emission rate is 0.5 lb/ton \times 179 \text{ ton/h} = 89.5 \text{ lb/h}, and for nitrogen oxides, 3884 \text{ lb/h}.\]
Example 4.5. If all of the ash in the coal in Example 4.4 were emitted with the gas stream, what would the emission factor for particulates be?

The factor is $10A \text{ lb/ton}$, where $A$ is the ash percentage in the coal. If the coal is $A$ percent ash, then the coal contains

$$\text{Ash content} = \frac{A}{100} \times \frac{2000 \text{ lb}}{\text{ton}} = 20A \text{ lb/ton}$$

and thus, if all of it were emitted, the factor would be $20A$ instead of $10A$. \hfill \blacksquare$