
Estimating Air Emission Rates

Course No: C02-011

Credit: 2 PDH

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INTRODUCTION

Air pollution is considered an important public health issue in the United States and other portions of the world. For example, a major issue confronting the 2008 Summer Olympics in Beijing was the high concentration of air pollutants that can affect the performance of the athletes and the health and enjoyment of the spectators. The problem resulted in great costs to the organizers, as well as major negative publicity for China.

In the US, concern over air pollution has consistently been at the top of the polls as far as environmental issues are concerned. Tens of thousands of Americans are conservatively estimated to die prematurely every year because of exposure to pollutants through air pathways. The public health cost of premature death, hospitalization, and missed work time due to air-related problems is staggering. Laws have been promulgated to reduce emissions from industrial sources as much as is practical. To determine compliance, predict potential health impacts, need for and design air pollution control equipment, and manage such an air program, it is critical to estimate the rates at which contaminants enter the atmosphere from the processes the facilities are in control of. In other words, one cannot manage an air program until one estimates or measures what one emits.

Please note, by the way, the use of the term “estimation” of emissions. Because processes and their emission rates are dynamic emission rates developed are probably not absolutely accurate at all times. The hope is that the rate estimated will be either reasonably close to the actual emission rate most of the time the process is operating or is a “conservative” estimate, a rate that is not likely to be exceeded at any time in practice.

There is no easy, inexpensive way to estimate accurately air emissions from sources. Many different techniques exist. The user must determine the right method to estimate the emission rate of the air contaminant in question. Factors that must be considered include:

- appropriateness for contaminant in question
- accuracy required
- changeability of process
- cost effectiveness.

Also, there is no single technique for all situations. The engineer normally must compromise and select a technique that may sacrifice some accuracy for the sake of practicality and cost effectiveness. In addition, processes and compounds change. While one estimation technique may be viable, over time with changes in the process, the technique must be repeated or a new estimation technique may need to be used. It is likely that different techniques will need to be used for different segments of the plant. What is most important for the engineer is to develop a program to regularly estimate emissions of needed accuracy from different processes.

The four major techniques for estimating emission rates are:

- direct measurement
- material balance
- emission factors
- engineering equations.

DIRECT MEASUREMENT OF AIR EMISSION RATES

There are techniques and procedures to perform direct measurement (commonly known as “stack testing”) of many regulated air pollutants for most source categories. It is common that to demonstrate compliance with an emission limit found in a permit or regulatory standard one must perform a direct measurement using a procedure approved by the USEPA or other recognized regulatory authority.

Please note that performing a stack test acceptable to a regulatory authority is very technically complex. It is strongly urged that if your company is required to perform one, it hire an experienced testing firm, particularly for the specific methods required. What follows is general background information about direct measurement of air pollutants. A facility should not use the information provided to perform tests on your own.

The components of a direct measurement for which there are procedures include:

- collection of a representative sample of gas from the exhaust or stack,
- pre-treatment of the gas sample to remove any other components which may interfere with the testing,
- analysis to measure the compound in question,
- computations of emission rate in different forms.

QA/AC procedures accompany each step. Typically, the method measures the concentration of the compound in the exhaust. Simultaneously collecting the exhaust flow rate enables the tester to convert the concentration into an emission rate (typically, in pounds per hour).

Basic Accepted Direct Testing Methodology

The basis of direct measurement is the group of procedures published by the USEPA found in 40 CFR Part 60, Appendix A. Some states and industrial organizations have published additional or slightly different methods. However this course will focus on the USEPA methods as they are uniform across industry in the US. Virtually all regulatory agencies recognize these methods. Finally, these methods have very exacting standards as to how to perform the procedure, QA/QC steps, and what data to record. Not following the procedure to the letter strongly risks the integrity and acceptability of results.

The first Appendix A procedure to be discussed is Method 1. This is a general procedure applicable to virtually all testing on how to collect sample for analysis. It provides basic guidelines to how to set up a testing “train”. A schematic of a typical train (applied to

measuring particulate matter emissions) is shown in the diagram below, from Figure 5-1 of USEPA Method 5.

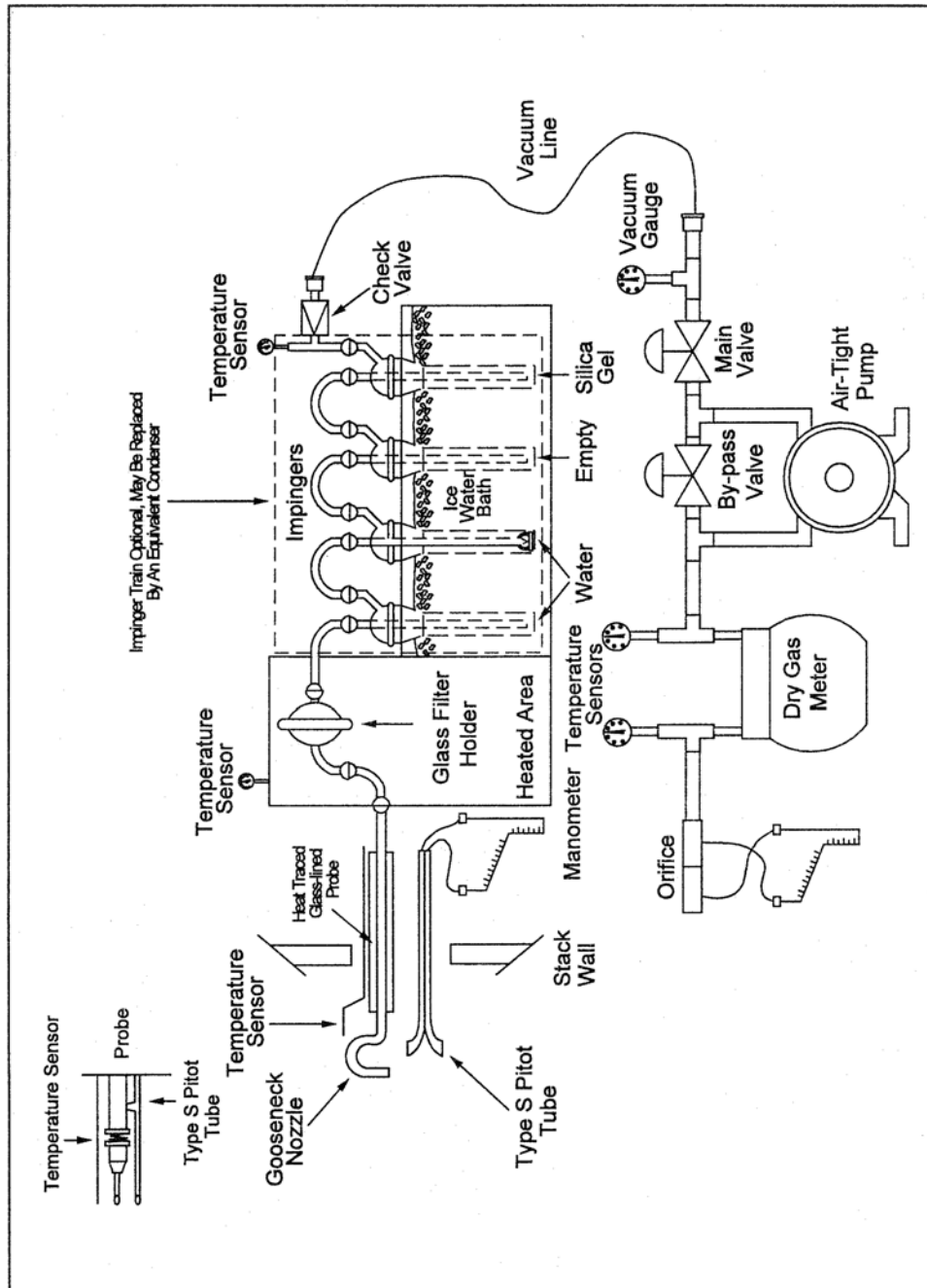


Figure 5-1. Particulate Sampling Train.

For any method, a testing “probe” must be inserted in a hole in the exhaust or stack. The end of the probe must have an opening to allow the collection of some exhaust flow. This flow moves through the inside of the probe outside of the exhaust to an area that typically pre-treats the exhaust sample before it is tested for the contaminant of concern. The sample must be maintained at $248^{\circ} \pm 25^{\circ}\text{F}$ to prevent condensation. This is generally maintained and monitored through a thermocouple.

Most trains also contain an S-type pitot tube to measure stack gas velocity by detecting a pressure difference proportional to velocity. Given the stack diameter, a flow rate can be estimated which can be used together with the pollutant concentration to determine a mass emission rate.

The sample of most trains then flows through a heated filter box to remove particulate matter from the sample. This is necessary either as part of Method 5 or related methodology to measure the particulate emission rate or to remove particulates which may interfere with analysis of other compounds.

The sample of most trains then flows through an impinger box containing a series of tubes containing certain chemicals to remove and measure the presence of certain compounds. In most cases the tubes are chilled by ice to condense out water. The sample leaving the impinger box can now be directed to the appropriate analyzer to measure the concentration of the pollutant in question. A sample train contains a pump box containing a pump to pump sample at a uniform rate throughout the system. There is also a centralized control box which houses a dry gas meter, temperature controllers, temperature display, manometer, flow adjustment valves and timer. Isokinetic sampling through the system is maintained by comparing the dry gas meter orifice pressure and the Pitot pressure reading and then adjusting the pump rate accordingly. Sample enters the control box through an umbilical, containing many lines, including sample and pitot and thermocouple and other lines.

Method 1 contains guidance for the selection of sampling ports and traverse points for acceptable sampling of a representative aliquot of exhaust. A key concern is collecting a uniform sample within the exhaust over time. For measuring a gaseous compound, the placement of the probe within the exhaust is less important as the concentration of the gas should be uniform as it flows through the width of the exhaust. The exception is cyclonic or swirling flow. Sample should not be taken from a section of exhaust exhibiting this type of flow. Method 1 contains procedures for determining whether there is cyclonic or swirling flow.

However, sample capture is most critical for measuring particulate matter as it does not mix equally with exhaust air. Particles are highest in concentration along and near exhaust walls, as its flow is slowest (the wall slows down its movement as a result of collisions). Particulate matter flow is fastest and is thus less held up (and more dilute) in the center of the exhaust. Therefore, to collect a true representative sample of particulate matter, the probe must be moved in stages during the test from just inside the wall to the center of the exhaust (traverse points) based on an equation in Method 1. This formula is

shown below for particulate matter flowing through a circular stack in Figure 1-1 of Method 1 below.

Another effect on flow and particulate or gaseous concentration within the diameter of an exhaust is disturbances in flow, such as bends, contractions, or expansions in the pipe. Ideally, a probe should be placed at least eight diameters in length downstream and two diameters upstream of any such disturbance. The probe must be adjusted during the sample collection period to collect exhaust throughout the interior of the duct (traverse points) based on a table. There are separate tables for particulate collection and non-particulate collection, from circular- and rectangular-shaped stacks. Figure 1-1 below shows the number of sampling points required to be taken for sampling locations below “8 & 2” diameters from the nearest disturbances. Table 1-2 from Method 1 follows. It proscribes the distances for particulate collection from circular stacks.

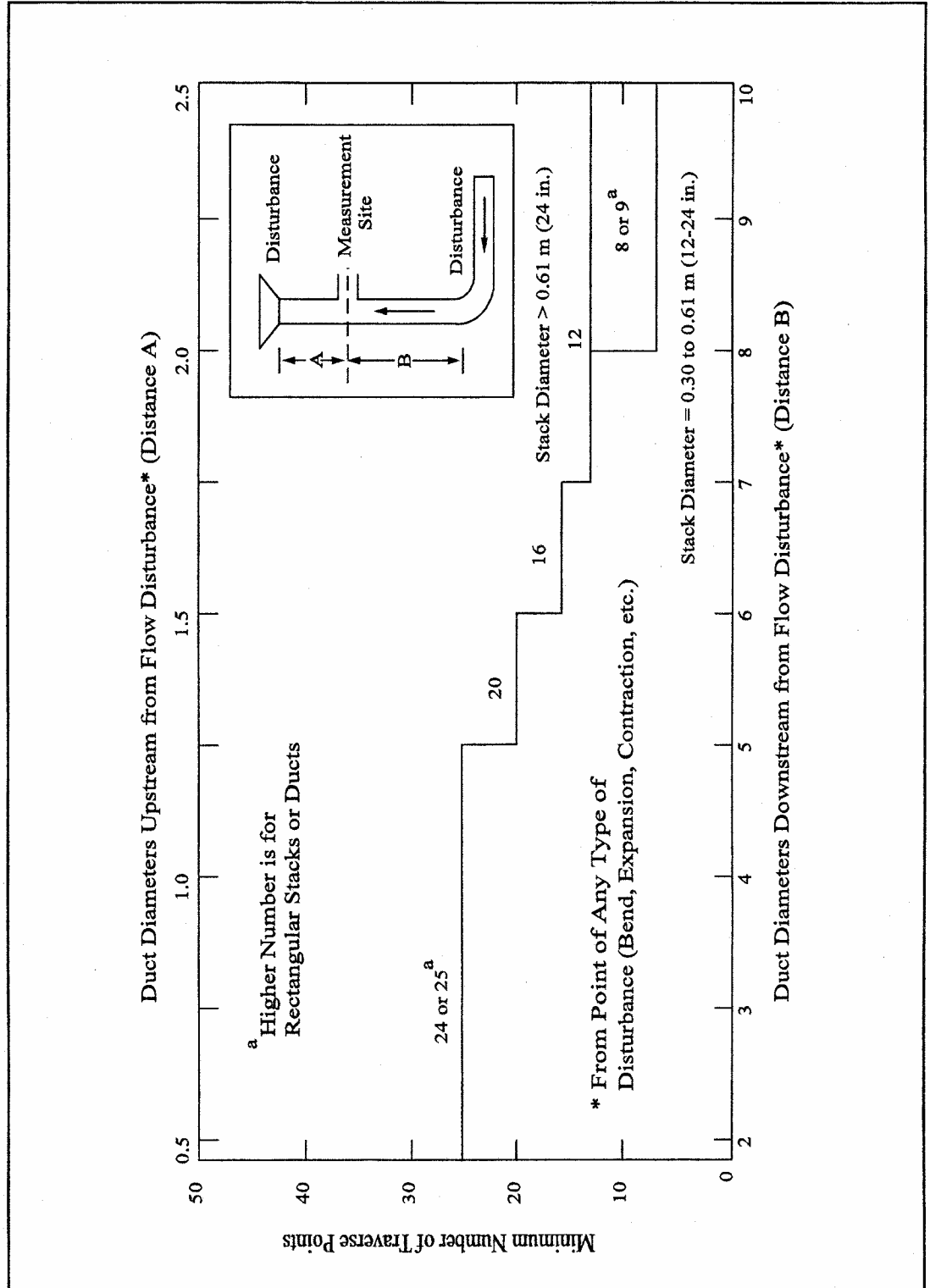


Figure 1-1. Minimum number of traverse points for particulate traverses.

TABLE 1-2 LOCATION OF TRAVERSE POINTS IN CIRCULAR STACKS (Percent of stack diameter from inside wall to traverse point)

Traverse Point Number on a Diameter	Number of traverse points on a diameter											
	2	4	6	8	10	12	14	16	18	20	22	24
1	14.6	6.7	4.4	3.2	2.6	2.1	1.8	1.6	1.4	1.3	1.1	1.1
2	85.4	25.0	14.6	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2
3		75.0	29.6	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5
4		93.3	70.4	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9
5			85.4	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5
6			95.6	80.6	65.8	35.6	26.9	22.0	18.8	16.5	14.6	13.2
7				89.5	77.4	64.4	36.6	28.3	23.6	20.4	18.0	16.1
8				96.8	85.4	75.0	63.4	37.5	29.6	25.0	21.8	19.4
9					91.8	82.3	73.1	62.5	38.2	30.6	26.2	23.0
10 ...					97.4	88.2	79.9	71.7	61.8	38.8	31.5	27.2
11 ...						93.3	85.4	78.0	70.4	61.2	39.3	32.3
12 ...						97.9	90.1	83.1	76.4	69.4	60.7	39.8
13 ...							94.3	87.5	81.2	75.0	68.5	60.2
14 ...							98.2	91.5	85.4	79.6	73.8	67.7
15 ...								95.1	89.1	83.5	78.2	72.8
16 ...								98.4	92.5	87.1	82.0	77.0
17 ...									95.6	90.3	85.4	80.6
18 ...									98.6	93.3	88.4	83.9
19 ...										96.1	91.3	86.8
20 ...										98.7	94.0	89.5
21 ...											96.5	92.1
22 ...											98.9	94.5
23 ...												96.8
24 ...												99.9

Method 2 contains the procedure for measuring stack velocity with which to measure exhaust velocity and volumetric flow rate. As mentioned earlier, an S-type pitot tube generally composed of stainless steel is placed next to the end of the probe and placed inside the exhaust tube or stack. Most sampling trains are equipped with a 10 in. (water column) inclined-vertical manometer, having 0.01 in. H₂O divisions on the 0 to 1 in. inclined scale, and 0.1 in. H₂O divisions on the 1 to 10 in. vertical scale. This type of manometer (or other gauge of equivalent sensitivity) is satisfactory for the measurement of Δp values as low as 1.27 mm (0.05 in.) H₂O. Magnehilic gauges may be used, but have more extensive calibration procedures. A thermocouple, liquid-filled bulb thermometer, bimetallic thermometer, mercury-in-glass thermometer, or other gauge capable of measuring temperatures to within 1.5% of the minimum absolute stack temperature may be used. The temperature sensor is generally attached to the pitot tube such that the sensor tip does not touch any metal and not interfere with the pitot tube face openings. A mercury- or water-filled U-tube manometer capable of measuring stack pressure to within 2.5 mm (0.1 in.) Hg must be used. A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.54 mm (0.1 in.) Hg must be used.

After average differential pressure (Δp) and temperature data is collected for each traverse point, the velocity and flow rate can be calculated using this data, the pitot tube coefficient, the dry molecular weight of the stack gas, the stack diameter, and other information. Special procedures exist for small diameter ducts and exhausts transporting gasoline vapor or landfill gas.

Method 3 is the procedure for measuring exhaust components in order to estimate dry molecular weight, necessary for the calculations of Method 2. It focuses on estimating content of the four largest components in any gaseous stream: nitrogen, oxygen, carbon monoxide, and carbon dioxide. N₂ and CO are not measured, as their concentrations are assumed to change only negligibly in any emission context. Method 3 calls for the use of an Orsat or Fyrite analyzer, which contains reagents which remove (absorb) the two remaining compounds. The N₂ concentration is considered constant and CO concentration is subtracted from 100. For QA/QC, standard concentrations of O₂ and CO₂ must be used.

Method 4 is the procedure for measuring the moisture content of an exhaust stream. Moisture must be subtracted out to determine dry molecular weight in order to determine velocity and flow rate in Method 2. Silica gel is placed in at least two impingers in the cooled box which collects the moisture for measurement.

Method 5 is the most common procedure for measuring particulate matter (PM). It measures PM from two sources: "filterable" PM and "condensable" PM found condensed in impingers downstream of the filter. In some procedures, the PM measured in both locations must be combined. In most procedures, only filterable PM needs to be calculated and reported. The setup is as discussed earlier. A heated sample flows through a heated filter. Glass fiber filters, without organic binder, exhibiting at least 99.95% efficiency (<0.05% penetration) must be used. The sample is then condensed in a chilled impinger box, containing four impingers, the first two with measured quantities of water,

one empty one, and, finally, one with silica gel. The content of the four impingers must be weighed and compared with pre-test weights.

Other Method 5 procedures exist for specific circumstances from specific source types (i.e., wood heaters, asphalt industry, etc.). Methods 201 and 202 are more modern particulate matter methodologies that should be considered.

One critical item involved in the integrity of the sampling train and the integrity of any test is the fact that it is a closed system and minimal outside (clean) air has leaked in to dilute the concentration of the pollutant in the exhaust sample. It is critical to ensure that all connections of the sampling train be fully fitting and sealed, normally with silicone grease. Method 5 requires and other methods recommend that a leak check be determined before and after the sampling event occurs to determine the degree of leakage. Method 5 provides the procedures for performing the leak check and acceptable leakage levels. If a leak check demonstrates that leakage exceeds the allowable rate, then the sample and results must be discarded and repeated from the beginning.

Most of the remaining Appendix A methods pertain to measurement of gaseous pollutants, and may be summarized as follows.

Method #	Pollutant
6	Sulfur dioxide
7	Nitrogen oxides
8	Sulfuric acid and sulfur dioxide
10	Carbon monoxide
11, 15, 16	Hydrogen sulfide and reduced sulfides
12	Lead
13	Fluoride
18, 24, 25	Volatile organic compounds (VOCs)
201, 202	PM-10

There are other more recent methods for other compounds, such as specific VOCs and metals. Typical of these methods the sample is collected through a heated probe and is pre-treated appropriate to the method to remove compounds that may interfere (particulate matter, water, or other compounds) with the analysis. Then the sample enters a monitor which measures the content of the pollutant in question. For example, Method 6 requires the sample to flow through an isopropanol sampler to remove fluorides and other halogens and hydrogen peroxide and potassium iodide to remove SO₃ and H₂SO₄ which may interfere with the analysis for SO₂. The SO₂ fraction is measured by a barium-thorin titration method, thorin is an indicator of SO₂ concentration and may be compared to a known standard to determine actual concentration.

Usually, when one tests using these methods, the tester complies with Methods 1-4 to establish the volumetric flow rate so that the concentrations of compound determined by the method can be converted to a mass rate.

Tips on Performing a Stack Test

As is apparent, performing a stack test is very complicated. There are many items that could go wrong or add potential error to the results. For that reason, virtually all agencies require that emissions be reported as an average of three successful runs (obtaining sample throughout the run and successful leak tests). Each run is generally one hour in length. However, for pollutants found in very dilute concentrations in the exhaust a longer sampling time for each run may be necessary to collect sufficient sample to measure. This is the approach commonly for trace metals.

In addition, because of the complexity of the methodology most regulatory agencies require a formal written protocol that they must approve before the test is sanctioned. Normally prepared by the testing firm, these protocols should not merely state the names of the test methods, but should also describe the method thoroughly and provide necessary calculations, such as the number and location of traverse points. Once approved, the facility and testing firm should set a mutually agreeable date with the regulatory agency. The agency may send an inspector to observe the test. Generally, a stack test report, summarizing the methodology, showing the results and attaching raw data must be submitted to the regulatory agency within 30 days of completion of the field work of the stack test (an extension may be requested).

Results are often given as a concentration or mass emission rate based on the measured volumetric flow through the exhaust. Because of constraints of the methods a lower limit is often defined, below which the pollutant cannot be measured. For trace metals and individual VOCs, in particular, this is an important point as the individual pollutant may be present in a very dilute concentration. If the lower limit of measurability is a relatively high concentration, then not enough sample was taken.

Another critical aspect of direct measurement is coordination with the operating process. A successful run is also considered successful if the operation ran successfully during that time. If it “turned off” during that time, then potentially no or non-normal amounts of pollutants were emitted and this cannot be legitimate for the run. For many methods, the probe can be removed when an upset begins and the run can be stopped at a certain point to be resumed when the process is operating normally again to reach the one hour of sampling time.

Besides upsets, it is critical to record operating conditions during a run. If there was some unusual activity that may affect emissions, then the facility would want to know that. After the fact, it may be legitimate to remove one run from the testing (if it can be traced to a non-normal activity during the run), and the final emission rate be based on the average of two “normal” runs.

It is critical to work with the operating engineers during the planning, set up, and during the testing itself. As mentioned earlier, the dates of the field testing must be coordinated between the facility, tester, and regulatory agency. It must also be coordinated with Manufacturing because they may know if special operations will occur those days that

are atypical. During the testing, if the temperature or some other parameter normally varies over time, it is important to know what the variations are and determine whether it correlates to any change in emission rate during the run. If the process is run in different modes, it will be necessary to perform triplicate runs of each mode and important to keep operations at the individual mode for each test. Coordination between manufacturing operators, testers, and environmental engineers is critical.

Continuous emission monitoring

A further advance to performing one-time direct measurement is to perform continuous measurements of the pollutant. This can be performed using a Continuous Emissions Monitor (CEM, sometimes referred to as a system: CEMS). A CEM has many of the same attributes as a stack test. A probe is inserted in the stack and the sample is conditioned appropriately before it enters into the analyzer for determination of concentration. Flow rate may also be determined. A Data Acquisition System (DAS) calculates, stores, and organizes emission rates. Typically, sample is taken regularly (every minute) and results can be averaged for hourly or other types of rates.

The USEPA has QA/QC procedures for ensuring a CEM's accuracy for compliance purposes. Daily calibration and evaluation of drift from zero must be performed. Regular audit testing must be performed, such as running an audit (known concentration sample of the compound being measured) and running a test in the exhaust piping versus another outside CEM (relative accuracy).

Purchasing and maintaining a CEM is expensive but can provide a reliable, consistent means to evaluate emissions over not just a short period but a long period of time and provide information about emissions during various time cycles of your production.

One other type of monitor is an ambient monitor. The USEPA and states operate thousands of these units throughout the US to measure ambient concentrations of criteria pollutants. Facilities may operate ambient monitors at different locations around their facility to assess their impact (ground level concentration) at the various locations. Teamed with wind and other meteorological data, ambient monitors can advise how much a facility's or background emissions is contributing to the ground level concentration around a site. An ambient monitor has a pump to pump in ambient air at a discrete rate and analyze for a particular compound.

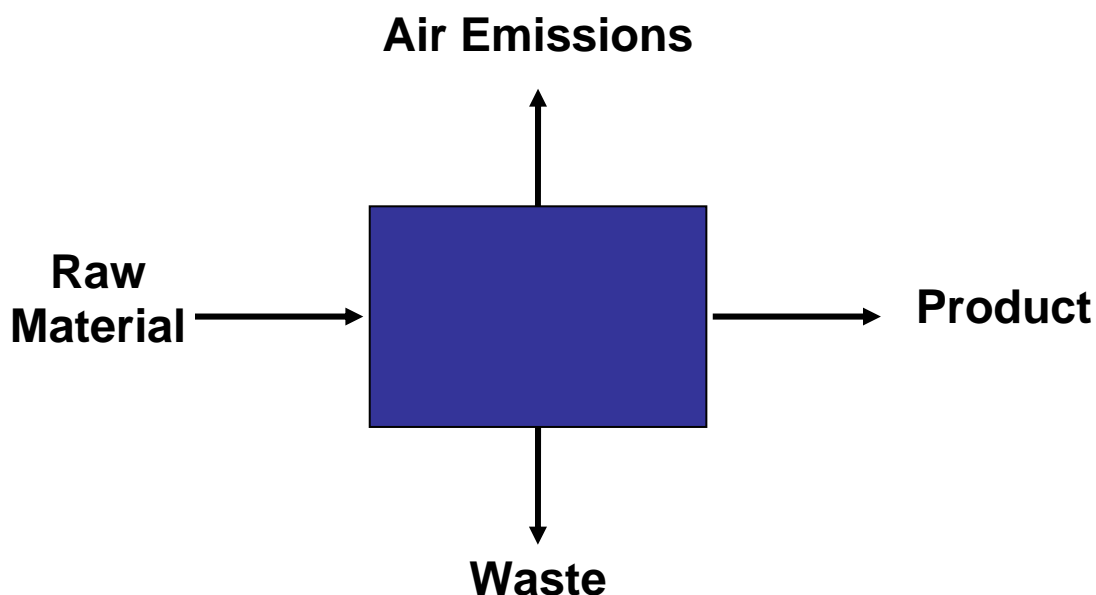
Summary

In summary, direct measurement of air pollutant emission rates has the major advantage of measuring real time emissions during a process operation. These are real measurements, not theoretical calculations. Direct measurement is favored, when practical, by regulatory agencies and considered the "final word" concerning emissions. The disadvantages include its complexity and cost and its error given the small potential errors that may occur during the many steps involved in sampling and analysis. Particularly given its cost, stack testing cannot practically be used to measure emissions

of all process situations from all pieces of equipment of a moderately sized or larger manufacturing facility.

MATERIAL BALANCE

Material balance is simply the principle of what quantity of a chemical enters a process or into a piece of equipment must either leave that process or piece of equipment, stay in the process or piece of equipment, or be converted by a chemical reaction. In this case, we can eliminate the middle option, assuming that in a dynamic process, the material does not stay long term in the process or equipment. The figure below illustrates a simple material balance through a process or a piece of equipment.



The total quantity of chemical entering the process or piece of equipment must equal the sum of the quantities that leave it:

- contained in the product that leaves the process or equipment,
- through liquid and solid waste,
- by volatilization (air), and
- converted by chemical reaction.

As an alternative to direct measurement of emissions into the air (which we have seen is expensive and difficult), if one can measure the other parameters (quantity of the compound incorporated into the product, chemically converted, content in solid waste, and content in liquid waste), the balance would be air emissions.

Fortunately, the quantity of a compound entering the process or equipment can be accurately measured or calculated, as can the quantity leaving as product. The contaminants leaving the process can reasonably be measured in the solid and liquid waste, leaving the air emissions. The advantage of this technique is simplicity. It is easy

and inexpensive to perform as not many complex measurements need to be taken. Many of these measurements are already compiled.

The major disadvantage of material balance is accuracy. Often air emissions represent the smallest component of the material balance. Measuring the other components has small, but discernable errors in technique. This compounds the errors in estimating the air portion. For example, if 100 pounds of Compound A enters a reactor during a batch process and it is determined that 80 pounds of this total is chemically converted into another compound which is part of the final product, 12 pounds are found in the solid waste, and 7 pounds are found in the wastewater, a material balance would conclude that the emission rate is 1 pound of Compound A per batch or per 100 pounds of Compound A use. But what if the measurements are in error? What if 79 pounds are incorporated into the final product instead of 80 (an error of only 1.25%)? What if there was an error in measuring the solid waste and 11.5 pounds of Compound A in reality ends up there (an error of 4.1%)? And, what if there was an error in measuring the Compound A content of the wastewater and the equivalent of 6.8 pounds are found there (error of less than 3%)? Then the balance – the total emitted into the air – would not be 1 pound, but 2.7 pounds, an error of 270%! And this would be an underestimation as well, which would not be satisfactory to a regulatory agency. These errors are typical and if anything on the low side for these type of measurements.

Therefore, it is possible to end up with unreasonably high or low air emissions just because of the errors involved in measuring the other parameters. The error bars are potentially greater than the air emissions itself. In fact, it is possible to measure quantities of the compound in the product, waste, etc. that total a greater value than the known input. Subtracting this sum from the input would result in a “negative” emission rate which, of course, is not possible and invalidates the entire material balance.

Therefore, material balance should only be used in simple systems where there are not many pathways for the chemical and are easy to measure and for systems where the air component is considerable. One example is painting (coating) processes. All of the solvent contained in a paint applied to a substrate will evaporate into the air, leaving behind the solid. So the air emissions would equal the entire solvent portion of the paint since it is intended to volatilize and leave behind the solid on the substrate. Particulate matter (solid) emissions from coating processes can be estimated by material balance, as well. One needs to estimate the “overspray”, the quantity of paint that misses the substrate and potentially is captured in the exhaust of the paint spray booth and take into consideration any filter or baghouse that controls particulate emissions. Caution should be taken not to use material balance for much more complicated systems than this unless accurate measurements can be assured.

PUBLISHED EMISSION FACTORS

A growing number of emission factors have been published over the years for a greater diversity of equipment and process situations. They are published to save facilities time in determining emissions and in “leveling the playing field” allowing many firms to use

the same emission factors. These are often calculated and published by equipment vendors, trade associations, the USEPA and other agencies. Often these emission factors are published in normalized terms such as lb of pollutant per 1000 gal of a certain fuel combusted, lb per Kw electricity produced, etc. Manufacturers often provide emission factors as guarantees to enable the user to properly estimate emissions from the proposed equipment and to permit the unit.

The USEPA has a well known compilation of emission factors for different types of equipment or operations called AP-42, accessible from its website. Emission factors are used in calculating most instances of greenhouse gas (GHG) emissions. The World Resources Institute (WRI) has published a document called the “GHG Protocol” with highly developed GHG emission factors for different types of sources, direct and indirect. These emission factors are modified every year or two based on changes observed, such as the relative sources of electricity in a region.

The advantage of emission factors is, like material balance, their simplicity as they allow the user to readily calculate emissions. The emission factor multiplied by the rate of usage (following the examples above, gallons of fuel combusted per year, Kw production) simply estimates emissions.

However, their disadvantage is that they are applicable to a limited number of situations or pieces of equipment that operate consistently in a certain way. An emission factor cannot be used for a process that varies in its operations and emissions profile. In many cases, such as AP-42, the emission factors are based on dozens of measurements of emissions from related equipment, sometimes used back in the 1950’s when pollution minimization was not a design consideration. Emission factors from equipment vendors tend to represent a single unit they manufacture or similar group, unlike AP-42 whose factors represent units of different manufacturers and different vintages. In addition, equipment vendors who use their emission factors as guarantees against which additional effort and cost is possible, will wish to make these emission factors high to better ensure their equipment will “pass”. In both cases, emission factors tend to be “conservative” (overestimated emissions) and not very accurate. For equipment vendors, their guarantees tend to be high so their equipment will pass. For the USEPA, this is because their emission factors tend to average emission from old, less efficient equipment. Conservative emissions may be advantageous in terms of ensuring that the “real” emissions from the equipment will not be higher than the emission factor. However, conservative emissions may be a detriment if accuracy is necessary or if the higher emission factor causes calculated total facility emissions to be higher than expected and may cause the facility to be subject to more stringent regulations as a result.

ENGINEERING EQUATIONS

Equations exist to estimate emissions from a process based on its likely chemical and physical properties and the degree of volatilization of the contaminants during their processing. These are specific in terms of the evaluation of what really “goes on” in the reactor, tank, etc. (See illustration below). There are equations that estimate the degree of

volatilization of different compounds at different temperatures, pressures, and other external factors.

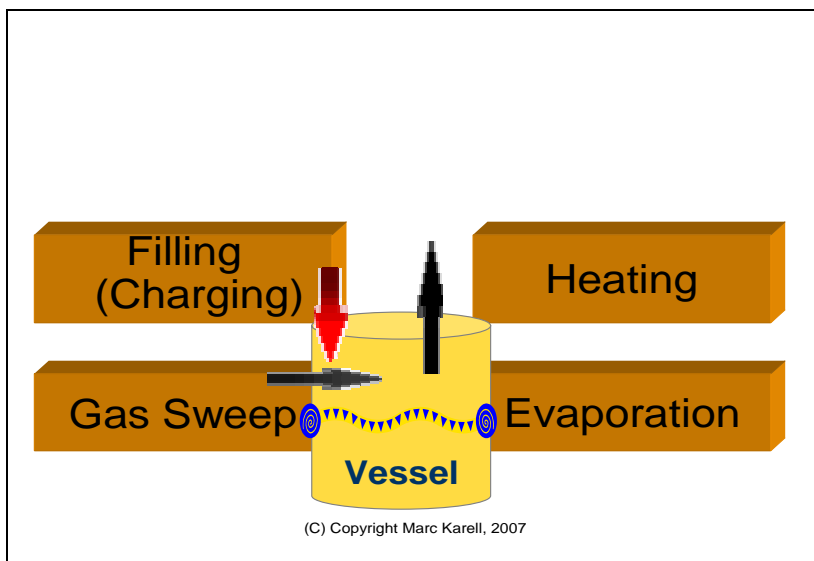
Engineering equations are most useful in the chemical and pharmaceutical industries, tracking the emissions from the myriad of individual process steps necessary to add raw materials to a reactor, form the product, and isolate and remove byproducts and other impurities. The Pharmaceutical Maximum Achievable Control Technology (MACT) rule, found in 40 CFR Part 63, Subpart GGG, contains the engineering equations for its processes, and recommends engineering equations be used as the preferred method for emissions estimation. Though not complete, the following are process steps in a chemical or pharmaceutical plant that lend themselves toward the use of engineering equations.

- Filling (or charging). When a piece of equipment (i.e., a reactor or a tank) is filled with solvent that volume of solvent displaces an equal volume of vessel headspace to the atmosphere. That vapor stream is laden with the solvents being added and those volatilized from that already in the equipment based on their concentrations and volatilities. The emission rate is based on the material filling rate. This is the most common chemical/pharmaceutical emitting step, as the reactor is often filled with many solvents and reactants before the reaction takes place; and the solution is transferred to additional tanks before the final product is developed. Please note that fills include fills of solid material, as they displace headspace, as well.
- Gas sweep. Empty equipment is often purged with an inert gas, such as nitrogen or air in preparation for its re-use by removing all residual solvent. In a different application, a gas sweep is common during the manufacturing process as a safety measure in order to prevent the buildup of too high a concentration of solvent in the headspace (which could approach its lower explosivity limit). The sweep gas carries out solvent in the headspace based upon the gas sweep rate and the vapor pressure of the components.
- Evacuation. Some process steps must be performed under vacuum. Therefore, the headspace must be evacuated, causing the removal of some or all of its components.
- Heating. Many reactions take place at elevated temperature and, therefore, the components of a reactor must be heated. The temperature rise causes a thermal expansion of the liquid, displacing headspace. Given that this occurs at an elevated temperature, this headspace would contain more solvent than at room temperature based on greater volatility at the elevated temperature.
- Vacuum distillation. This is a common separation technique in the chemical and pharmaceutical industries. The creation of a vacuum and heating of the material to

separate components causes volatilization of solvents into the vapor phase and, based on the degree of condensation, the atmosphere.

- Drying. The wet chemical or pharmaceutical product is placed in large ovens (sometimes under vacuum) for final drying – often for many hours, as rules call for the complete removal of organic solvent from the final product. In practice, most of the solvent is emitted in the initial hours. The emission rate profile is usually an exponential decay curve.
- Gas evolution. In some cases, chemical reactions result in the formation of new compounds that are volatile and make its way to the headspace and eventually the atmosphere.
- Storage tank working and breathing losses. Storage tanks are often filled with material, causing headspace potentially to be emitted (see Filling above). In addition, each tank undergoes “breathing” losses, depending on the conditions of the tank and regional average temperature.

Figure 2 – Common industrial process operations leading to volatilization



Most of these equations derive from the Ideal Gas and Raoult’s Laws, as shown below.

$$E = \frac{(V)}{(R)(T)} \times \sum_{i=1}^n (P_i)(MW_i)$$

where:

E = mass of compound emitted

V = volume of gas displaced from the vessel
 R = ideal gas law constant
 T = temperature of the vessel vapor space; absolute
 P_i = partial pressure of the individual compound
 MW_i = molecular weight of the individual compound
 n = number of compounds in the emission stream
 i = identifier for the compound

The volume of gas displaced from the vessel and partial pressure of the compound must be determined by other equations based on the chemical's unique properties and data pertaining to the process step.

Information needed to calculate emissions may be summarized by the table below (with typical, but not exclusive, units).

Step Type	Parameters	Typical Units
Filling	System temperature Fill duration	°F minutes
Evacuation	System temperature Time to evacuate Initial pressure Final pressure Total volume of contents	°F minutes mm Hg mm Hg gallons
Gas Sweep	System temperature Duration Gas sweep rate Empty or full vessel	°F minutes scfm
Heating	Time to heat (not to maintain the temperature) Initial temperature Final temperature Total volume of contents	minutes °F °F gallons
Vacuum Distillation	System temperature Receiving vessel temperature Duration Leak rate System pressure	°F °F minutes scfm mm Hg
Drying	System temperature	°F

	Duration Leak rate (if under vacuum) System pressure Loss on drying Exponential decay factor	minutes scfm mm Hg
Gas Evolution	System temperature Duration	°F minutes
Storage Tank	Solvent throughput Size and condition of tank Location (mean temperature) Max. and min. solvent heights	gallons/year

Commercial software exists to conveniently input chemical and physical data and develop emission rates. Many chemical or pharmaceutical products manufactured involve dozens of potential air emitting steps like those listed above, each utilizing many chemicals. Therefore, software use reduces errors in managing the sheer volume of input data, keeping historical records of emissions, and in developing the emissions inventory consistently.

Several emission estimating software packages are commercially available. Features to look for in emission estimation software include:

- a comprehensive chemical database. The software should have an existing chemical library of information, including Antoine's Constants to calculate vapor pressure at a variety of system temperatures. If a chemical is used in a process that is not already found in the library, the user should be able to input the necessary information only once, and have information available whenever that chemical is utilized;
- an equipment database, including the names and capacities of all process equipment, as well as the appropriate information to determine the effectiveness of each type of air pollution control equipment;
- a process step database where the steps and necessary data that compose the process in question can be constructed and easily available. This is particularly important as process characteristics often change over time (new equipment or changes in steps to improve yield and efficiency), and it is important to have a historical record;
- an emission model database where the calculations are recorded for each process and set of chemicals.

A software program also allows the user to keep historical records of actual and potential emissions based on the processes of that time. It provides a defense that an advanced

method to determine air emissions was implemented. Software provides a convenient historical record of input data saving the user time in trying to determine where it came from if questions arise years later and outliving employee turnover.

A major advantage of engineering equations is that while these are theoretically derived, they are considered fairly accurate (provided accurate data is inputted!) when compared to actual measurements. Once a system (or software) is installed, then engineering equations can calculate emissions speedily and consistently. It is also good for “What if” scenarios that develop. The disadvantage is that these may need to be applied to dozens of potential emissions steps in a process, resulting in the necessary gathering or estimation of enormous quantities of process data, requiring additional time and effort. Software systems do ease this burden somewhat. Also, because the estimates derive from equations that are correct only under ideal circumstances, it is unknown whether emissions that derive from this method are conservative or not.

TIPS TO IMPROVE YOUR EMISSION ESTIMATION

Identify all steps and phases

It is beneficial to perform a total review of your processes, including a detailed walkthrough of your plant, to ensure that you have captured all of your equipment and ancillary activities related to your processes. Know where all major exhausts are travelling and understand the forces that contribute to the development of air emissions.

It is possible that your plant manufactures so many products that it may be too many to conduct the techniques demonstrated in this course (too many engineering equation estimates, too many material balances). Understanding your products and the steps involved in their production will enable you to select true representative products to evaluate.

Validate supporting data

Virtually all of the emission estimation techniques presented in this course depend on quality data concerning the process or the equipment for them to be successful (provide accurate, reliable results). For direct measurement, it is important to know all compounds potentially present in the exhaust that may affect the use of a methodology; it is also important to know about any disturbances in your exhaust piping. For material balance, as discussed earlier, the accurate measurement of the various inputs to and outputs from the process or equipment is critical. For emission factors, it is important to be sure that the factor is correct as applied to your process or equipment and there are no extenuating circumstances that may cause you to use a different factor. Finally, for engineering equations, as was apparent, input data (chemical composition, temperature, pressure, etc.) at every stage in the process is integral to estimating the emission rate.

Your facility may be depending on the results for critical reporting to a regulatory agency or for planning or for meeting emission reduction goals. Therefore, it is important to do a

little extra “homework” to ensure that all data used to estimate emissions is current, transparent, and accurate. Often it is helpful to work with the operators at the plant who have experience with the process. If feasible, it may be helpful to seek outside, independent review and verification of input data.

Check emission estimates

After the emission estimates are complete, spend some time checking them. Initially, perform a “sanity” check to determine whether they make “sense” or not. As mentioned earlier, with a material balance, any emission rates of zero or negative should immediately set off concerns. With any technique, human involvement will result in errors which can affect results. Review input data where feasible to ensure that no mis-estimations were made. Revisit estimates periodically.