Chapter 8

This chapter will take approximately 1 hour to complete.

Introduction to Ambient Air Sampling for Air Toxics

OBJECTIVES

Terminal Learning Objective

At the end of this chapter, the student will be able to describe ambient air sampling for air toxics.

Enabling Learning Objectives

8.1 Define *toxic air pollutants*.

8.2 Describe risk assessment and risk characterization.

8.3 Describe the air toxics methods for the air toxics monitoring program.

8.1 Introduction

What are Toxic Air Pollutants?

Toxic air pollutants are poisonous substances in the air that come from natural sources (such as radon gas coming up from the ground) or from manmade sources (such as chemical compounds given off by factory smokestacks) and can harm the environment or your health. Inhaling toxic air pollutants can increase your chances of experiencing health problems. For example, inhaling the benzene fumes that are given off when you pump gas into your car can increase your chances of experiencing health effects that have been associated with exposure to benzene, such as leukemia.

Some air toxics are also involved in the formation of other pollutants, principally ozone and particulate matter (PM). If we can significantly reduce volatile organic compounds (VOCs), this will not only help with air toxics risk, but also help reduce ozone and PM formation.

Here are some more facts about air toxics:

- Air toxics are also known as hazardous air pollutants (HAPs).
- These pollutants are known or suspected to cause cancer or other serious health effects.
- The principle pathway for most HAPs is inhalation.
- High concentration locales are often heavily industrialized areas.
- Analysis of ambient air monitoring data can be an effective means of assessing air quality and associated potential health risks, and assessing trends and regulatory program effectiveness.

Several technical tools have been developed to help EPA and their partners in the state, local, and academic communities. These tools include emission inventories, air quality modeling, data analysis, and monitoring programs. The

models, inventories, and data analyses are the planning and assessment tools that directly support numerous assessments across the air toxics programs. The first National Scale Air Toxics Assessment (NSATA, also known as "1996 NATA") provided county level summaries of HAP exposures based predominantly on modeling and emissions data from the year 1996. Monitoring data indirectly—and, in some cases, directly—support all the technical tools as well as the larger programs. The challenge faced in monitoring for air toxics is effectively marrying observations with these program elements.

Clean Air Act of 1990

In 1990, the United States promulgated the Clean Air Act (CAA) of 1990. This was major landmark legislation on many levels. For the first time, air toxics were regulated. Section 112 of the Clean Air Act states the powers that the federal government has in regulating, monitoring, and reducing HAPs within the country. Section 112 originally listed 189 HAPs. However, because one was de-listed, currently the CAA recognizes 188 listed HAPs. Figure 8-1 shows the breakdown of the makeup of the HAPs listed in Section 112.

As can be seen from Figure 8-1, well over half of the HAPs listed in the Clean Air Act are volatile compounds, or VOCs. These are a class of compounds that *volatilize* in normal ambient conditions. *Volatile* means that they are in the gaseous phase. Semi-volatile compounds (SVOCs) are compounds of a molecular weight such that their volatility is dependent on the temperature and pressure of the atmosphere. For instance, the compound naphthalene is considered to be a SVOC. Compounds such as naphthalene can be solid, liquid, or gas phase depending on ambient conditions. At higher atmospheric temperatures, naphthalene acts like a gas. However, in colder times of the year, naphthalene is a solid. Non-volatile compounds are those that are never gaseous in ambient air, such as particulate matter or particles. Particles in the air can contain HAP compounds, such as arsenic, cadmium, or lead.

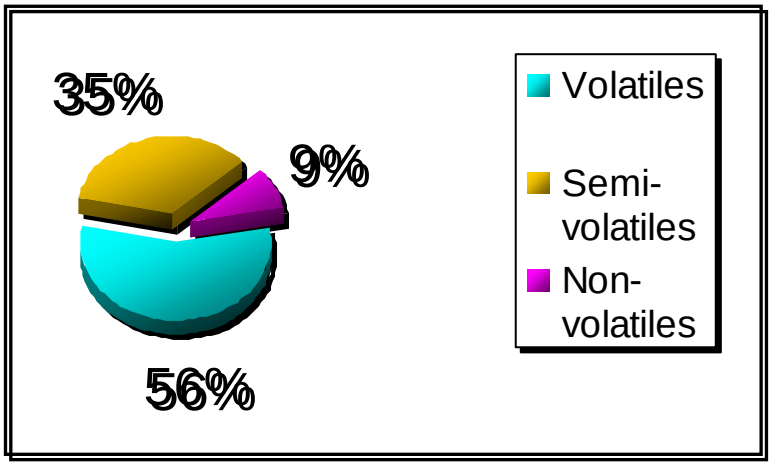

Figure 8-1. Breakdown of HAPs by class.

Timeline for Air Toxics Monitoring

Figure 8-2 illustrates the timeline for the development of air toxics monitoring in the United States. The 1990 CAA amendments provide the framework for the air toxics program. The air toxics program is designed to characterize, prioritize, and equitably address the serious impacts of HAPs on public health and the environment through a strategic combination of regulatory approaches, voluntary partnerships, ongoing research and assessments, and education and outreach. In addition to promulgating Section 112 for HAPs, the CAA also created a program in the early 1990s known as the Photochemical Assessment Monitoring Stations (PAMS) program. The PAMS program called for the measurement of VOCs that are highly reactive and can lead to the formation of ozone. Many VOCs that are HAPs are also reactive. For example, benzene, formaldehyde, and 1,3-butadiene are both PAMS compounds and HAPs. Two methods were developed by the EPA to measure these compounds: Toxic Organics (TO) 11 and TO-14. Both of these methods were useful in developing updated methods: TO-11A and TO-14A.

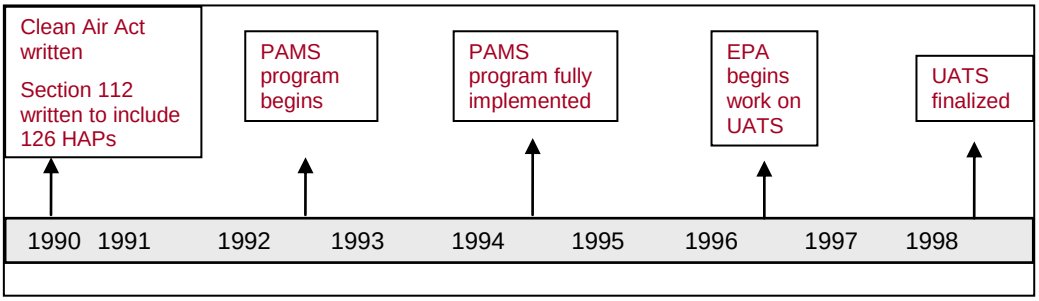

Figure 8-2. Timeline for air toxics monitoring, 1990 to 2000.

In 1996, the EPA started work on the Urban Air Toxics Strategy (UATS). The major components of the Integrated Urban Air Toxics Strategy (standards, risk initiatives, air toxics assessments, and educational outreach) are the same as the major components of our overall national air toxics program. The EPA is continuing to develop a number of national standards for stationary and mobile sources as a part of the national air toxics program. These standards, as well as standards developed by state and local authorities, are expected to improve air quality in urban and rural areas. As part of the national air toxics program, we will be assessing what additional actions, both at the national and local level, are needed to further improve air quality. The UATS complements the existing national efforts by focusing on achieving further reductions in air toxics emissions in urban areas. The UATS includes state and local governments particularly in planning UATS activities and other initiatives under the national air toxics program to assess and address local air quality concerns. The UATS was finalized in 1998.

The EPA and its partners cannot monitor everywhere. So, in order to better understand public exposure, the EPA has created the National Air Toxics

Assessment (NATA). The NATA helps us identify areas of concern, characterize risks, and track our progress toward meeting our overall air toxics program goals. NATA activities include expansion of air toxics monitoring, improvements and periodic updates to emissions inventories, national- and local-scale modeling of air quality and exposure, continued research on health effects and exposures to both ambient and indoor air, and development and use of improved risk and exposure assessment tools.

Figure 8-3 illustrates the development of several air toxics monitoring programs. From 1998, EPA and its stakeholders worked together to create the Air Toxics Concept Paper. It established the framework for future monitoring throughout the United States. The monitoring network should be incrementally designed to first address the highest priority needs of the air toxics program: to focus on pollutants and sources which pose the greatest risk to the largest number of people and the greatest risk to the environment. Because of limited knowledge in measuring many of the 188 HAPs, the program should initially focus on those pollutants that EPA, state, and local agencies have identified as having the most significant potential health impacts and routine measurement methods. The list of HAPs in the UATS is a logical starting point. Several UATS pollutants are also important from an ecosystem risk assessment perspective. As additional priority air toxics are identified and as monitoring capabilities improve, additional HAPs can be added to the monitoring program.

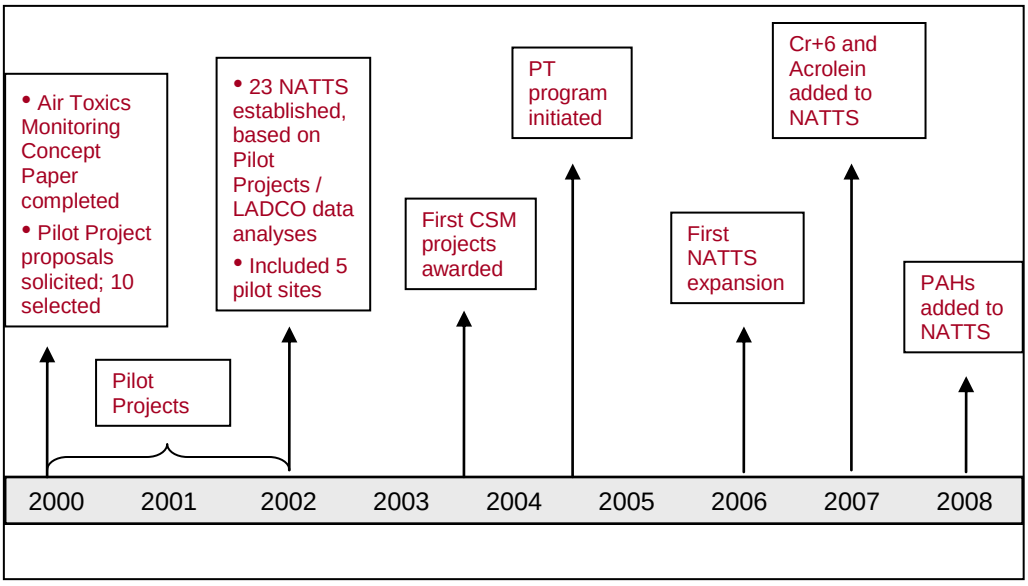

Figure 8-3. Timeline for air toxics monitoring, 2000 to 2008.

This is not to say that all UATS HAPs must be measured at all locations and that non-UATS HAPs should not currently be measured at some locations. To permit comparisons among HAPs and to facilitate dispersion and deposition

model evaluation, however, some number of "core" UATS HAPs should be initially measured at a number of locations nationwide. The HAPs measured should include those associated with the highest toxicity-weighted emissions or those that are judged responsible for a large percentage of the risk associated with exposures to ambient air toxics. Similarly, as many UATS HAPs as possible should be measured at an agreed upon, albeit initially small, number of comprehensive monitoring locations. Such comprehensive platforms should be selected to reflect a broad representative mix of UATS HAP emissions. As monitoring capabilities improve and available resources increase, the list of compounds and locations can change.

The outcome of the Air Toxics Concept Paper was to create a Pilot Project. The EPA funded and worked with the regional offices to establish 10 sites throughout the country to pilot a national network. Pilot Project sites would be operated by state and local government agencies, but overseen by the EPA and its regional partners. The Pilot Project stations operated for 1–2 years and gave its partners valuable information about level of detection, day-to-day variability, operating procedures, and quality assurance. The compounds selected were confirmed by earlier conclusions from the 1996 NATA and prevailing judgment, and illustrated the variant nature of air toxics both within and across cities. With the exception of relatively consistent motor vehicle signals, the data showed extreme variation in the relative levels of particular pollutants that largely were influenced by proximity to sources.

Once the Pilot Project was over, EPA and its partners began planning for a long-term, fixed network that would allow us to understand trends. Thus the National Air Toxics Trends Stations (NATTS) were proposed in 2002. Information from the Pilot Project illustrated that a single trends site should rarely be viewed as being representative of the many disparate locations throughout a metropolitan area. Accordingly, a more realistic expectation of the NATTS emerged, suggesting that these sites should adequately track the progress of mobile-source-oriented emission reduction programs at a national level, but provide only a limited perspective on characterizing a city's air quality. More focused studies that either address fairly specific source categories or provide greater spatial resolution (i.e., more stations) are needed to complement the NATTS.

It was decided that more in-depth studies would be needed rather than a long-term trends network. Therefore, EPA initiated the Community Scale Monitoring (CSM) projects in 2003. The CSM projects are intense, focused monitoring projects that look to answer specific questions about HAPs in an area or city and understand the risk and exposure of the population to those specific HAPs.

8.2 What is Risk?

Health risks, put simply, are a measure of the chance that you will experience health problems. Exposure to toxic air pollutants can increase your health risks. For example, if you live near a factory that releases cancer-causing chemicals and

you inhale contaminated air, your risk of getting cancer can increase. Risk is defined as function of exposure and toxicity as stated in the following equation:

RISK = f [(Measure of Exposure) (Measure of Toxicity)]

Exposure to HAPs can come in many forms. HAPs are released into the atmosphere from factories, our automobiles, and other processes. HAPs disperse into the atmosphere and can be affected by local and long distance meteorology. HAPs can deposit into lakes, oceans, and streams by wet deposition in the form of rain or snow. Dry deposition of HAPs usually occurs as SVOCs or particles. This type of deposition is considered to be "dry" because it is not associated with rainfall.

We are exposed to these compounds by three modes: ingestion, dermal, and inhalation. People uptake and intake HAPs at different rates and in different ways. Most HAPs are excreted by the body, but some are taken into target organs, which over time causes a number of health effects. Figure 8-4 illustrates the pathways and endpoints of HAPs.

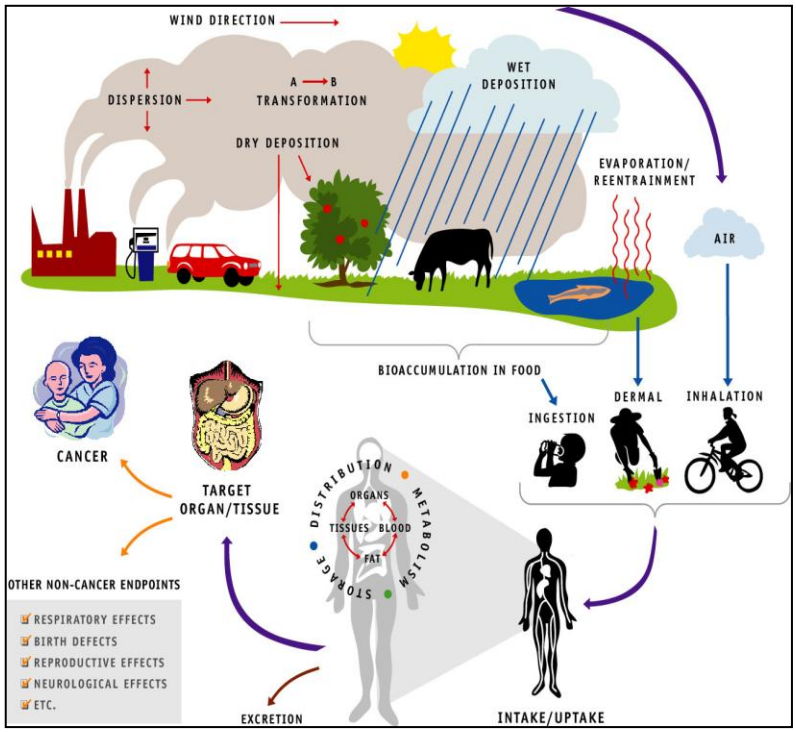

Figure 8-4. Various pathways of exposure to HAPs.

What is a Risk Assessment?

In order to understand how the public is at risk to HAPs, scientists and government officials perform risk assessments. One of several tools used in risk management, risk assessments estimate the increased risk of health problems in people. A risk assessment for a toxic air pollutant combines results of studies on

the health effects of various animal and human exposures to the pollutant with results of studies that estimate the level of people's exposures at different distances from those sources (see Figure 8-5).

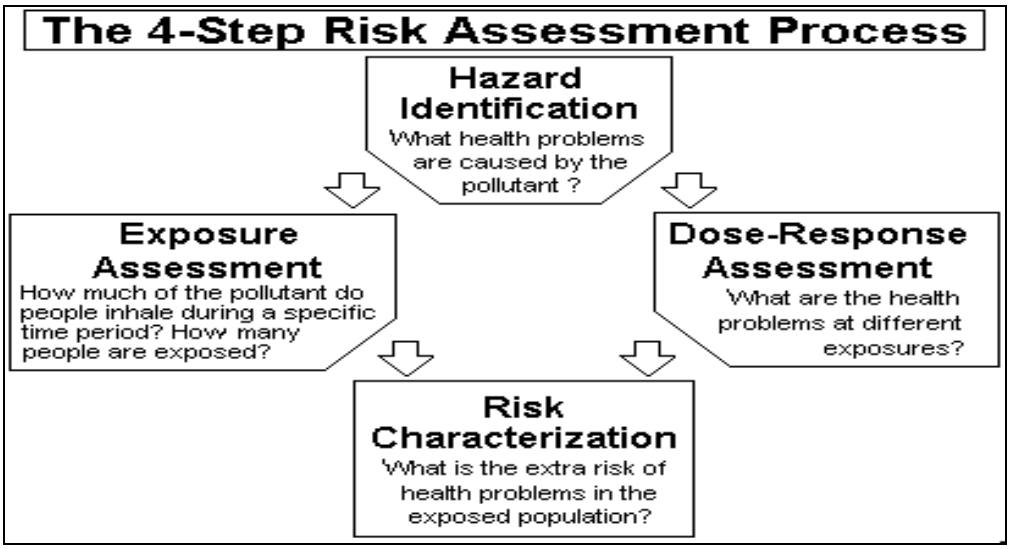

Figure 8-5. Risk assessment flow chart.

While the estimates provided by these risk assessments are far from perfect, they do help scientists evaluate the risks associated with emissions of toxic air pollutants. Using risk estimates and other factors, the government can set regulatory standards to reduce people's exposures to toxic air pollutants and thus reduce the risk of experiencing health problems.

Hazard Identification

The toxic air pollutants of greatest concern are those that cause serious health problems or affect many people. Such health problems can include cancer, respiratory irritation, nervous system problems, and birth defects. Some health problems occur very soon after a person inhales a toxic air pollutant. These immediate effects may be minor, such as watery eyes. Or they may be serious, such as life-threatening lung damage. Other health problems, such as cancer, may not appear until many months or years after a person's first exposure to the toxic air pollutant. Risk is also affected by whether exposure is acute or chronic. Acute exposure is of severe but short duration, while chronic exposure lasts for a long period of time or is marked by frequent recurrence.

Weight of Evidence for Health Problems of Concern

In hazard identification, scientists evaluate all available information about the effects of a toxic air pollutant to estimate the likelihood that a chemical will cause a certain effect in humans. The better the evidence, the more certain scientists can be that a toxic air pollutant causes specific health problems. The amount,

type, and quality of evidence are all important. The best type of evidence comes from human studies. This evidence may be in the form of case reports, such as physicians' reports of an unusual number of cases of a specific illness. Other more formal studies can be done that compare the number of cases of a particular illness in groups of people with different levels of exposures (for example, cases of leukemia in rubber manufacturing workers).

Because human information is very limited for most toxic air pollutants, scientists often conduct studies on laboratory animals, such as rats. Animal studies are performed under controlled laboratory conditions. Scientists can study a variety of health effects by exposing animals to pollutants at varied concentrations and for varied time periods. When relying on animal studies only, scientists need to be satisfied that health effects in humans are likely to be the same as those in the animals tested. Scientists try to use animal species with body functions that are similar to humans.

Exposure Assessment

An exposure assessment estimates how much of a pollutant people inhale during a specific time period, as well as how many people are exposed. Because there are many possible sources of toxic air pollutants, such as a factory smokestack or thousands of automobiles crossing a busy intersection each day, the first step in an exposure assessment is to decide which sources are giving off the pollutant of concern. Once the identity and location of the source(s) are known, the next step is to determine the amounts of the toxic air pollutant released in a specific time period and how it moves away from the source(s). Scientists use either monitors or computer models to estimate the amount of pollutant released from the source and the amount of pollutant at different distances from the source. Monitors are used to sample the air and measure how much of the pollutant is present. Computer models use mathematical equations to represent the processes that occur when a facility releases a pollutant and the movement of pollutants through the air. Factors such as distance from the source to exposed persons, wind speed and direction, and smokestack height (for factories) affect these estimates.

The number of people exposed at different distances from the site of release can be estimated with computer models that use information from the census and from maps. Some models can even estimate exposures for the different places people are each day—including indoor, automobile, outdoor, and workplace exposures. The final step in an exposure assessment is to estimate the amount each person inhales. To do this, scientists combine estimates of the breathing rate and lifespan of an average person with estimates of the average amount of pollutant in that person's air.

Dose-Response Assessment

The following description applies to how HAPs enter the body, interact within the body, and are eliminated from the body. First, toxic air pollutants get into the body mainly through breathing. They can also be ingested (for example, children eating soil contaminated with lead) or absorbed through the skin. Once a pollutant enters the body, it can stay in the lungs (like asbestos), be exhaled, or

move into the blood from the lungs (like the oxygen we breathe) or from the digestive system or skin. In the blood it is carried to all parts of the body. As it moves around the body, a pollutant can undergo chemical changes, especially as it passes through the liver, becoming less, or more, toxic. Finally, the pollutant can be exhaled, it can leave the body in urine, bowel movements, sweat, or breast milk, or it can be stored in hair, bone, or fat.

Toxic air pollutants can cause health problems by interfering with normal bodily functions. Most commonly they change chemical reactions within individual cells, the building blocks of living things. These changes can kill cells, impair cell function, or redirect cell activity. The results can be damaged organs, birth defects when the cells of an unborn child are damaged, or cancer that develops when cells begin to grow at an uncontrolled rate.

Dose-Response Relationships

The dose-response relationship for a specific pollutant describes the association between exposure and the observed response (health effect). In other words, it estimates how different levels of exposure to a pollutant change the likelihood and severity of health effects. Just as in hazard identification, scientists use results of animal and human studies to establish dose-response relationships.

Dose-response relationship for cancer: In the absence of clear evidence to the contrary, EPA assumes that there are no exposures that have "zero risk" -- even a very low exposure to a cancer-causing pollutant can increase the risk of cancer (albeit a small amount). EPA also assumes that the relationship between dose and response is a straight line -- for each unit of increase in exposure (dose), there is an increase in cancer response.

Dose-response relationship for noncancerous effects: A dose may exist below the minimum health effect level for which no adverse effects occur. EPA typically assumes that at low doses the body's natural protective mechanisms repair any damage caused by the pollutant, so there is no ill effect at low doses. However, for some substances, noncancerous effects may occur at low doses. The dose-response relationship (the response occurring with increasing dose) varies with pollutant, individual sensitivity, and type of health effect.

Risk Characterization

Information is presented in different ways to illustrate how individuals or populations may be affected. Some of the most common risk measures are described here. Combining the results of the exposure assessment and the dose-response assessment gives an estimate of the increased lifetime risk of cancer for an individual exposed to the maximum predicted long-term concentration.

Maximum Lifetime Exposure	X	Dose-Response Relationship	=	Maximum Individual Lifetime Risk

Many people may be exposed to less than the maximum level. Depending on the amount of exposure, an individual's risk of cancer will vary. The distribution of individual risk is usually expressed as the number of people estimated to be at

various levels of risk. Distributions of individual risk are used to calculate population risk. The population cancer risk is usually expressed as the expected increased incidence of cancer (that is, the number of new cases each year) for all people exposed to the pollutant. For example, the estimated population cancer risk may be the number of new cancer cases per year expected among residents within 30 miles of a certain large source. Health reference levels refer to exposure levels that will not cause significant risks of noncancerous health effects. Long-term exposure to levels below these levels are assumed to produce no ill effects.

Health reference levels are an example of one index that government agencies use in characterizing noncancerous health risks. These levels are generally developed from exposure levels that do not produce ill effects in experimental animals. These exposure levels are adjusted to account for animal-human differences (such as breathing rate) and for underlying uncertainties (such as the difference in sensitivity between healthy adults and more sensitive people like children and the elderly). Risk analysts then compare the health reference levels with the exposure estimates to determine how many people are exposed to concentrations higher than the health reference level. Some of these people might experience ill effects.

Although scientists can estimate risks caused by toxic air pollutants in animals experimentally or in humans who have unusual exposures, converting these estimates to those expected in people under a wide range of conditions is difficult and can be misleading. By their nature, risk estimates cannot be completely accurate. The main problem is that scientists don't have enough information on actual exposure and on how toxic air pollutants harm human cells. The exposure assessment often relies on computer models when the amount of pollutant getting from the source(s) to the people can't be easily measured. Dose-response relationships often rely on assumptions about the effects of pollutants on cells for converting results of animal experiments at high doses to human exposures at low doses. When information is missing or uncertain, risk analysts generally make assumptions that tend to prevent them from underestimating the potential risk -- that is, these assumptions provide a margin of safety.

8.3 Introduction to Air Toxics Methods

Monitoring Program Goal and Objectives

The goal of the air toxics monitoring program is to support reduction of public exposure to HAPs. Monitoring data will provide a critically important role by characterizing HAP concentrations to support three very basic monitoring objectives, and also several sub-objectives. These objectives are:

- *Trends:* Measurements of key HAPs in representative areas of the nation provide a basic measure of air quality differences across cities and regions and over time in specific areas. Trends measurements provide one basis for accounting for program progress.

- *Exposure Assessments*: Ambient measurements may serve as a surrogate for actual human exposure. However, understanding the relationships between ambient concentrations and personal exposure, and how human activities impact these relationships, is critical for true exposure assessments. Therefore, ambient measurements *support* exposure assessments by providing ambient concentration levels. In addition, ambient measurements may also provide direct input into more detailed human exposure models that can be used to estimate actual human exposures.
- *Air Quality Model Evaluation:* Measurements provide basic ground truthing of models which in turn are used for exposure assessments, development of emission control strategies, and related assessments of program effectiveness. In addition, measurements provide direct input into source-receptor models, which provide relatively direct linkage between emission sources and receptor locations.

Sub-objectives to aid the overall program in general, and state and local jurisdictions in particular, are as follows:

- *Program Accountability:* Monitoring data provide perhaps the most acceptable measure of air program progress, i.e., observed changes in the atmosphere consistent with expectations of emissions strategies. Accountability is the closest direct match to measurements in addressing agency goals as outlined in the Government Performance and Results Act of 1993 (GPRA), and applies to all programs (MACT, residual risk, area sources, mobile source rules, and local-scale projects).
- *Problem Identification:* Measurements are used to uncover a suspected air quality issue associated with a specific source or source group, or confirm that a problem does not exist. Given the numerous HAPs and variation in issues across the nation, this particular objective probably contributed to much of the historical toxics monitoring as well as the emerging local-scale project studies. Local-scale project studies are used to pinpoint a particular pollutant that may be present in only one city or even a part of a city. This type of project is usually very intensive, short in duration, and targets very specific compounds.
- *Science Support:* Routine network measurements often provide a backbone of basis measurements that more extensive research studies can utilize in the areas of model process development, exposure studies, and health effects. By themselves, data from the network should provide a basis for a wealth of long-term epidemiological studies associating adverse health impacts with observations, particularly where toxics measurements are grouped with multiple pollutants. In addition, given the current limited research efforts on methods development, the national air toxics program can also provide opportunities to test and advance measurement methodologies for air toxics.

Air toxics methods are generally classified into two groups: organic and inorganic. Organic refers to the class of compounds that contain carbon. Inorganic refers to the analyses of non-carbon elements and matrices. EPA created what is known as the Compendium (plural: compendia), which is a

compilation of sampling and analytical methods brought into a larger set of volumes. Originally developed by the Office of Research and Development (ORD) in late 1990s, they have since been reviewed and revised, and new methods have been created. The Office of Air Quality Planning and Standards (OAQPS) now develops air toxics methods. All of these organic and inorganic methods are available on the EPA's Technology Transfer Network (ttn) websites:

- http://www.epa.gov/ttn/amtic/inorg.html
- http://www.epa.gov/ttn/amtic/airtox.html

Figure 8-6 is the front cover of the Compendium Methods for the Determination of Toxic Organic Compounds in Ambient Air. An additional Compendium, Determination of Inorganic Compounds in Ambient Air, is also available on the EPA's website. Before these methods could be added to the Compendium, they went through very thorough review by EPA and its stakeholders. Although these methods have their flaws, they are the backbone of the HAPs methods.

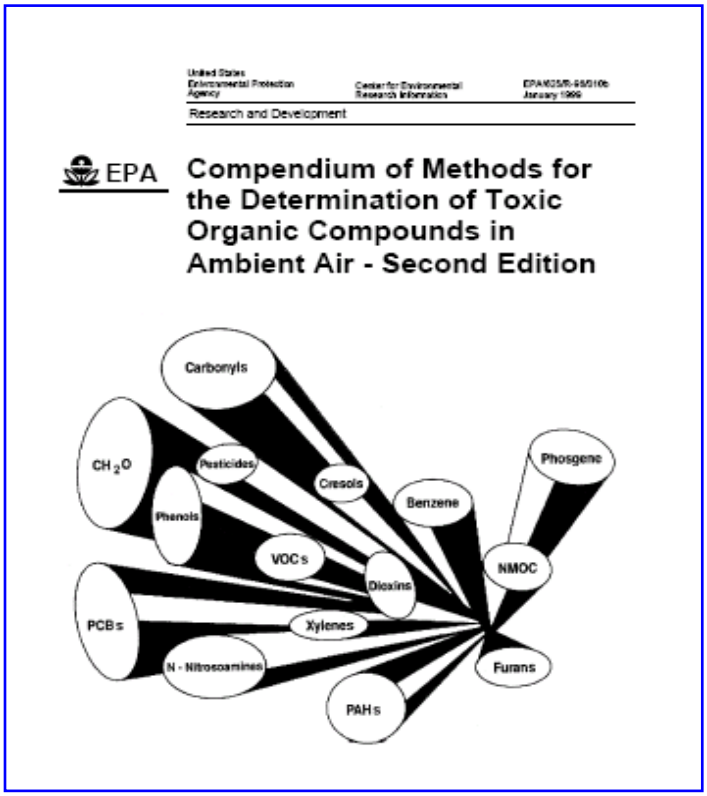

Figure 8-6. Front cover of the TO Compendium.

One additional document, the Technical Assistance Document for the National Ambient Air Toxics Trends and Assessment Program (NATTS TAD) is also useful to operators and laboratory staff. This document describes the most current recommendations on the toxic organic (TO) and inorganic (IO) methods. It can be found at: http://www.epa.gov/ttn/amtic/airtox.html.

Description of the Methods

This section will describe the most widely utilized methods in the Compendia. Please note that these are guidance documents and describe the general procedures to obtain data. Many laboratories use these as their starting point and detail their modifications in their individual standard operating procedures.

The objective of the Compendia is for the EPA to document and standardize methods for measuring atmospheric pollutants of interest and publish them in standardized format, with each having been extensively reviewed by several technical experts having expertise in the methodology presented. Tables 8-1 and 8-2 illustrate how the TO and IO Compendia are organized.

Table 8-1. Toxic Organic Methods.

Method No.	Compounds
TO-1	VOCs
TO-2	VOCs
TO-3	VOCs
TO-4A	Pesticides and polychlorinated biphenyls
TO-5	Aldehyde and ketones
TO-6	Phosgene
TO-7	Amines
TO-8	Phenols
TO-9A	Dioxin/furans
TO-10A	Pesticides and polychlorinated biphenyls
TO-11A	Aldehydes and ketones
TO-12	Non-methane organic compounds
TO-13A	Polycyclic aromatic hydrocarbons
TO-14A	Nonpolar VOCs by flame ionization
TO-15A	Polar VOCs by mass spectroscopy
TO-16	VOCs by open path spectroscopy
TO-17	VOCs collection by diffusion tubes

Table 8-2. Toxic Inorganic Methods.

Method No.	Compounds/Technique
IO-1	Sampling of particle matter 10 microns or less
IO-2	Sampling of total suspended particles
IO-3	Chemical speciation of particle matter
IO-4	Determination of reactive acidic and basic gases
IO-5	Sampling and analysis of mercury

The remainder of this section will focus on the four methods that are used extensively throughout the air toxics networks. They are:

- **TO-11A:** Carbonyls (ketones and aldehydes) by dinitrophenylhydrazine coated cartridge and liquid chromatography,
- **TO-13A:** Polynuclear aromatic hydrocarbons by polyurethane foam sampler and gas chromatography/mass spectrometry (GCMS),
- **TO-15A:** Volatile organic compounds (VOCs) by canister and GCMS, and
- **IO-3.5:** Metals by high-volume sampler on quartz filter using ion coupled plasma with mass spectrometer (ICP/MS).

Compendium Method TO-11A

This method is applied to the determination of formaldehyde and other carbonyl compounds (aldehydes and ketones) in ambient air. EPA Compendium Method TO-11A utilizes a coated solid adsorbent for collection of carbonyl compounds from ambient air followed by high pressure liquid chromatography (HPLC) analysis with ultraviolet (UV) detection. Carbonyl compounds, especially low molecular weight aldehydes and ketones, have received increased attention in the regulatory community due in part to their effects on humans and animals. Exposure to formaldehyde and other specific aldehydes (acetaldehyde, acrolein, and crotonaldehyde), even short-term, has been proven to cause irritation of the eyes, skin, and mucous membranes of the upper respiratory tract. High concentrations of carbonyls, especially formaldehyde, can injure the lungs and may contribute to eye irritation and affect other organs of the body. Aldehydes may also cause injury to plants. Sources of carbonyl compounds in ambient air range from natural occurrences to secondary formation through atmospheric photochemical reactions.

In general, natural sources of carbonyls do not appear to be important contributors to air pollution. Aldehydes are commercially manufactured by various processes, including production of alkenes, dehydrogenation of alcohols, and addition reactions between aldehydes and other compounds. Formaldehyde and other aldehyde production in the United States has shown a substantial growth over the last several years due in part to use of these compounds in a wide variety of industries, such as the chemical, rubber, tanning, paper, perfume, and food industries. The major industrial use of carbonyl compounds is as an intermediate in the syntheses of organic compounds, including alcohols, carboxylic acids, dyes, and medicines.

A major source of carbonyl compounds in the atmosphere may be attributed to motor vehicle emissions. In particular, formaldehyde, the major carbonyl compound in automobile exhaust, accounts for 50 to 70% of the total carbonyl burden in the atmosphere. Furthermore, motor vehicles also emit reactive hydrocarbons that undergo photochemical oxidation to produce formaldehyde and other carbonyl compounds in the atmosphere.

To address the need for a measurement method that determines carbonyl compounds with the sensitivity required to perform health risk assessments (i.e., 10^{-6} risk level), a combination of wet chemistry and solid adsorbent methodology was developed. Activating or wetting the surface of an adsorbent with a chemical

specific for reacting with carbonyl compounds allowed greater volumes of air to be sampled, thus enabling better sensitivity in the methodology. Various chemicals and adsorbent combinations have been utilized with various levels of success. The currently accepted technique is based on reacting airborne carbonyls with 2,4-dinitrophenylhydrazine (DNPH) coated on a silica gel adsorbent cartridge, followed by separation and analysis of the hydrazone derivative by HPLC with UV detection. The methodology used to accomplish carbonyl compounds measurements is EPA Compendium Method TO-11A (http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-11ar.pdf). EPA Compendium Method TO-11A provides sensitive and accurate measurements of carbonyl compounds and includes sample collection and analysis procedures. In this method, a cartridge containing a coated solid sorbent is used to capture the compounds of interest (see Figure 8-7). The sampling cartridge is extracted and the extract is analyzed using HPLC with UV detection.

Figure 8-7. Examples of DNPH cartridges.

Organic compounds that have the same HPLC retention time and significant absorbance at 360 nanometers (nm) (the absorption of the DNPH derivative of formaldehyde) will interfere. Such interferences can often be overcome by altering the chromatographic separation conditions (e.g., using alternative HPLC columns or mobile phase compositions). Ozone has been identified as an interferent in the measurement of carbonyl compounds when EPA Compendium Method TO-11A is used. To eliminate this interference, removal or scrubbing of O_3 from the sample airstream in the field is mandatory. Ozone at high concentrations has been shown to interfere negatively in the sampling process by reacting with both the DNPH and its carbonyl derivatives (hydrazones) on the cartridge. The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds and the

duration of sampling. Significant negative interference from O_3 has been observed at concentrations of formaldehyde and ozone typical of clean ambient air. Because of these issues, it is recommended that the ozone interference should be removed before the ambient air sample stream reaches the coated cartridge.

Figure 8-8 illustrates a block diagram of a typical TO-11A sampler. Note that the air is drawn in through a manifold, then through a denuder. The denuder scrubber is constructed using a saturated solution of potassium iodide (KI) to selectively remove ozone from the sample air.

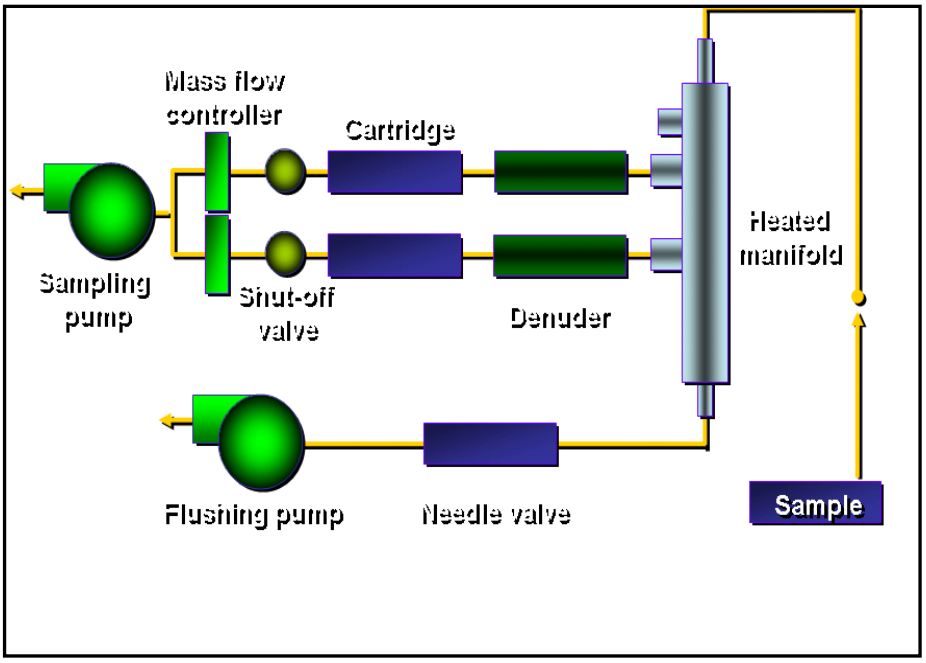

Figure 8-8. Diagram of a TO-11A sampler.

Compendium Method TO-13A

Method 13A is the method best suited for determining SVOCs in ambient air. SVOCs are the class of organic compounds that can be either gases or solids under ambient conditions. Compounds like naphthalene, anthracene, and benzoapyrene are examples of SVOCs.

Sample collection for quantitative determination of SVOCs is accomplished by pulling ambient air at a known and constant flow rate through a quartz fiber filter followed by a sampling cartridge with a polyurethane foam (PUF) plug sandwiched between an adsorbent material, XAD-2®. The sampler pulls ambient air through the filter/PUF/XAD-2® media for a 24-hour collection period. Figure 8-9 illustrates a block diagram of a PUF sampler.

The sampler should be located in an unobstructed area at least 2 meters from any obstacle to airflow. The inlet of the high-volume sampler must be positioned

in the breathing zone, 4 to 10 feet above ground level. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air into the sampling head.

The high-volume sampler is calibrated using a calibrated orifice transfer standard (i.e., high-volume sampler calibrator) in accordance with the specifications of EPA Compendium Method TO-13A. The individual orifice plates are placed in the sampling flow stream, and the differential pressure across the orifice plate is documented. Simultaneously, a corresponding Magnehelic® pressure reading is recorded. The differential pressure and the Magnehelic® readings are used to create a curve that establishes the flow characteristics of each individual sampler.

The prepared XAD-2® cartridge is placed and secured into the sampling head of the high-volume sampler. The quartz fiber filter is placed and secured onto the inlet of the high-volume sampler. The system is activated manually and the desired Magnehelic® reading is achieved by adjusting the ball valve located at the exit of the sampling head.

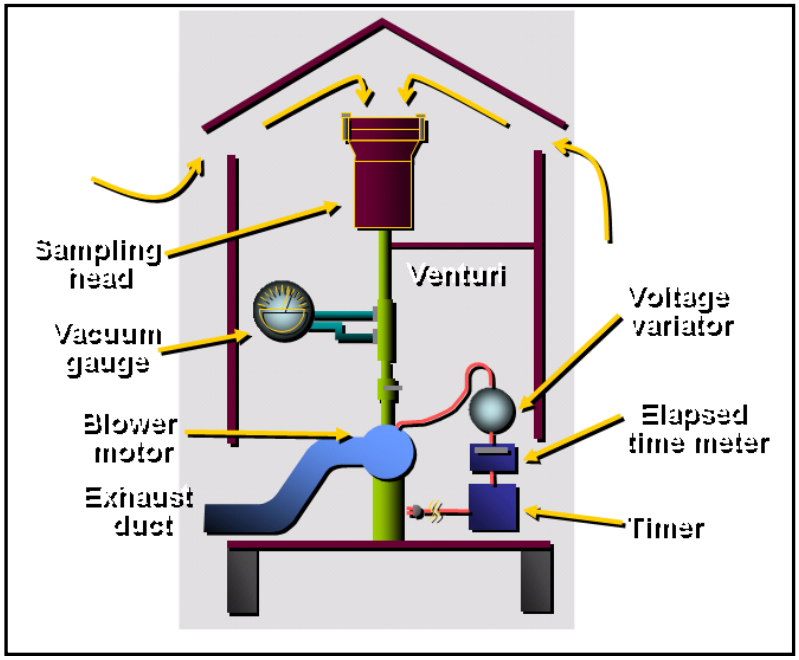

Figure 8-9. Block diagram of a PUF sampler.

Note that the Magnehelic® readings associated with use of a glass frit XAD-2® cartridge will be significantly lower than the readings typically achieved using polyurethane foam (PUF) cartridges because the glass frit material is more restrictive of flow. Readings in the range of 8 to 30 inches H_2O for glass frit XAD-2® cartridges are not unusual. Please see Figure 8-10 for a diagram of the PUF/XAD-2® sandwich.

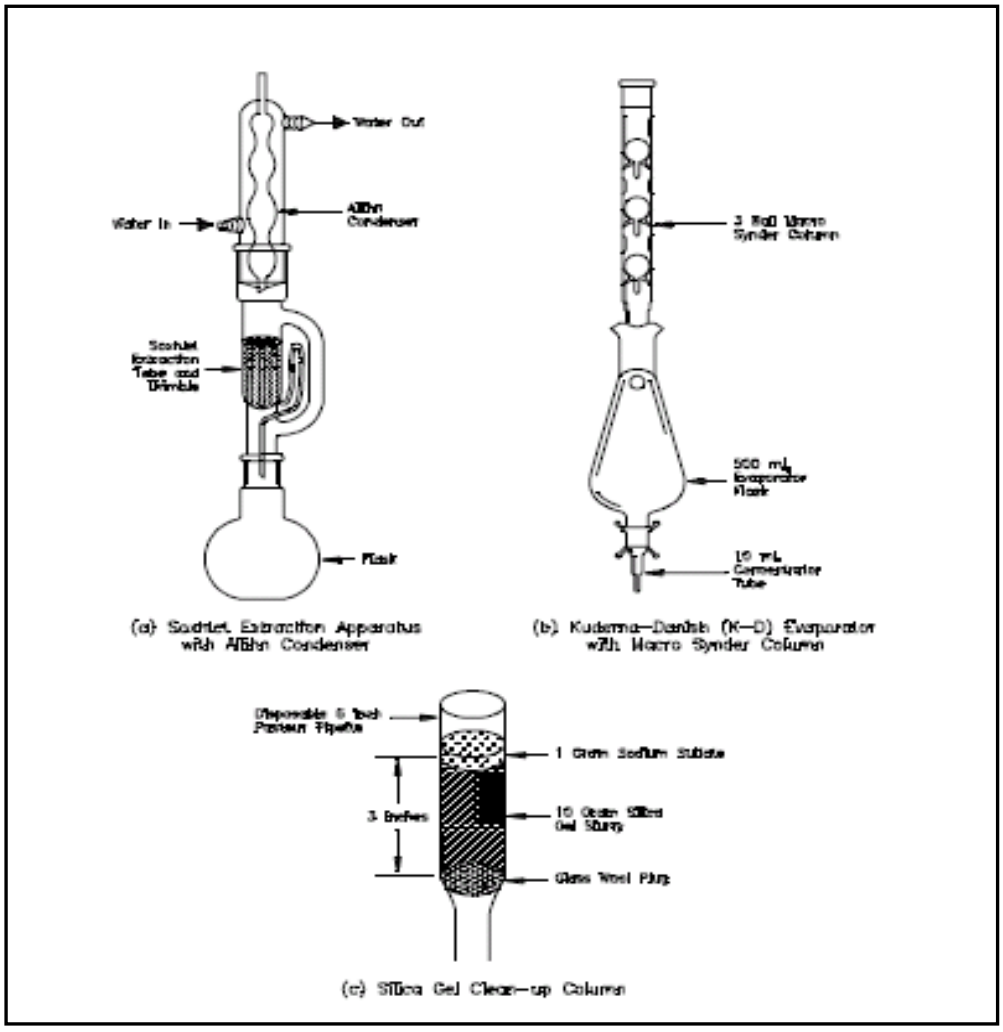

Figure 8-10. Diagrams of the Soxlet, K-D, and PUF/XAD-2® sandwich.

The analysis is performed by extracting the filters, XAD-2®, and PUF plug using a Soxhlet flask with an appropriate solvent. The extract is concentrated by a Kuderna-Danish (K-D) evaporator, followed by silica gel cleanup using column chromatography to remove potential interferences prior to analysis by GC/MS. The eluent is further concentrated by K-D evaporation, then analyzed by GC/MS. The analytical system is verified to be operating properly and is calibrated with five concentration calibration solutions.

Compendium Method TO-15A

Compendium Method T0-15A is the one of EPA's recommended methods for determining VOCs. Examples of VOCs that are characterized well by this method are benzene, vinyl chloride, and carbon tetrachloride.

The ambient air is drawn into a specially prepared stainless steel canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling, and into the pre-evacuated and passivated canister. After the air sample is collected, the canister valve is closed and then transported to the laboratory. Figure 8-11 is a picture of a passivated canister that is widely used today.

Figure 8-11. Passivated canister.

These canisters can be reused many times over many years. They must be cleaned using clean, purified, humidified air. This process is outlined in the method.

To analyze the sample, a known volume is directed from the canister through a mass flow controller to a solid multisorbent concentrator. As a whole air sample, ambient humidity (i.e., water vapor) levels will be present. This water vapor can complicate the analysis. A portion of the water vapor will pass through the concentrator during sample concentration. The water vapor content of the concentrated sample can be reduced by dry purging the concentrator with dry helium.

Figure 8-12 illustrates a block diagram of the flow path of the VOCs. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and then focused into a small volume by trapping on a reduced temperature trap or small volume multisorbent trap. The VOCs are then released from the trap by thermal desorption and swept by the carrier gas onto a gas chromatographic column for separation.

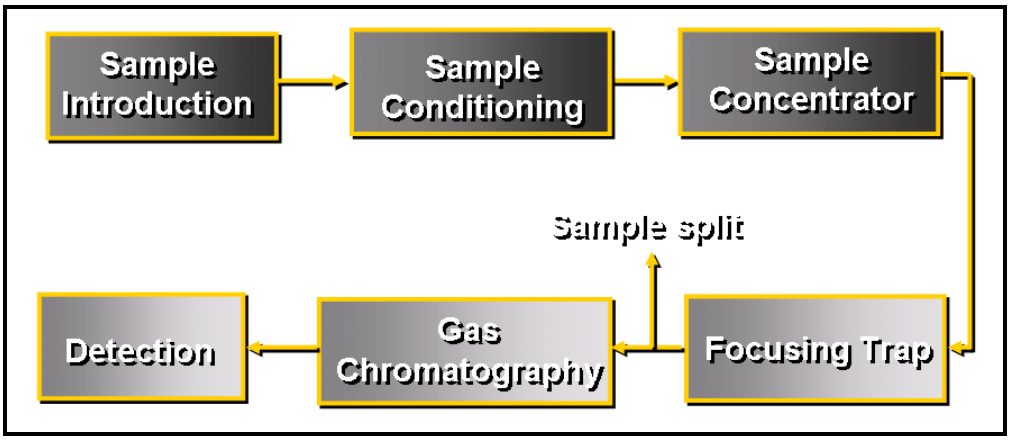

Figure 8-12. Flow diagram of the TO-15A method.

The analytical strategy involves using a high-resolution gas chromatograph (HRGC) coupled to a mass spectrometer (MS) operated by selective ion monitoring (SIM) mode. The fragmentation pattern from interaction of individual molecules with the MS ionization source (electron beam) is compared with stored spectra taken under similar conditions in order to calibrate for and identify the compounds. For any given compound, the intensity of the given fragment is compared with the system response to the given fragment for known amounts of the compound to establish the compound concentration that exists in the sample.

Canisters should be manufactured using high-quality welding and cleaning techniques, and new or reconditioned canisters should be filled with humidified zero air and then analyzed after 24 hours to evaluate cleanliness. Although the 24-hour period is not a method requirement, new and reconditioned canisters have a higher potential for contamination due to the manufacturing processes, and it is therefore prudent to allow the humidified zero air to remain in the canister for a longer period to ensure that contaminants are desorbed from active sites. The cleaning apparatus, sampling system, and analytical system should be assembled from clean, high-quality components, and each system should be demonstrated to be free of contamination.

Compendium Method IO-3.5

EPA Compendium Method IO-3.5 is the measurement method used for sampling and analytical procedures for the measurement of metals in ambient air. Representative compounds would be arsenic, lead, or cadmium. The method involves collection on total suspended particulate (TSP) or particulate material $\leq$ 10 micron (PM_{10}) filters and detection by inductively coupled plasma/mass spectrometry (ICP/MS). ICP/MS uses an argon plasma torch to generate elemental ions for separation and identification by mass spectrometry. This analysis technique allows many more than 60 elements to be quantitatively determined simultaneously, and the isotopes of an element can also be determined.

Figure 8-13 illustrates two types of high-volume samplers: TSP and PM_{10} samplers. Ambient air is pulled through filter media using a high-volume sampler. The particulate phase sample is collected on the filter, and the filter is digested yielding the sample material in solution. Sample material in solution is introduced by pneumatic nebulization into a radio frequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially-pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height. The ions transmitted through the quadrupole are registered by a continuous dynode electron multiplier, and the ion information is processed by a data-handling system.

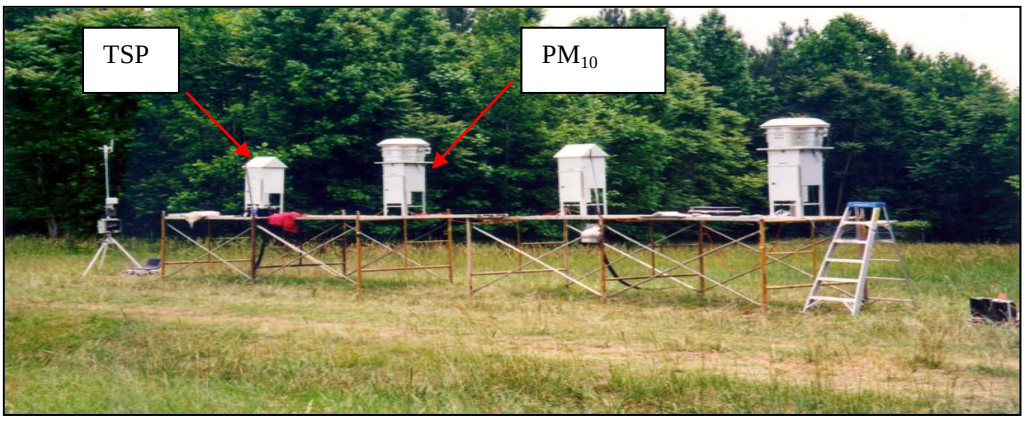

Figure 8-13. High-volume TSP and PM_{10} samplers.

Sample collection for quantitative determination of metal species is accomplished by pulling ambient air at a known and constant flow rate through a filter over a 24-hour collection period.

The glass fiber filter is 8 in. x 10 in. and is constructed of spectro-quality-grade glass fiber material with a pH of approximately 7.5. The filters must have a collection efficiency of 99% for particles of 0.3 µm in diameter or larger. Each filter must have a unique ID number that is a permanent part of the filter.

If the sampler is located on a roof or other structure, there must be a minimum of a 2-meter separation from walls, parapets, penthouses, etc. No furnace or incineration flues should be nearby. This separation distance from flues is dependent on the height of the flues, type of waste or fuel burned, and quality of fuel (ash content). In the case of emissions from a chimney resulting from natural gas combustion, the sampler should be placed at least 5 m from the chimney as a precautionary measure. On the other hand, if fuel oil, coal, or solid waste is burned and the stack is sufficiently short so that the plume could reasonably be expected to impact on the sampler intake a significant part of the time, other buildings/locations in the area that are free from these types of sources should be considered for sampling. Trees provide surfaces for particulate deposition and also restrict airflow. Therefore, the sampler should be placed at

least 20 m from the drip line and must be 10 m from the drip line when the tree(s) acts as an obstruction. The sampler must also be located away from obstacles such as buildings, so that the distance between obstacles and the sampler is at least twice the height that the obstacle protrudes above the sampler, except for street canyon sites. Sampling stations that are located closer to obstacles than this criterion allows should not be classified as neighborhood, urban, or regional scale, since the measurements from such a station would closely represent middle-scale stations. Additional information for siting samplers is provided in 40 CFR Part 58, Appendix E.

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