# REVISED AMBIENT AIR MONITORING PROGRAM FOR THE DONA PARK NEIGHBORHOOD DURING ACTIVE REMEDIATION ACTIVITIES AT THE FORMER ASARCO/ENCYCLE FACILITY

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# LIST OF ACRONYMS

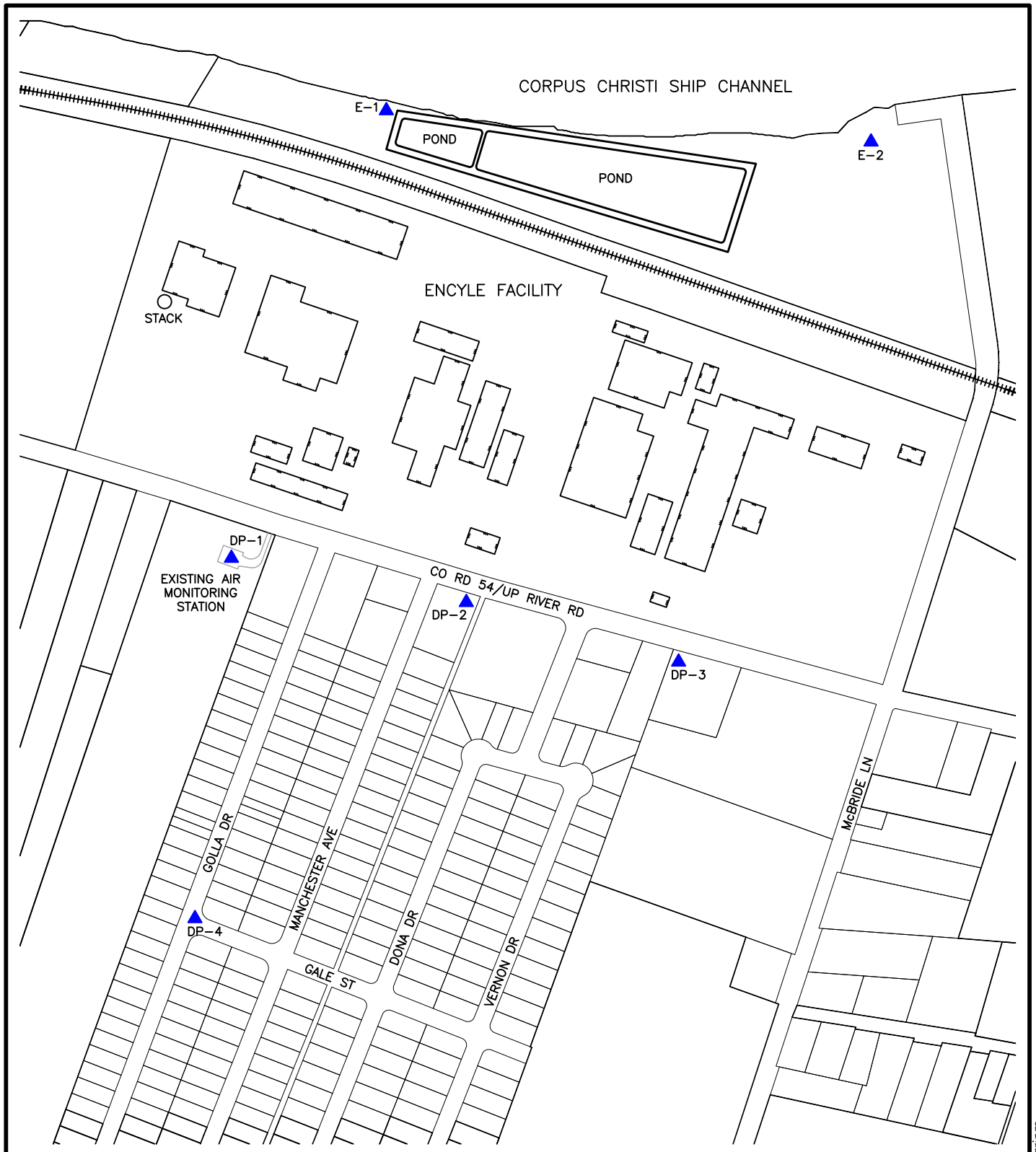
| | |
|---|---|
| AAMP | ambient air monitoring program |
| ASARCO | American Smelter and Refining Co. |
| BAM | beta-attenuation monitors |
| CSI | Campbell Scientific, Inc. |
| EDDs | electronic data deliverables |
| EM | Equivalent Method |
| EPA | Environmental Protection Agency |
| ESLs | Effects Screening Levels |
| GPS | global positioning system |
| ICP | inductively coupled plasma |
| LPM | liters per minute |
| Met One | Met One Instruments, Inc. |
| mL/min | milliliters per minute |
| mph | miles per hour |
| NAAQS | National Ambient Air Quality Standard |
| NEMA | National Electrical Manufacturers Association |
| NCDC | National Climate Data Center |
| NIOSH | National Institute for Safety and Health |
| $PM_{10}$ | particles less than 10 microns aerodynamic diameter |
| $PM_{2.5}$ | particles less than 2.5 microns aerodynamic diameter |
| QA | quality assurance |
| QAPP | Quality Assurance Project Plan |
| QC | quality control |
| SOPs | Standard Operating Procedures |
| TCEQ | Texas Commission on Environmental Quality |
| TSP | total suspended particulates |
| VSCC | Very Sharp Cut Cyclone |
| WESTON | Weston Solutions, Inc. |
| XRF | X-ray fluorescence |

# 1. INTRODUCTION AND BACKGROUND

Weston Solutions, Inc. (WESTON®) has prepared this revised ambient air monitoring program (AAMP) at the request of the Texas Commission on Environmental Quality (TCEQ) for use in the Dona Park and Manchester Place neighborhoods (community) and the former American Smelter and Refining Co. (ASARCO)/Encycle Facility (Facility) in Corpus Christi, Texas. The AAMP will be implemented during active remediation activities at the Facility located at 5500 Up River Road. The Facility is on the north side of Up River Road across from the existing TCEQ / University of Texas air monitoring station. Figure 1-1 shows the general site setting subject to implementation of the AAMP.

Multiple environmental assessments have been performed in the Dona Park neighborhood to evaluate the levels of lead, cadmium, zinc, and other metals in residential soils of the community potentially deposited via air migration from the ASARCO stack during zinc smelting operations. The TCEQ has overseen or performed the remediation of all residential properties with soil concentrations of metals exceeding health-based benchmarks. Community concerns over the possibility that emissions from demolition and remediation activities at the Facility could adversely impact the community prompted the TCEQ to conduct ambient air quality monitoring during demolition activities. This effort will be sustained during active remediation activities at the Facility. The air quality monitoring program being performed by the TCEQ, and described herein, has been designed to supplement the on-site ambient air monitoring program being implemented at the Facility by the ASARCO/Encycle Bankruptcy Trustee charged with the remediation of the Facility.

This revised AAMP includes ambient air quality monitoring requirements implemented during demolition activities from April 2011 through July 2012 (demolition phase). This revised AAMP also includes modifications to the program based on the ambient air quality data set collected during the demolition phase. The revised AAMP provides the TCEQ with real-time ambient air quality information in the community to assess the effectiveness of on-site emissions controls and to direct the modification of remediation activities as required.




LEGEND:

FACILITY BUILDING

RAILROAD TRACK

DESIGNATED AIR MONITORING LOCATION

N

0 50 100

SCALE IN FEET

WESTON SOLUTIONS

# FIGURE 1-1

## DEFAULT DONA PARK AIR MONITORING LOCATIONS

CORPUS CHRISTI, TEXAS

| DATE | PROJECT NO. | SCALE |
|---|---|---|
| APR 11 | 02444.019.005 | AS SHOWN |

SOURCE: CITY OF CORPUS CHRISTI, TX, DEPARTMENT OF DEVELOPMENT SERVICES, 2009

H:\TCEQ (02444)\02444.019.005 Dona Park\06.0 Data and Figures\Figures\FIGURE 1-1 AIR MONITORING LOCATIONS.dwg

November 22, 2011 – 4:52pm User: herrinm

## 1.1 GEOGRAPHY AND CLIMATOLOGY

The climatology and broader geographic setting of the Corpus Christi area are described in the climate narrative for the National Weather Service station at Corpus Christi International Airport:

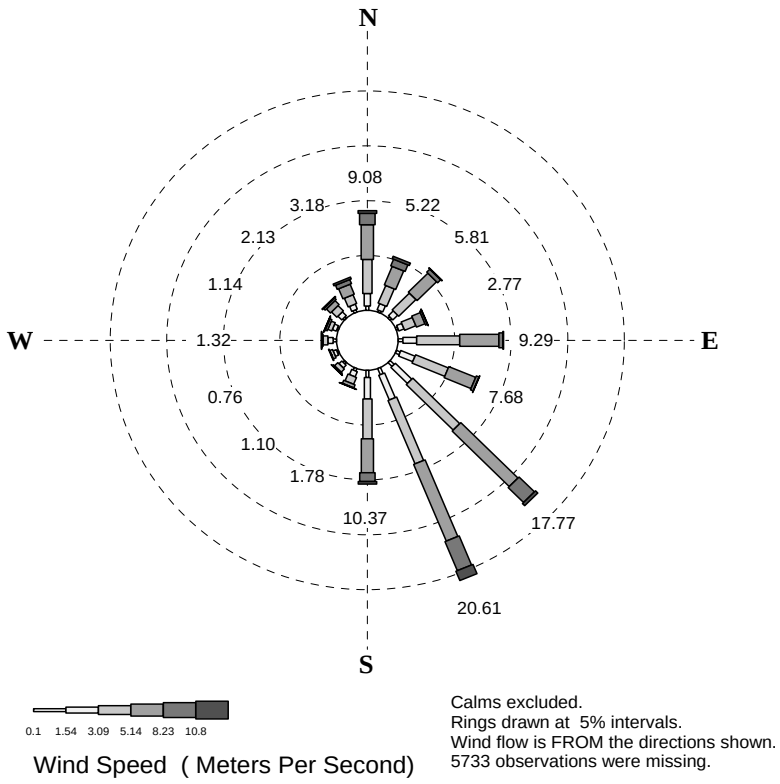
> Corpus Christi is located on Corpus Christi Bay, an inlet of the Gulf of Mexico, in south Texas. The climatic conditions vary between the humid subtropical region to the northeast along the Texas coast and the semi-arid region to the west and southwest. Temperatures at the International Airport, which is about 7 miles west of downtown Corpus Christi, may be substantially different than those in the city during calm winter mornings and during summer afternoon sea breezes.
>
> Peak rainfall months are May and September. Winter months have the least amounts of rainfall. The hurricane season from June to November can greatly affect the rainfall totals. Dry periods frequently occur. Several months during the years of record have had no rainfall, or only a trace. Snow falls on an average of about one day every two years.
>
> There is little change in the day-to-day weather of the summer months, except for an occasional rain shower or a tropical storm in the area. High temperatures range in the high 80s to mid 90s, except for brief periods in the high 90s. The sea breeze during the afternoon and evening hours moderates the summer heat. Low temperatures are usually in the mid 70s. Mornings are generally warm. Summertime temperatures rarely reach 100 degrees near the bay, but occasionally do in most other parts of the city. Temperatures above 100 degrees are frequent about 30 to 60 miles to the west and southwest. Summertime afternoons are more pleasant than mornings because they are usually clear and windy. In the summer season the region receives nearly 80 percent of the possible sunshine.
>
> The fall months of September and October are essentially an extension of the summer months. November is a transition to the conditions of the coming winter months, with greater temperature extremes, stronger winds, and the first occurrences of northers. The winter months are relatively mild, but with temperatures sufficiently low to be stimulating. Temperatures below 32 degrees seldom occur near the bay, but are more frequent inland. January is the coldest month with a prevailing northerly wind. The most extreme cold weather, in which daytime highs do not exceed 32 degrees, does not occur more than once every three or four years. The earliest occurrence of a temperature below 32 degrees is in early November and the latest occurrence in the spring is mid to late March.
>
> Relative humidity, because of the nearness of the Gulf of Mexico, is high throughout the year. However, during the afternoons the humidity usually drops to between 50 and 60 percent.
>
> Severe tropical storms average about one every ten years. Lesser strength storms average about one every five years. The city of Corpus Christi has a feature not

> found in most other coastal cities. A bluff rises 30 to 40 feet above the level of the lowlands area near the bay. This serves as a natural protection from high water. Protection for the main city is now furnished by sea walls.
>
> Chief hurricane months are August and September, although tropical storms have occurred as early as June and as late as October. The majority of the storms pass either to the south or east of the city. Tornadoes are an infrequent occurrence in the area, and hail occurs only about once a year.
>
> (Source: National Climatic Data Center Online, 2011)

Hourly data from the years 2003 through 2008 were obtained from the National Climate Data Center (NCDC) for the Corpus Christi International Airport. This data was used to generate the wind rose in Figure 1-2. The wind rose has petals whose lengths indicate the relative frequency (amount of time) that the wind was observed blowing from the general direction the petal is pointing. Specifically, each of the 16 petals actually represents all wind directions that fall in the 22.5-degree wide range that extends halfway to the two adjoining petals.

Based on the 6-year Corpus Christi data, the prevailing winds in the study area are from the south to southeast. There are secondary peaks in frequency from the east and north.

## Figure 1-2
## Corpus Christi Wind Rose




PERCENT OCCURRENCE: Wind Speed ( Meters Per Second)
LOWER BOUND OF CATEGORY

| DIR | 0.1 | 1.54 | 3.09 | 5.14 | 8.23 | 10.8 |
|---|---|---|---|---|---|---|
| N | 0.40 | 1.13 | 3.10 | 3.17 | 1.03 | 0.25 |
| NNE | 0.19 | 0.59 | 1.73 | 1.84 | 0.65 | 0.22 |
| NE | 0.19 | 0.60 | 2.14 | 2.44 | 0.37 | 0.06 |
| ENE | 0.18 | 0.49 | 1.07 | 0.82 | 0.17 | 0.04 |
| E | 0.41 | 1.21 | 3.80 | 3.46 | 0.35 | 0.06 |
| ESE | 0.36 | 1.35 | 3.13 | 2.56 | 0.26 | 0.02 |
| SE | 0.50 | 2.05 | 5.87 | 7.14 | 1.93 | 0.29 |
| SSE | 0.60 | 2.43 | 6.24 | 7.55 | 2.87 | 0.91 |

TOTAL OBS = 68388 MISSING OBS = 5733

PERCENT OCCURRENCE: Wind Speed ( Meters Per Second)
LOWER BOUND OF CATEGORY

| DIR | 0.1 | 1.54 | 3.09 | 5.14 | 8.23 | 10.8 |
|---|---|---|---|---|---|---|
| S | 0.65 | 1.96 | 3.63 | 3.08 | 0.80 | 0.24 |
| SSW | 0.25 | 0.51 | 0.67 | 0.30 | 0.04 | 0.01 |
| SW | 0.20 | 0.34 | 0.42 | 0.12 | 0.02 | 0.00 |
| WSW | 0.14 | 0.31 | 0.25 | 0.06 | 0.00 | 0.00 |
| W | 0.28 | 0.48 | 0.42 | 0.10 | 0.02 | 0.01 |
| WNW | 0.15 | 0.37 | 0.37 | 0.18 | 0.06 | 0.02 |
| NW | 0.19 | 0.49 | 0.67 | 0.50 | 0.20 | 0.08 |
| NNW | 0.25 | 0.49 | 0.86 | 0.98 | 0.41 | 0.19 |

CALM OBS = 0

(Source: National Climatic Data Center Integrated Surface Hourly Observations, 2003-2008 [Data CD-ROM]).

## 1.2 AMBIENT AIR QUALITY STANDARDS & GUIDELINES

There are currently two short-term Primary National Ambient Air Quality Standards (NAAQS) for particulate matter, based on two particle size ranges: particles less than 10 microns aerodynamic diameter ($PM_{10}$) and particles less than 2.5 microns aerodynamic diameter ($PM_{2.5}$). The Primary NAAQS are designed to be protective of human health and welfare. The 24-hour NAAQS for $PM_{10}$ is an average of 150 micrograms per cubic meter ($\mu g/m^3$), and the 24-hour NAAQS for $PM_{2.5}$ is an average of 35 $\mu g/m^3$. The current PM NAAQS are summarized in Table 1.1.

**Table 1-1**
**Particulate Matter NAAQS**

| Pollutant | Primary Standard | Averaging Time |
|---|---|---|
| Particulate Matter ($PM_{10}$) | 150 $\mu g/m^3$ | 24-hour[1] |
| Particulate Matter ($PM_{2.5}$) | 35 $\mu g/m^3$ | 24-hour[2] |

[1] Not to be exceeded more than once per year on average over 3 years.

[2] To attain this standard, the 3-year average of the 98th percentile of 24-hour concentrations at each population-oriented monitor within an area must not exceed 35 $\mu g/m^3$.

The NAAQS values for $PM_{10}$ and$PM_{2.5}$ will be used to develop conservative and protective real-time particulate matter action levels as described in Section 2.3. In addition, the TCEQ's Effects Screening Levels (ESLs) will be used to develop conservative and protective action levels. ESLs are screening levels used by the TCEQ, for example, to evaluate air dispersion modeling's predicted impacts in the air permitting process. They are used to evaluate the potential for adverse health effects to occur as a result of exposure to constituents in the air for the applicable exposure duration (e.g., acute, chronic). ESLs are based on data concerning health effects, the potential for odors to be a nuisance, and effects on vegetation. If predicted ambient levels of constituents in air exceed the screening levels, it does not necessarily indicate a problem, but rather triggers a more in-depth review. The ESLs for the metals of concern associated with on-site demolition and remediation activities are listed as action levels on Table 4-1.

## 1.3 PROGRAM GOALS

The goals of the Dona Park Neighborhood Ambient Air Monitoring Program are as follows:

- Supplement the on-site ambient air monitoring program by collecting $PM_{10}$ and $PM_{2.5}$ real-time data to evaluate and adjust on-site emissions controls as necessary, and mitigate the potential for ambient air particulate concentrations in Dona Park from exceeding conservative and protective action levels based on the 24-hour NAAQS values for $PM_{10}$ and $PM_{2.5}$.

- Supplement the on-site ambient air monitoring program by collecting speciated metals in ambient air data to evaluate and adjust on-site emissions controls as necessary and to adjust on-site and/or community $PM_{10}$ and $PM_{2.5}$ action levels as necessary to mitigate the potential for long-term ESL exceedances in the community.

- As a back-up to the on-site ambient air monitoring program, alert TCEQ, WESTON, and Encycle Trustee if real-time particulate measurements attributable to on-site operations reach or exceed the action levels (discussed in Section 2.3) as necessary.

- Deploy mobile "roving" stations with real-time monitors for $PM_{10}$ and $PM_{2.5}$ and speciated metals analytical samplers at least twice a week, or when wind conditions favor a northerly component during active remediation activities. Asbestos ambient air sampling may also be performed at the discretion of TCEQ, based on the type of remediation activities being performed.

# 2. PROGRAM OVERVIEW

WESTON has set up a primary ambient air monitoring station at the existing TCEQ / University of Texas monitoring location adjacent to the Facility along Up River Road. Continuous monitoring for $PM_{10}$ and $PM_{2.5}$ along with periodic ambient air sampling for metals will be conducted during active remediation activities at the Facility. Asbestos ambient air sampling may also be performed at the discretion of the TCEQ.

## 2.1 PRIMARY STATIONS

The primary station is the existing TCEQ / University of Texas monitoring station. The station is equipped with Environmental Protection Agency (EPA) approved Federal Equivalent Method (EM) continuous monitors for $PM_{10}$ and $PM_{2.5}$. In addition to the EM samplers, a portable real-time $PM_{10}$ monitor is currently deployed at the primary station. This portable monitor will measure particulates in real-time (averaging time less than 1 hour). As remediation of the Facility progresses, the portable $PM_{10}$ monitor may be relocated (as practicable within the fenced area) to continue the 24-hour real-time monitoring. Descriptions of the monitoring equipment are presented in Section 3.

## 2.2 ROVING STATIONS

Two roving monitoring stations (E-BAMs) will be deployed routinely into the community during active remediation. The roving stations will be deployed at a minimum of twice per week for the duration of active remediation activities. The roving stations will consist of a portable real-time $PM_{10}$ or $PM_{2.5}$ monitor. Each of the units has been modified to provide portable battery operation and produce measurements in real-time (averaging times less than 1 hour).

If predominant wind with a northern component is observed or forecasted, a roving station will be placed upwind (north of the ASARCO/Encycle facility), while the second station is placed downwind near or within the Dona Park neighborhood for a minimum of 8 hours. The roving unit positioned within the Dona Park neighborhood will be the $PM_{2.5}$ monitor by default. The default locations of the roving ambient air monitoring stations are shown in Figure 1-1. The exact location used will depend on the observed or forecasted wind direction for the monitoring period each day. If predominant wind with a northern component is not observed or forecasted,

only the $PM_{2.5}$ roving station will be deployed in the community for a minimum period of two hours. If a new monitoring location is utilized (not shown on Figure 1-1), a hand-held global positioning system (GPS) receiver will provide latitude and longitude coordinates for the new location.

One of the portable instruments will collect $PM_{10}$ measurements, while the other portable instrument will collect $PM_{2.5}$ measurements. As previously stated, the $PM_{2.5}$ instrument will always be used in the downwind, most sensitive areas for public health near or within the Dona Park neighborhood. Prior to use, each roving unit will be leak-checked, and clocks on the data logger and particulate monitors will be synchronized. Whenever a new location is to be monitored, the field team will input the latitude and longitude of the roving station into the data logger.

In conjunction with the roving particulate monitors, ambient air sampling equipment will also be routinely deployed to collect time-integrated ambient air samples for trace metals. Ambient air samples for asbestos may also be periodically collected. This equipment will use pumps to draw air at a fixed rate through sample filters or cartridges. The ambient air samples will be collected during the daylight hours and for a period of 8 hours to during on-site remediation activities. Samples collected will be sent to CHESTER LabNet of Tigard, Oregon for total metals analyses. CHESTER LabNet will send any asbestos samples collected to Chemoptix Microanalysis, LLC of West Linn, Oregon for analysis.

## 2.3 PARTICULATE ACTION LEVELS

As shown in Table 1-1, the NAAQS for $PM_{10}$ and $PM_{2.5}$ are 150 $\mu g/m^3$ and 35 $\mu g/m^3$, respectively, for a 24-hour period. Conservative and protective action levels set at a fraction of the NAAQS time period (a 1 hour averaging time versus the 24-hour NAAQS averaging time) will be in place during active remediation activities to supplement on-site ambient air monitoring data in an effort to prevent ambient air quality particulate levels attributable to on-site operations from approaching the NAAQS values. Remediation action levels and appropriate responses to action level exceedances are listed in Table 2-1.

**Table 2-1**
**Action Levels for $PM_{10}$ and $PM_{2.5}$**

| Pollutant Monitor | Action Level | Averaging Time | Response |
|---|---|---|---|
| Primary Station Particulate Matter and/or Roving Station Particulate Matter ($PM_{2.5}$) | 45 µg/m3 | 1-hour | Stop work triggered; may resume in 30 minutes |
| Primary Station Particulate Matter and/or Roving Station Particulate Matter ($PM_{10}$) | 150 µg/m3 | 1-hour | Stop work triggered; may resume in 30 minutes; |
| Roving Station Particulate Matter ($PM_{2.5}$) | 45 µg/m3 | Two consecutive 15-minute averages | Increase emissions controls; decrease demolition rates |
| Primary & Roving Station Particulate Matter ($PM_{10}$) | 150 µg/m3 | Two consecutive 15-minute averages | Increase emissions controls; decrease demolition rates |

The data from the particulate monitors will be recorded by digital data loggers (described in Section 5) using the analog signal outputs of the monitors. The $PM_{10}$ and $PM_{2.5}$ data from the primary monitors will be recorded as hourly and daily (midnight-to-midnight) averages. The $PM_{10}$ and $PM_{2.5}$ roving monitors will be recorded as 15-minute and hourly averages. If a $PM_{10}$ or $PM_{2.5}$ 1-hour average concentration attributable to remediation activities at the site triggers a stop-work response as described in Table 2-1, work may resume in no less than 30 minutes, provided the NAAQS 24-hour average has not been exceeded. All remediation work must cease for the day if a second stop-work action level is reached that same day. Although NAAQS compliance is not a primary objective of this AAMP, it is by design that by setting action levels with stop-work provisions at a fraction of the NAAQS time period, adherence to the $PM_{10}$ and $PM_{2.5}$ NAAQS by site operations is expected.

## 2.4 SPECIATED METALS ACTION LEVELS

A total of 11 metals will be analyzed during remediation activities. Based on data collected during demolition phase, samples for mercury analysis will no longer be required. The action levels based on the ESLs for each of the 11 metals is shown in Table 2-2, below.

**Table 2-2**
**Action Levels for Metals**

| Metal | Action Level ($\mu g/m^3$) |
|---|---|
| Antimony | 5 |
| Arsenic | 0.1 |
| Barium | 5 |
| Cadmium | 0.1 |
| Chromium | 3.6 |
| Copper | 10 |
| Lead | 0.15 |
| Nickel | 0.15 |
| Selenium | 2 |
| Silver | 0.1 |
| Zinc | 20 |

The action level required by the TCEQ for asbestos is 0.01 fibers per cc (f/cc).

As was discussed in Section 1.2, the TCEQ's ESLs will be used as conservative and protective action levels to supplement the on-site ambient air monitoring data. Because the collection of real-time speciated metals data is generally not possible, laboratory data is the only speciated metals data that will be collected. However, laboratory results for samples collected during northwind conditions will be expedited by using X-ray fluorescence (XRF) spectroscopy analyses with the minimum possible laboratory turnaround time, as discussed in Section 4.1.1.

In the event an action level for a metal or asbestos has been exceeded, the particulate action level may be adjusted downward to the extent of the exceedance. The real-time particulate action level for both $PM_{10}$ and $PM_{2.5}$ may be lowered by the corresponding metals or asbestos percent exceedence for a minimum period of two weeks. If no additional metals or asbestos action level exceedences are observed within this two week period, the default particulate action levels listed in Table 2-1 may resume.

## 2.5 ALERTS

When an action level has been triggered, the data loggers and data telemetry system will send email and text message alerts to assigned WESTON and TCEQ personnel as described in the

Remediation Phase AAMP Alert Logic in Appendix A. Table 2-2 shows the distribution list to receive alerts when demolition commences. If personnel changes occur during the remediation phase, WESTON will be notified so additional contact information may be added to the programming.

**Table 2-2**
**Action Level Alert Contact List**

| TCEQ | WESTON |
|---|---|
| omar.valdez@tceq.texas.gov | dayna.pelc@westonsolutions.com |
| mark.arthur@tceq.texas.gov | phil.bredfeldt@westonsolutions.com |
| steve.mauch@westonsolutions.com | ryan.mccarthy@westonsolutions.com |

Additional actions may be taken by the TCEQ if winds have any sustained northern component (270 to 90 degrees) per the on-site Air Monitoring Program, as this condition will trigger provisions to direct the Encycle Trustee to cease certain remediation activities, including any kind of excavation. Detection of this condition will be the responsibility of TCEQ personnel using online data available from the meteorological station on Up River Road that includes dedicated meteorological equipment installed and maintained by WESTON during the remediation phase.

## 2.6 DEPLOYMENT FREQUENCY

Roving monitoring stations and samplers will be deployed into the adjacent Dona Park neighborhood at least twice a week during active remediation activities at the Facility. The recurring, scheduled deployment of the roving stations will occur during the work week only (Monday through Friday), with Mondays and Thursdays as default deployment days unless weather or remediation conditions warrant other or additional days of monitoring and sampling (as directed by the TCEQ). Additional monitoring beyond two days per week may be required to address changes in remediation activity and/or wind direction forecasts indicating the likelihood of predominant winds with a northerly component. The TCEQ may deploy roving monitoring stations whenever the predominant wind direction is expected to have a sustained northerly component (270 to 90 degrees). The TCEQ will monitor the weather predictions and local current conditions using dedicated Dona Park weather station and instruct WESTON to deploy the roving monitors whenever such a weather condition is predicted or observed. Using the

available weather forecasting, advanced notice of such a deployment will be made whenever possible.

The particulate monitors, ambient air samplers, or a combination of both, will typically operate for a period of 8 hours during daylight to provide coverage during remediation operations. The deployment of roving monitors and the duration of monitoring may vary commensurate to wind direction, observed $PM_{10}$ and $PM_{2.5}$ levels, and with periods of inactivity at the former ASARCO/Encycle facility.

# 3. AMBIENT AIR MONITORING EQUIPMENT

## 3.1 PARTICULATE MATTER

Beta-attenuation monitors (BAM) manufactured by Met One Instruments, Inc. (Met One) were selected to continuously monitor $PM_{10}$ and $PM_{2.5}$. The Met One BAM-1020 monitors will be used for continuous $PM_{10}$ and $PM_{2.5}$ measurements at the Dona Park air monitoring station. Met One E-BAM monitors will be used for continuous, real-time $PM_{10}$ measurements at the Dona Park air monitoring station and for use as roving monitors. Both instruments operate on the principle of beta attenuation.

The BAM-1020 $PM_{10}$ monitor has received EPA's designation as an Automated Equivalent Method (EQPM-0798-122) when operated for 24 1-hour average measurements with a filter change frequency of 1 hour and glass fiber filter tape. The BAM-1020 $PM_{2.5}$ FEM Configuration monitor has received EPA's designation as an Automated Equivalent Method (EQPM-0803-111) when operated for 24 1-hr average measurements with a BGI Very Sharp Cut Cyclone (VSCC) particle size separator, a filter change frequency of 1 hour, and glass fiber filter tape.

The portable E-BAM monitor design is descended directly from the BAM-1020 and modified to provide portable battery operation and produce measurements in real-time (averaging times less than 1 hour).

The beta attenuation process uses a small source of beta particles (carbon-14, 60 microcuries) coupled to a sensitive detector that counts the emitted beta particles. The dust particles are collected on a filter tape that is placed between the beta source and the detector. Dust on the filter will intercept some of the beta particles. The reduction of beta particles is proportional to the amount of dust on the filter, which allows the mass of dust to be determined from the beta particle counts. The dust mass is combined with the air volume collected during the filter exposure time to determine the PM concentration.

Both the BAM-1020 and E-BAM monitors will be equipped with particle size selective inlets. The design of the inlets is such that particles larger than the desired size range will be removed from the air flow, based on the air flow rate. All units will be equipped with an inlet head to separate $PM_{10}$. One BAM-1020 and one E-BAM will have an additional separator (VSCC

cyclone) downstream of the $PM_{10}$ inlet to separate the $PM_{2.5}$ fraction. Sampling flow rate is critical to maintain the proper particle size cut points of the inlets. Flow rates are maintained at 16.7 liters per minute (LPM) in the BAM-1021 and E-BAM monitors using an integral flow meter, pressure sensor, and ambient temperature sensor on board each monitor.

The data from the BAM-1020 and E-BAM units will be recorded by digital data loggers (described in Section 5), using the analog signal outputs of the monitors. The $PM_{10}$ and $PM_{2.5}$ data from the BAM-1020 monitors will be recorded as hourly and daily (midnight-to-midnight) averages. The $PM_{10}$ and $PM_{2.5}$ data from the E-BAM monitors will be recorded as 15-minute and hourly averages.

A total of three E-BAM monitors will be used in this AAMP. One E-BAM will monitor from the primary station in the Dona Park air monitoring station and be dedicated to 15-minute average $PM_{10}$ data. This unit may be relocated as remediation progresses across the site. The two additional E-BAMs (one $PM_{10}$ and one $PM_{2.5}$) will serve as the roving stations collecting 15 minute average data.

## 3.2 WIND SENSOR

As part of AAMP activities during remediation of the Facility, a dedicated wind direction and velocity sensor will be installed within the Dona Park Air Monitoring Station on Up River Road. The sensor (WindSonic 2-D Wind Sensor) is an ultrasonic anemometer manufactured by Gill Instruments. It contains no moving parts, requires no calibration, and outputs its data via an SDI-12 signal. The TCEQ will utilize the wind sensor to obtain timely air speed and wind vector data to allow for real-time assessment of on-site wind conditions and support as-needed modifications to the on-site and community monitoring programs and/or remediation activities.

## 3.3 WEB CAMERA

A pan, tilt, and zoom-capable camera will be installed at the TCEQ facility on Up River Road. The camera is the AutoDome Easy II, manufactured by Bosch. The TCEQ and WESTON will have the capability to remotely access and operate the camera at any time. The information provided by the camera will facilitate the enforcement of AAMP stop-work provisions and the

on-site air monitoring program stop-work provisions. The information provided by the camera will also facilitate the enforcement of various remediation work plan provisions.

# 4. AMBIENT AIR SAMPLING EQUIPMENT

## 4.1 SAMPLING & ANALYTICAL METHODS

### 4.1.1 Total Metals

BGI PQ200 Ambient Air Samplers were selected to collect ambient air samples for total metals analyses. The PQ200 ambient air sampler is capable of collecting either $PM_{10}$ and $PM_{2.5}$ air fractions. The PQ200 ambient air sampler monitors its own airflow rate and adjusts the pump speed to compensate for changes in load pressure and/or other forces which would otherwise hamper the flow of ambient air through a filter. The PQ200 has a standard airflow rate of 16.7 liters per minute (L/min), and can be programmed to begin its sampling job at a specific date and time and stop sampling after the user defined run time is depleted. The TCEQ standard procedure will be to collect ambient air samples using a standard 8-hour collection period to provide suitable ambient air monitoring coverage throughout a work day.

All air samples collected via the PQ200 will be set to collect $PM_{10}$ particulate fractions and be laboratory-analyzed for metals using XRF spectroscopy via EPA Compendium Method IO-3.3 (Appendix B). This approach is supported by the suitable correlation between XRF data and the inductively coupled plasma (ICP) spectroscopy data observed during months of AAMP implementation in the demolition phase and the XRF method detection limits for the metals of concern of approximately one order of magnitude lower than the action levels. The XRF analysis of the TSP filters will be performed by CHESTER LabNet of Tigard, Oregon. The turnaround time for XRF analysis will be 24 hours or as quick as possible so that any action level exceedances can be addressed in a timely manner and changes made to the on-site remediation activities and emissions controls as needed. It is anticipated that XRF results will generally be provided by the laboratory on the same day of their receipt of samples if received by noon. Samples collected during a southerly wind component away from the neighborhood may not be submitted for expedited analysis, and a standard turn-around time will be requested instead. Samples will be shipped to CHESTER LabNet on the same day as their collection whenever possible.

Following XRF analysis, the particle mass collected on each filter will be determined gravimetrically by the laboratory. The resultant mass divided by the total amount of ambient air passed through the filter during the sampling period will provide the calculated concentration of each analyte in ambient air during that time period. The TSP collected on the PQ200 membrane filter will then be stored for possible future analysis for metals using ICP via EPA Method IO-3.4 (Appendix C). Analysis by ICP will only be performed if XRF data are questionable, exceed action levels, or if requested TCEQ. The turnaround times for the laboratory analyses may vary with wind conditions. Analyses of samples collected in wind conditions with a northerly component may be expedited, whereas analyses of samples collected in wind conditions with a southerly component away from the neighborhood may undergo a standard laboratory turnaround time.

### 4.1.2 Asbestos

SKC Incorporated 224-PCWR8 Ambient Air Sampling Pumps were selected to collect asbestos samples in ambient air. These sampling pumps have an adjustable air inflow range of up to 5,000 milliliters per minute (mL/min). The flow rate of the unit will typically be adjusted in the field to approximately 3,000 mL/min. The sampling pump will then be operated for enough time to allow for the required laboratory detection limit. Although the required length of time to meet desired detection limit requirements will likely only be two to three hours in duration, the TCEQ standard procedure will be to collect ambient air samples using a standard 8-hour collection period to provide suitable ambient air monitoring coverage throughout a work day.

One sampling pump will be used for asbestos analysis. Additional pumps may be operated for the analysis of total metals as a backup to PQ200 samples, at the request of the TCEQ.

The asbestos samples will be collected on a 25 millimeter (mm), three-piece cassette. The cassette samples are analyzed with a light microscope where fibers are manually counted. The samples will be shipped to CHESTER LabNet; however, the analyses of the asbestos filters will be performed by Chemoptix Microanalysis, LLC of West Linn, Oregon.

## 4.2 SAMPLE SCHEDULING & HANDLING

Ambient air samples for total metals analyses will be collected at a minimum of twice per week in conjunction with the deployment of the roving monitors (E-BAMs) during active remediation of the Facility. Sampling frequency may increase due to forecasted or observed wind conditions with a northern component towards the community. The TCEQ may request the collection of additional samples based on their monitoring of weather forecasts and local weather data using the dedicated meteorological equipment in the Dona Park air monitoring station.

Sampling information to be collected includes the ambient temperature and pressure conditions (as obtained from the TCEQ monitoring station) and volumetric sample flow rate. The volumetric flow rate will be used to calculate the actual ambient air concentrations of the analytes over the sampling period.

The ambient air sample cartridges and/or filters will be securely capped, labeled, and shipped to CHESTER LabNet of Tigard, Oregon for analysis. Total metals as measured by the XRF will be analyzed by the EPA Compendium Method IO-3.3. Total metals as measured by ICP will be analyzed using EPA Method IO-3.4. Sampling, particulate mass, and digestion will be performed in accordance with EPA Method IO-3.1. Chemoptix Microanalysis will conduct the analyses for asbestos by the NIOSH 7400 method.

Samples will be shipped in a timely fashion within corresponding sample holding time limits of the analytical methods to facilitate a rapid receipt of results as necessary. Expedited samples will be shipped via Federal Express Priority Overnight service.

## 4.3 METHOD QUANTITATION LIMITS

A total of 11 metals, as well as asbestos, will be analyzed. The method quantitation limit required by the TCEQ for each of these analytes is shown in Table 7-1.

# 5. DATA MANAGEMENT AND REPORTING

All data management will be accomplished using electronic databases. Raw data from the continuous monitors, sampling information from the integrated samplers, and the integrated sample results from the analytical laboratory will be collected in Microsoft Excel format for review and summary. Final lab reports will be generated in Adobe Acrobat format.

Data from the primary and roving stations will be collected using digital data loggers. These data will be automatically downloaded to a database at least daily via digital cellular modems. This automated system is described in Section 5.1.

Sample data for the integrated samplers will be collected manually in the field. Analytical results will be received as electronic data deliverables (EDDs) from the laboratory. The sample data and EDDs will be uploaded to a database for processing. The systems to manage integrated sample data are described in Section 5.2.

## 5.1 CONTINUOUS DATA RECORDING & TELEMETRY

### 5.1.1 Data Loggers

The digital data loggers are CR850 data loggers manufactured by Campbell Scientific, Inc. (CSI). The Campbell CR-series of data loggers are programmable, general-purpose data logging units that can accept a wide variety of sensors with analog outputs.

The loggers operate in outdoor environments and are housed in weather-tight National Electrical Manufacturers Association (NEMA) standard enclosures for moisture protection, along with their power supplies and telemetry equipment.

The loggers are powered by small 12 VDC rechargeable batteries, or by typical 12 VDC deep cycle marine batteries. Data are stored onboard the loggers in flash memory that is retained even if power is lost. Loggers also maintain their programming and internal clocks in the event of a power loss. No data will be collected if the battery becomes drained, but data collection will resume automatically when power is restored. The batteries at each station will be sufficient to power the loggers for several days if recharging power is lost.

### 5.1.2 Data Telemetry & Review

The telemetry equipment for the study will be RavenX Cellular Modems manufactured by AirLink Communications. The RavenX is a wireless networking device that will be used on the Verizon network. The RavenX allows direct connection to the data loggers for troubleshooting, programming, and data retrieval. The RavenX also provides the capability for the data loggers to directly transmit email notifications. The RavenX modem uses 12 VDC power, which will be provided by the datalogger at each station.

The data from each station will be polled daily from WESTON's home office in West Chester, Pennsylvania. The retrieved data will be uploaded to a database for review and processing. The data from the Dona Parks monitoring network will be reviewed on a daily basis during the work week by WESTON meteorologists who are experienced with continuous monitoring data.

## 5.2 SAMPLE INFORMATION MANAGEMENT

The sample information management system for the study will be based on a uniform sample identification system. Each sample will receive a unique ID that is based on the unique combination of site location, sampling date, and the pollutant being sampled.

The sample ID will be structured as follows:

DP-TCEQ-YYMMDD-LOC-LOC2-XX[-QQ], where

| | | |
|---|---|---|
| DP-TCEQ | = | Project (Dona Park-TCEQ) |
| YYMMDD | = | Sampling date (e.g., 04/06/2011 = 110406) |
| LOC | = | Sample Location (e.g. UW = Upwind, DW = Downwind) |
| LOC2 | = | Sample Location 2 (e.g. DP-1, DP-2, E-2, etc.) |
| XX | = | Lab analysis (ML = Metals, ASB = Asbestos) |
| QQ | = | Optional QA sample flag (TB = trip blank, FB = field blank, SC = duplicate, PQ = PQ200) |

For example, a metals sample collected at roving site the upwind station E-2 on 30 September 2012 would be identified as DP-TCEQ-20120930-UW-E-2-ML.

### 5.2.1 Field Data

Field sampling data, such as sample load/unload times, sampler flow readings, or elapsed timer readings will be documented into a standardized database. Field sampling data will be manually

recorded in a logbook and field data sheet (Appendix D). A single dedicated logbook will be used to document AAMP implementation throughout the remediation phase, and entries will be made by the field technician(s) at the time of loading or unloading. Information from the daily sampling event will be given to WESTON in the West Chester, Pennsylvania office to be inputted into the database.

### 5.2.2 Laboratory Data

Laboratory data will be received as hard copy reports and in Microsoft Excel format. The digital reports are provided to allow efficient electronic uploading of the analytical results to the project databases and eliminate data entry errors.

The laboratories will provide analytical results in units of total mass of pollutant per sample. In order to determine the ambient air concentrations of the pollutants, the masses will be divided by the volume of air pulled through the media for each sample.

## 5.3 DELIVERABLES

### 5.3.1 TCEQ Website

A dedicated private website will host raw real-time data from the continuous particulate monitors for TCEQ internal use. The BAM-1020 data will display $PM_{10}$ and $PM_{2.5}$ 1-hr average concentrations. The primary station E-BAM data will display $PM_{10}$ 15-minute average concentrations. E-BAM data from the roving particulate monitoring stations will display $PM_{10}$ and $PM_{2.5}$ 15-minute average concentrations and denote the roving status. Corresponding hourly wind velocity and direction data from the TCEQ wind sensor will be associated with all $PM_{10}$ and $PM_{2.5}$ time-averaged data. Wind speed and direction as well as upwind data will be used for source attribution and may be used by the TCEQ to request unscheduled monitoring and sampling events.

### 5.3.2 Public Website

A public website will be offered for community viewing. Data will be downloaded remotely to the West Chester, Pennsylvania office. WESTON meteorologists familiar with continuous ambient air monitoring will review and validate the previous day's data and post to the public

website by the close of the business day. Validated hourly data from the BAM-1020 and primary E-BAM will be uploaded to the site. The 24-hr average $PM_{10}$ and $PM_{2.5}$ concentrations will be calculated and compared with the NAAQS values for $PM_{10}$ and $PM_{2.5}$. Corresponding hourly wind velocity and direction data from the TCEQ wind sensor will be associated with all $PM_{10}$ and $PM_{2.5}$ time-averaged data posted on the public website.

### 5.3.3 Analytical Results Report

WESTON will provide the TCEQ a summary report of non-expedited laboratory results within 3 business days of receiving the data package from the lab. WESTON shall ensure that all preliminary and final data reports for expedited analyses are submitted concurrently to TCEQ and WESTON for the sake of expediency. WESTON shall perform a cursory review of all preliminary analytical reports received from the laboratory immediately upon receipt and send TCEQ an email notification on a determination of whether the reported concentrations are above or below action levels. WESTON shall immediately notify TCEQ of any action level exceedances. WESTON shall also provide the TCEQ with the tabulated sampling data results for each type of analyses every two weeks.

# 6. QUALITY ASSURANCE / QUALITY CONTROL

Quality assurance (QA) refers to the planned and systematic actions necessary to provide adequate confidence that a product or service will satisfy a given requirement for quality. QA is applied to location and equipment selection, equipment acquisition and installation, routine site operation, and data processing and reporting.

Quality control (QC) refers to the operational techniques and activities that are used to fulfill requirements for quality. QC procedures applied at each step provide checks for acceptable conditions with corrective procedures specified when necessary.

The purpose of QC procedures is to assess and document data quality and to define remedial corrective actions when operating conditions exceed pre-established limits. Routine QC procedures are designed to focus on areas most likely to have problems, based on experience and guideline documents. Table 6-1 shows the frequency of audits and routine QC measures for the ambient air quality study. The following subsections describe the QC, calibration, and auditing procedures to be used in the ambient air quality study. Applicable TCEQ SOPs are provided in Appendix E.

**Table 6-1**
**Schedule of Audits, Calibrations, and Quality Control Checks**

| Frequency | Activity |
|---|---|
| Start of Program | Instrument Installation, Leak Check and Calibration |
| Weekly | Routine Checks of Monitors (Tape, Clocks, Housekeeping) |
| Monthly | Leak Checks of Primary Instruments |
| Quarterly | Ambient Air Sampling Equipment Audit |
| End of Program | Ambient Air Sampling Equipment Audit |

## 6.1 AMBIENT AIR QUALITY MONITORS

### 6.1.1 Quality Control

The BAM-1020 and E-BAM particulate monitor beta detectors are calibrated at the factory. The beta source strength will theoretically not vary significantly for over 500 years. The beta detector calibrations remain fixed for the life of the unit, and no user adjustments are required.

Both units have test membranes that are placed in the beta particle pathway to verify performance of the detector. The test membranes are thin sheets of material that absorb a fraction of beta particles equivalent to a known mass of particulate matter. Each instrument has an individually matched membrane, and the factory-provided equivalent mass reading is stored in the instrument. The reference membrane tests are performed automatically every hour by the BAM-1020 and will be manually performed once every quarter for the E-BAM (the manufacturer recommends a frequency of 1-2 times per year for the E-BAM). The units are also equipped with zero-check inserts that are used in the same manner as the reference membranes.

Periodic QC flow checks will be made to ensure that the correct sample flow rate is being maintained to provide proper particle size separation. The BAM-1020 and E-BAM particle size selective inlets are designed to function at a flow rate of 16.7 L/min to maintain proper particle separation. The flow checks of both the BAM-1020 and E-BAM instruments will use a reference thermometer, a reference barometer, and a calibrated manometer. The thermometer and barometer will be used for volumetric flow corrections to standard reference conditions and will be factory calibrated to NIST-traceable standards. The manometer will be calibrated to a primary volumetric flow standard (BIOS DryCal piston flow meter). As part of the flow check for the BAM-1020, the reference temperature and barometric pressure readings will be compared to the corresponding readings produced by the BAM-1020's internal sensors.

The size selective inlets on the particulate monitors also require periodic cleaning. The larger particles that are removed from the air flow are captured inside the $PM_{10}$ inlet heads and in the secondary $PM_{2.5}$ cyclones. To maintain proper operation of the inlets, the particle deposits must be cleaned periodically. The manufacturer recommends cleaning the inlets every 6 months. During this program, the inlets will be inspected every quarter and cleaned as necessary according to manufacturer's instructions.

### 6.1.2 Quality Assurance

The audit of the BAM-1020 and E-BAM samplers will consist of a check of the inlet flow rates to verify proper functioning of the size selective inlet. Audits will be performed at the midpoint and the end of the study, using the same procedures as the routine flow checks. Audits will be performed using equivalent equipment; personnel conducting audits will not be involved in the routine project operation of instruments.

## 6.2 AMBIENT AIR QUALITY SAMPLERS

### 6.2.1 Quality Control

Periodic QC flow checks will be made to ensure that the correct sample flow rate is being maintained. During sample runs, the PQ200 microprocessor maintains an airflow rate of 16.7 LPM by adjusting the pump speed to compensate for changes in load pressure and/or other forces which would otherwise hamper the flow of ambient air through the filter cassette. The PQ200 flow check will also use a reference thermometer, a reference barometer, and a calibrated manometer. The calibrator will give a direct indication of volumetric flow rate, standard flow rate, barometric pressure, and ambient temperature.

Field and trip blank quality control samples will be collected. Field blank samples assess the possible contamination introduced by field sampling procedures, sampling media, sampling equipment, or shipment of the samples. Trip blanks verify the cleanliness of the sampling media.

The field blank will be shipped to the field, prepared, handled as the other samples, and returned to the laboratory without drawing air through the sampler, for analysis. One field blank for metals analysis will be collected each week. Trip blanks will be set aside each day that samples are collected for XRF analysis. A trip blank will be submitted for laboratory analysis on sampling events in northerly wind conditions and as requested by the TCEQ. Trip blanks will be shipped from the laboratory to the field, left sealed in their packaging, and then returned to the laboratory for analysis, as needed.

### 6.2.2 Quality Assurance

Precision and accuracy checks are both elements of QA. Precision checks are a measure of agreement among individual measurements of the same parameter, usually under prescribed similar conditions. Accuracy is the degree of agreement between an accepted reference measurement and the field measurement. Accuracy may be expressed as a total difference, or as a percentage of the reference value, or as a ratio. Precision checks are performed as collocated measurements.

Accuracy of ambient air sampling equipment is measured in terms of the accuracy of the flow rate measurement. Accurate determination of the air volume drawn through the sampler is

essential to the concentration calculation. Flow rate accuracy of the ambient air samplers will be audited quarterly, using calibrated equipment appropriate to the sampling device.

Collocated samplers will be used periodically to assess precision of the methods being used. An additional sampler of the same type will be located near the primary sampler, but with inlets no closer than 2 meters to avoid interactions between the sampler inflows. Both samplers will be set to collect a sample using the same operational settings and for the same time period. The samples will be returned to the same laboratory for analysis. The method precision will be expressed as the relative percentage difference between the primary and duplicate sample concentrations. One duplicate sample will be collected every two weeks. Duplicate samples will always be collected from the sample location in the community.

Preventative maintenance will be part of the samplers' QA program. Preventive maintenance is a combination of preventive and remedial actions taken to prevent or correct failure of the monitoring systems. Preventive maintenance for the high volume samplers includes inspection and cleaning of the inlets.

# 7. LABORATORY ANALYSIS

### 7.1.1 Analysis

Metals will be prepared and analyzed using the EPA IO-3.3 (XRF) and IO-3.4 (ICP) methods. Asbestos will be prepared and analyzed by the NIOSH 7400 method. Whenever possible, all laboratory analyses will be conducted following the procedures outlined in the TCEQ Federal Superfund Quality Assurance Project Plan (QAPP), Document Control No. QTRACK #12-463 (or the most current revision) (TCEQ, 2012).

CHESTER LabNet has reviewed this AAMP and the QAPP and will comply with the analytical requirements. CHESTER LabNet's method quantitation limits for the analysis are provided in the table below:

**Table 7-1**
**Method Quantitation Limits for Metals**

| Metal | XRF Quantitation Limit ($\mu g/m^3$) | ICP Quantitation Limit ($\mu g/m^3$) | AAMP Action Level ($\mu g/m^3$) |
|---|---|---|---|
| Antimony | 0.023 | 0.0312 | 5 |
| Arsenic | 0.003602 | 0.0624 | 0.1 |
| Barium | 0.1776 | 0.005 | 5 |
| Cadmium | 0.016484 | 0.0031 | 0.1 |
| Chromium | 0.002098 | 0.0025 | 3.6 |
| Copper | 0.001801 | 0.0125 | 10 |
| Lead | 0.00839 | 0.0312 | 0.15 |
| Nickel | 0.001801 | 0.0062 | 0.15 |
| Selenium | 0.002987 | 0.0624 | 2 |
| Silver | 0.016187 | 0.0125 | 0.1 |
| Zinc | 0.002098 | 0.0037 | 20 |

Note: Quantitation Limits above are based on an 8-hour sampling period and normal inflow rates.

The detection limit required by the TCEQ for asbestos is 0.001 fibers per cc (f/cc).

### 7.1.2 Data Review and Data Validation

CHESTER LabNet will provide the results of each ambient air sample collected to WESTON with an EDD that contains all pertinent information. CHESTER LabNet will submit the data

package as specified in QAPP Element A.9.2 and will review the data as specified in QAPP Element D.2.1.1. All internal Standard Operating Procedures (SOPs) will be followed by the analytical lab, and any deviation from SOPs will be noted in the final data package for review.

An independent data review and data validation will be completed as specified in QAPP Elements D. 2.1.2 and D.2.1.3, respectively, with the following conditions:

- Data reviews will be performed on all samples analyzed by EPA IO-3.3 and EPA IO-3.4 collected in northerly wind conditions;
- Data validation will be performed on 10% of all samples analyzed by EPA IO-3.3 and EPA IO-3.4 collected in northerly wind conditions.

A data usability summary will be prepared as specified in Element D.2.3.1 as requested by the TCEQ. Minor deviations from QAPP requirements may be necessary due to ambient air monitoring techniques. However, any deviation from QAPP requirements will not be performed without prior approval from the TCEQ.

# 8. REFERENCES

NCDC (National Climatic Data Center). "Integrated Surface Hourly Observations." *2003-2008*. CD-ROM. National Climatic Data Center.

NCDC Online. 2011. *Corpus Christi International Airport*. Retrieved from http://www4.ncdc.noaa.gov/cgiwin/wwcgi.dll?wwDI~StnSrch~StnID~20024190#ABOUT

TCEQ (Texas Commission on Environmental Quality), Remediation Division. 2012. *Quality Assurance Project Plan for the Federal Superfund Program.*

# APPENDIX A
# ALERT LOGIC FOR PARTICULATE MONITORS

# Appendix A
# Alert Logic for Particulate Monitors

## PRIMARY STATIONS

The Primary Station BAM-1020 $PM_{10}$ and $PM_{2.5}$ monitors, within the Dona Park Air Monitoring Station on Up River Road, record hourly averages based on fixed blocks bracketed by the top of each hour (00 minutes past the hour). The Primary Station monitors will issue 60-min Action Level Exceedance alerts when their respective Action Levels (ALs) are exceeded for the hourly concentrations being recorded.

## EBAM STATIONS

All EBAM monitors will be programmed to issue alerts based on 15-minute and rolling 60-minute periods. The rolling 60-minute periods will be synchronized with each 15-minute block of data (logged at 15, 30, 45, and 00 past each hour). The logic used to issue alerts is shown in the flow diagram of Figure 1.

*30-Minute Action Levels*

The 30-minute ALs are based on two consecutive 15-minute averages above the threshold values. The first 15-minute period over the threshold value will generate a "30-minute Action Level Warning" alert. The Action Level Warning provides notice that the 30-minute AL may be triggered in 15 minutes if concentrations do not decrease. A second *consecutive* 15-minute average above the threshold will trigger a "30-minute Action Level Exceedance" alert.

The count of consecutive 15-minute values above the threshold continues to accumulate until one 15-minute concentration below the threshold occurs. A "60-minute Action Level Warning" is issued at three consecutive 15-minute periods over threshold. If concentrations do not decrease, exceeding the 60-minute AL (four consecutive periods) may trigger a work stoppage, depending on wind and site conditions. No further alerts are issued based on 15-minute concentrations past the third consecutive period.

*60-Minute Action Levels*

For the 60-minute ALs, a rolling average of the four most recent 15-minute averages is used. Any rolling 60-minute average above the threshold will trigger a "Stop Work Alert".

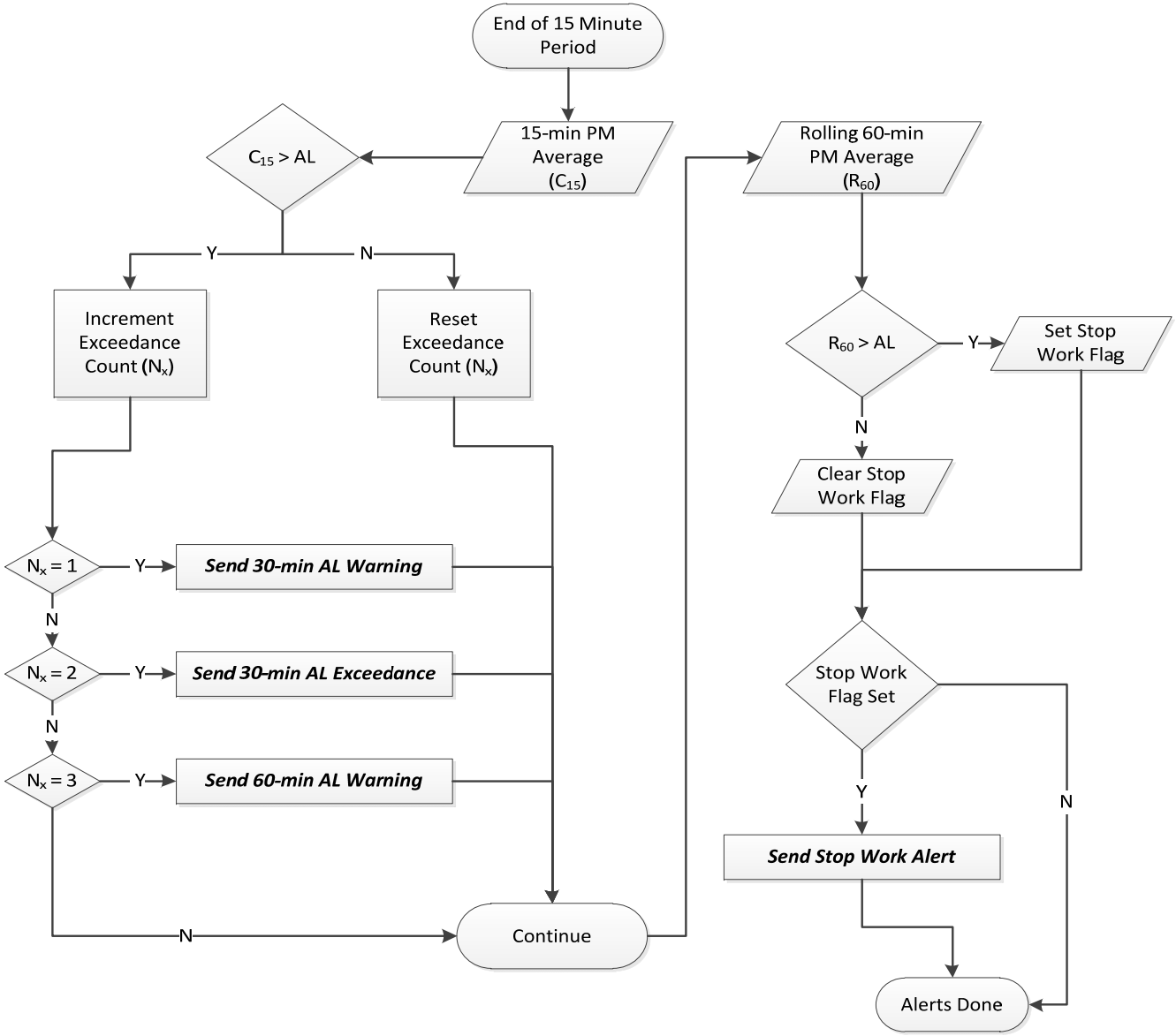
## WIND CONDITIONS

Wind information will be incorporated into the text of all alerts. The following wind information from the latest 15-minute period will be included in the messages:

- Mean wind speed and direction
- Fastest 1-minute wind speed and associated direction
- Total number of 1-minute mean wind directions with northerly component

A "wind direction with northerly component" refers to a wind direction coming from between 271 and 89 degrees, inclusive.

## Figure 1. EBAM Station Alert Flowchart



# APPENDIX B
# COMPENDIUM METHOD IO-3.3

EPA/625/R-96/010a

# Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air

## Compendium Method IO-3.3

# DETERMINATION OF METALS IN AMBIENT PARTICULATE MATTER USING X-RAY FLUORESCENCE (XRF) SPECTROSCOPY

**Center for Environmental Research Information**
**Office of Research and Development**
**U.S. Environmental Protection Agency**
**Cincinnati, OH 45268**

**June 1999**

Method IO-3.3

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This Method is the result of the efforts of many individuals. Gratitude goes to each person involved in the preparation and review of this methodology.

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DISCLAIMER

***This Compendium has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.***

**Method IO-3.3**
**Determination of Metals in Ambient Particulate Matter Using**
**X-Ray Fluorescence (XRF) Spectroscopy**

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# Chapter IO-3
# CHEMICAL SPECIES ANALYSIS OF FILTER-COLLECTED SPM

## Method IO-3.3
## DETERMINATION OF METALS IN AMBIENT PARTICULATE MATTER USING X-RAY FLUORESCENCE (XRF) SPECTROSCOPY

### 1. Scope

**1.1** During a span of more than two decades, the U. S. Environmental Protection Agency (EPA) has developed and applied x-ray fluorescence (XRF) to the analysis of ambient and source aerosols using both energy and wavelength dispersive spectrometers. Inorganic Compendium Method IO-3.3 briefly describes the agency's experience with XRF and informs the reader of its capability in elemental aerosol analysis and attempts to give a brief account of what is involved in its application. The procedures described have been in a continual state of evolution beginning with those in use on a special purpose spectrometer designed by Lawrence Berkeley Laboratory (LBL) and eventually applied to a commercially available instrument manufactured by Kevex. It is for the Kevex spectrometer to which this method applies.

**1.2** The area of toxic air pollutants has been the subject of interest and concern for many years. Recently the use of receptor models has resolved the elemental composition of atmospheric aerosol into components related to emission sources. The assessment of human health impacts resulting in major decisions on control actions by Federal, state, and local governments is based on these data. Accurate measures of toxic air pollutants at trace levels is essential to proper assessments.

**1.3** Suspended particulate matter (SPM) in air generally is considered to consist of a complex multi-phase system consisting of all airborne solid and low vapor pressure, liquified particles having aerodynamic particle sizes ranging from below 0.01 microns to 100 (0.01 Fm to 100 Fm) microns and larger. Historically, measurement of SPM has concentrated on total suspended particulates (TSP) with no preference to size selection.

**1.4** The most commonly used device for sampling TSP in ambient air is the high-volume sampler, which consists essentially of a blower and a filter, and which is usually operated in a standard shelter to collect a 24-hour sample. The sample is weighed to determine concentration of TSP and is usually analyzed chemically to determine concentration of various inorganic compounds. When EPA first regulated TSP, the National Ambient Air Quality Standard (NAAQS) was stated in terms of SPM with aerodynamic particle size of $< 100$ Fm captured on a filter as defined by the high-volume TSP sampler. Therefore, the high-volume TSP sampler was the reference method. The method is codified in 40CFR50, Appendix B.

**1.5** More recently, research on the health effects of TSP in ambient air has focused increasingly on particles that can be inhaled into the respiratory system, i.e., particles of aerodynamic diameter of $< 10$ Fm. These particles are referred to as $PM_{10}$. It is now generally recognized that, except for toxic materials, it is this $PM_{10}$ fraction of the total particulate loading that is of major significance in health effects. The reference method for $PM_{10}$ is codified in 40CFR50, Appendix J and specifies a measurement principle based on extracting an ambient air sample with a powered sampler that incorporates inertial separation of $PM_{10}$ size range particles and collection of these particles on a filter for a 24-hour period. Again, the sample is weighed to determine concentration of $PM_{10}$ and is usually analyzed chemically to determine concentration of various inorganic compounds.

**1.6** Further research now strongly suggests that atmospheric particles commonly occur in two distinct modes, the fine ( < 2.5 µm) mode and the coarse (2.5 to 10.0 Fm) mode. The fine or accumulation mode (also termed the respirable particles) is attributed to growth of particles from the gas phase and subsequent agglomerization, whereas the coarse mode is made up of mechanically abraded or ground particles. Because of their initially gaseous origin, the fine range of particle sizes includes inorganic ions such as sulfate, nitrate, and ammonium as well as combustion-form carbon, organic aerosols, metals, and other combustion products. Coarse particles, on the other hand, normally consist of finely divided minerals such as oxides of aluminum, silicon, iron, calcium, and potassium. Samplers which separate SPM into two size fractions of 0-2.5 µm and 2.5-10 µm are called dichotomous samplers. In 1997, the EPA promulgated a new standard with fine particles. The new $PM_{2.5}$ standard replaced the previously NAAQS for $PM_{10}$.

**1.7** Airborne particulate materials retained on a sampling filter, whether TSP, $PM_{10}$, $PM_{2.5}$, or dichotomous size fractions, may be examined by a variety of analytical methods. This method describes the procedures for XRF analysis as the analytical technique. The XRF method provides analytical procedures for determining concentration in $ng/m^3$ for 44 elements that might be captured on typical filter materials used in fine particle or dichotomous sampling devices. With the sample as a thin layer of particles matrix effects substantially disappear so the method is applicable to elemental analysis of a broad range of particulate material. The method applies to energy dispersive XRF analysis of ambient aerosols sampled with fine particle ( < 2.5 µm) samplers, dichotomous and VAPS (versatile air pollution sampler) samplers with a 10 µm upper cut point and $PM_{10}$ samples.

**1.8** The analysis of ambient aerosol samples captured on filterable material should be performed by a scientist that has been trained in energy dispersive x-ray fluorescence spectroscopy and its associated data processing system. The training should be performed by a scientist with an advance degree in the physical sciences with a minimum of 5 years experience in x-ray spectroscopy.

## 2. Applicable Documents

### 2.1 ASTM Documents

- D4096 Application of High Volume Sample Method For Collection and Mass Determination of Airborne Particulate Matter.
- D1356 Definition of Terms Related to Atmospheric Sampling and Analysis.
- D1357 Practice For Planning the Sampling of the Ambient Atmosphere.

### 2.2 U.S. Government Documents

- U.S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I: A Field Guide for Environmental Quality Assurance*, EPA-600/R-94/038a.
- U.S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Ambient Air Specific Methods (Interim Edition)*, EPA-600/R-94/038b.
- "Reference Method for the Determination of Particulate Matter in the Atmosphere," *Code of Federal Regulations*, 40 *CFR* 50, Appendix B.
- "Reference Method for the Determination of Particulate Matter in the Atmosphere ($PM_{10}$ Method)," *Code of Federal Regulations*, 40 *CFR* 50, Appendix J.
- "1978 Reference Method for the Determination of Lead in Suspended Particulate Matter Collected From Ambient Air." *Federal Register* 43 (194):46262-3.
- *Test Methods for Evaluating Solid Waste, Method 9022*, EPA Laboratory Manual, Vol. 1-A, SW-846.

### 2.3 Other Documents

- Kevex XRF TOOLBOX II Reference Manual
- Kevex 771-EDX Spectrometer User's Guide and Tutorial

## 3. Summary of Method

*[Note: This method was developed using the Kevex spectrometer. EPA has experience in the use of the Kevex spectrometer associated with various field monitoring programs involving analysis of filterable particulate matter for metals over the last two decades. The use of other manufacturers of x-ray spectrometers should work as well as long as the quality assurance and quality control specifications identified in Sections 12 through 14 of Method 10-3.3 are met. However, modifications to Compendium Method IO-3.3 procedures may be necessary if another commercial x-ray spectrometer is used.]*

The method described is x-ray fluorescence applied to $PM_{10}$, fine ( < 2.5 µm) and coarse (2.5-10 µm) aerosols particles captured on membrane filters for research purposes in source apportionment. The samplers which collect these particles are designed to separate particles on their inertial flow characteristics producing size ranges which simplify x-ray analysis. The instrument is a commercially available Kevex EDX-771 energy dispersive x-ray spectrometer which utilizes secondary excitation from selectable targets or fluorescers and is calibrated with thin metal foils and salts for 44 chemical elements. Spectra are acquired by menu-driven procedures and stored for off-line processing. Spectral deconvolution is accomplished by a least squares algorithm which fits stored pure element library spectra and background to the sample spectrum under analysis. X-ray attenuation corrections are tailored to the fine particle layer and the discrete coarse particle fraction. Spectral interferences are corrected by a subtractive coefficient determined during calibration. The detection limits are determined by propagation of errors in which the magnitude of error from all measured quantities is calculated or estimated as appropriate. Data are reported in $ng/m^3$ for all samples. Comprehensive quality control measures are taken to provide data on a broad range of parameters, excitation conditions and elements.

## 4. Significance

**4.1** The area of toxic air pollutants has been the subject of interest and concern for many years. Recently the use of receptor models has resolved the elemental composition of atmospheric aerosol into components related to emission sources. The assessment of human health impacts resulting in major decisions on control actions by federal, state and local governments are based on these data.

**4.2** Inhalable ambient air particulate matter ( < 10 µm) can be collected on Teflon® filters by sampling with a dichotomous sampler and analyzed for specific metals by X-ray fluorescence. The dichotomous sampler collects particles in two size ranges - fine ( < 2.5 µm) and coarse (2.5-10 µm). The trace element concentrations of each fraction are determined using the nondestructive energy dispersive X-ray fluorescence spectrometer.

**4.3** The detectability and sensitivity of specific elements may vary from instrument to instrument depending upon X-ray generator frequency, multichannel analyzer sensitivity, sample interferences, etc.

## 5. Definitions

*[Note: Definitions used in this document are consistent with ASTM Methods. All pertinent abbreviations and symbols are defined within this document at point of use.]*

**5.1 Accuracy**. The agreement between an experimentally determined value and the accepted reference value.

**5.2 Attenuation**. Reduction of amplitude or change in wave form due to energy dissipation or distance with time.

**5.3 Calibration**. The process of comparing a standard or instrument with one of greater accuracy (smaller uncertainty) for the purpose of obtaining quantitative estimates of the actual values of the standard being calibrated, the deviation of the actual value from a nominal value, or the difference between the value indicated by an instrument and the actual value.

**5.4 10 µm Dichotomous Sampler**. An inertial sizing device that collects suspended inhalable particles ( < 10 µm) and separates them into coarse (2.5-10 µm) and fine ( < 2.5 µm) particle-size fractions.

**5.5 Emissions**. The total of substances discharged into the air from a stack, vent, or other discrete source.

**5.6 Filter**. A porous medium for collecting particulate matter.

**5.7 Fluorescent X-Rays (Fluorescent Analysis)**. Characteristic X-rays excited by radiation of wavelength shorter than the corresponding absorption edge.

**5.8 Inhalable Particles**. Particles with aerodynamic diameters of < 10 µm which are capable of being inhaled into the human lung.

**5.9 Interference**. An undesired positive or negative output caused by a substance other than the one being measured.

**5.10 Precision**. The degree of mutual agreement between individual measurements, namely repeatability and reproducibility.

**5.11 Standard**. A concept that has been established by authority, custom, or agreement to serve as a model or rule in the measurement of quantity or the establishment of a practice or procedure.

**5.12 Traceability to NIST**. A documented procedure by which a standard is related to a more reliable standard verified by the National Institute of Standards and Technology (NIST).

**5.13 Uncertainty**. An allowance assigned to a measured value to take into account two major components of error: (1) the systematic error, and (2) the random error attributed to the imprecision of the measurement process.

**5.14 Chi-square**. A statistic which is a function of the sum of squares of the differences of the fitted and measured spectrum.

**5.15 Fluorescer**. A secondary target excited by the x-ray source and in turn excites the sample.

**5.16 FWHM**. Full width at half maximum, a measure of spectral resolution.

**5.17 NIST**. National Institute of Standards and Technology.

**5.18 Shape**. The actual shape of a background corrected pulse height spectrum for an element.

**5.19 SRMs**. Standard reference materials.

**5.20 Teflo®**. Trade name of a Teflon filter.

**5.21 Unknown**. A sample submitted for analysis whose elemental concentration is not known.

**5.22 XRF**. X-ray fluorescence.

## 6. Description of Spectrometer

The x-ray analyzer is a Kevex EDX-771 energy dispersive spectrometer with a 200 watt rhodium target tube as an excitation source. The machine has multiple modes of excitation including direct, filtered direct, and secondary which utilizes up to 7 targets or fluorescers. To minimize radiation damage to delicate aerosol samples only the secondary mode is used. Table 1 provides a listing of the fluorescers and the elements which they excite associated with energy dispersive spectrometers. Analysis atmospheres are selectable with choices of helium, vacuum or air; helium is used for all targets except Gd where air is employed because it gives a lower background. The detector is cryogenically cooled lithium-drifted silicon with a 5 µm Be window and a resolution of 158 eV at Fe $K_{\alpha}$ and comes with two manually changeable collimators. A 16 position rotating wheel accommodates the samples and provides sample changing.

The machine is operated by procedure files (or programs) written in Kevex's proprietary Job Control Language (JCL) which runs in a Windows 3.1 environment and provides setting of the analytical conditions and data acquisition. Using the JCL language, procedures have been written in-house to perform all the

functions necessary to acquire spectra and to assign to them file names in a structured manner to facilitate future spectral processing. These procedures are invoked in menu form.

## 7. Caveats

**7.1** The type of samplers mentioned in Section 1.7 must be operated in accordance with Inorganic Compendium Method IO-2.2 Sampling for Suspended Particulate Matter in Ambient Air Using a Dichotomous Sampler, or severe errors in x-ray analysis may occur. For example, errors in flow rate will not only give erroneous volumes but will cause a more serious condition of altering the cut points upon which the coarse particle x-ray attenuations are based. If samples are intended for x-ray analysis then the sampling protocol must conform to the constraints inherent within this method. Furthermore, the type of filter on which the sample is collected is very important. In general, thin membrane filters (Teflo® and Nuclepore®) are required so that the background is low and penetration of particles into the matrix of the filter is small. Thick depth filters such as quartz or glass fiber not only have high background but also allow particles to penetrate into the matrix of the filter - a condition which the spectral processing program cannot accommodate.

**7.2** Some internal contaminations consisting of Sn, Ni, Cu and Fe are present which sometimes appear in blanks. Routine analysis of blanks with samples will give the magnitude of the correction necessary to compensate for this.

**7.3** In general the elements analyzed by the Gd fluorescer have higher detection limits than the other fluorescers (see Table 2). The reason for this is due to limitations in the upper voltage limit of the x-ray tube power supply and the use of rhodium instead of a heavier element such as tungsten as a target material for the x-ray tube. As a secondary consequence of this, there are also higher detection limits for many of the elements below chromium because they overlap the elements analyzed by Gd.

**7.4** An inherent problem with a helium atmosphere is the diffusion of He through the detector window causing detector degradation and necessitating replacement. A lifetime of 3 to 4 years is expected.

**7.5** Due to an x-ray leak around the anode area of the x-ray tube the head must be shielded with additional lead cladding to prevent unwanted excitation of internal parts. This leak posed no threat to personnel but caused high background when operating at the maximum voltage. The additional shielding proved very effective at improving detection limits.

**7.6** Experience with wavelength dispersive spectrometers (WDXRF) has shown good agreement with energy dispersive instruments (EDXRF) over a broad range of elements. In spite of this agreement and the simpler spectral processing requirements of wavelength machines the preference remains with energy dispersive equipment for a variety of reasons. The very low power tubes in EDXRF machines leaves the sample intact and unaffected whereas in WDXRF the high power excitation embrittles the filter itself after 15 - 30 min exposure raising the possibility of altering particle morphology. This is a concern if electron microscopy is considered. Also, the vacuum environment, necessary for WDXRF, causes loss of some volatile materials.

## 8. Sample Preparation

**8.1** Sample preparation begins with the correct operation of the samplers employed. Inorganic Compendium Method IO-2.2, Sampling for Suspended Particulate Matter in Ambient Air Using a Dichotomous Sampler, covering the option of the samplers in the field and subsequent collection of ambient air particles on 37-mm Teflon® filter for XRF analysis. One of the greatest advantages of analyzing aerosols by XRF is that the sample can, in theory, be collected in a manner most advantageous to XRF by sampling for a duration that produces an ideal mass loading on the filter. An approximate maximum target mass is about 100 $\mu g/cm^2$ although much less is often collected in many environments.

**8.2** The types of filters used for aerosol sampling are 37-mm or 47-mm Teflo® with a pore size of 2 microns and, if electron microscopy is planned for the coarse fraction, then a 0.6 micron pore size Nuclepore® filter is used. The sample should be collected on the side of the Teflo® filter with the supporting ring to maintain the proper distance between the sample and detector during analysis. A properly collected sample will be a uniform deposit over the entire collection area of at least 25-mm in diameter. Samples which are not uniformly deposited over the whole collection area are not quantitatively analyzable.

**8.3** All filter samples received for analysis are removed with tweezers from their container and are checked for any invalidating conditions such as holes, tears, or a non-uniform deposit which would prevent quantitative analysis. If such a condition is found the sample is noted as invalid on the XRF data entry form; data from such samples are not reported. Teflo® filters are easily handled because of the supporting ring, however, Nuclepore® filters must have a supporting ring applied to them (after gravimetric assay) to help maintain their flatness and to securely hold them in the frame. The sample is then placed in a custom-designed commercially available two-part sample frame which snaps together holding the filter securely in place.

## 9. Spectral Acquisition and Processing

**9.1** Spectra are acquired in sets of 15 samples each. Up to 7 spectra are acquired for each sample depending on how many secondary excitation targets are selected. Utilizing all seven fluorescers requires approximately 4 hours machine time for 44 elements analyzed plus atmospheric argon.

**9.2** Elemental intensities are determined by spectral deconvolution with a least squares algorithm which utilizes experimentally determined elemental shape functions instead of the mathematical Gaussian function. This approach has been successfully implemented for many years on an earlier machine and is described in Section 15, Citation 10. Since the spectral shape is not a pure Gaussian the experimental shapes are a more realistic representation of a spectrum. In addition to this library of elemental shape spectra there is also a background shape spectrum for each of the types of filters. It is assumed that the background on an unknown sample is due to the filter and not to the sample. (This is one of the reasons for avoiding heavily loaded filters.) The least squares algorithm synthesizes the spectrum of the sample under analysis by taking a linear combination of all the elemental shapes spectra and the background shape spectrum. The coefficients on the linear combination of elemental shapes and background spectra are scaling factors determined by minimizing chi-square thus producing the best fit possible by least square minimization. Values of the chi-square statistic are calculated for each sample and fluorescer to give an indication of the quality of the fit.

**9.3** X-ray attenuation corrections are performed as described in Section 15, Citation 10 and are briefly described here. The mass absorption coefficients for the layer of fine particles is based on a typical composition of ambient aerosol particles so the actual x-ray attenuations on a given sample are simply a function of the mass loading. Coarse particle attenuations are more complex in that they are based on x-ray

attenuation by spherical particles with compositions of common crustal minerals with various size distributions. An average attenuation and uncertainty for each coarse particle element is based on this broad range of crustal minerals and is therefore a one-time calculation giving an attenuation factor useable for all subsequent coarse (2.5-10 µm) particle analyses. This treatment assumes low coarse particle loading so that the particles do not shadow one another - yet another reason for assuring that the sample mass loading is not too high. Attenuation corrections on $PM_{10}$ particles are deduced from elemental concentration data from samples taken with collocated $PM_{10}$ and dichotomous samplers.

**9.4** The need for interference corrections arises from overlaps that are not deconvoluted by the least squares algorithm. This can best be illustrated by an example: Barium and titanium are analyzed by the gadolinium and iron fluorescers, respectively. The barium L x-rays overlap with the K x-rays of titanium and require an interference correction because the elements analyzed by gadolinium do not include titanium. The interference correction technique is described by Gilfrich in Section 15, Citation 29. The interference coefficient, determined during calibration, represents the fraction of the concentration of an affecting element (barium in the present example) which must be subtracted from the concentration of the affected element concentration (titanium) to compensate for the interference.

**9.5** When samples are collected by the dichotomous or other samplers using virtual impaction, an additional correction must be employed because these type of samplers do not perfectly separate the fine and coarse particles. Due to virtual impaction requirements, about 10% of the fine particle mass is deposited on the coarse filter. Therefore, the attenuation corrections used for the particles on the coarse filter "over-correct" the attenuation because of these residual fines on the coarse filter. These effects are compensated for by the flow fraction correction.

## 10. Data Reporting

*[Note: In other Inorganic Compendium methods, the authors have provided detailed examples of calculations involving final metal concentration (in terms of µg/m$^3$) from filterable materials. However, due to the nature of overlapping spectra which is characteristic of energy dispersive spectormeters, calculations are required to be performed by computer due to the complexity of the deconvolution of the recorded spectra which uses least square algorithm involving experimentally determined elemental shape functions instead of the mathematical Gaussian function. To perform by hand would require second order calculus and considerable time and manpower. Thus, the application of a computer is mandatory to determine elemental intensities and the elemental concentrations by a polynomial fit using a model based on the fundamentals of x-ray physics process (see Section 11 for further explanation).]*

The two most important data output files are an ASCII file which contains a recapitulation of the field data and the final sample concentrations in ng/m$^3$ and a Lotus file with only the sample data. An example printout of a fine/coarse sample pair is shown in Table 3.

The uncertainty reported with each concentration is a 1F (68% confidence level) uncertainty and is determined by propagating the errors given in Section 12. Elements with concentrations below 3 times the uncertainty are flagged with an asterisk (*) on the printed record. If the true elemental concentration is zero then the fitting procedure implies that negative and positive results are equally probable. Therefore, negative numbers may be reported.

## 11. Calibration

**11.1** Calibration is performed only when a change in fluorescers or x-ray tubes or detector is made or a serious malfunction occurs requiring significant repairs. Calibration establishes the elemental sensitivity factors and the magnitude of the interference or overlap coefficients. It takes approximately 2 weeks to complete a calibration.

**11.2** Thin film standards are used for calibration because they most closely resemble the layer of particles on a filter. There are two types of calibration standards in use. One type consists of thin films deposited on Nuclepore substrates (Micromatter Co., Eastsound, WA). These standards are available for almost all the elements analyzed ranging in atomic number from 11 (Na) to 82 (Pb) with deposit masses gravimetrically determined to ± 5%. Another type consists of polymer films that contain known amounts of two elements in the form of organo-metallic compounds dissolved in a polymer and are not commercially available but their preparation is described in Section 15, Citation 9. These standards have been prepared for elements with atomic numbers above 21 (titanium and heavier). The same set of standards is used every time the spectrometer is calibrated. The standards are sufficiently durable to last many years, however occasionally one must be replaced due to accidents in handling. Approximately 200 calibration standards for 44 elements are in use (see Table 4.) and the acquisition of their spectra requires several days.

**11.3** The background files which are used for background fitting are created at calibration time. Thirty clean Teflo® and Nuclepore® blanks are kept sealed in a plastic bag and are used exclusively for background measurement. After acquiring spectra for all 7 fluorescers the spectra are added together to produce a single spectrum for each fluorescer. Options are available to omit a spectrum from the sum if one shows a contamination. It is these summed spectra that are fitted to the background during spectral processing.

**11.4** The shapes standards are thin film standards consisting of ultra pure elemental materials for the purpose of determining the physical shape of the pulse height spectrum. For this purpose it is not necessary for the concentration of the standard to be known - only that it be pure. A slight contaminant in the region of interest in a shape standard can have serious effect on the ability of the least squares fitting algorithm to fit the shapes to the unknown. For this reason the Se and elemental As standards, whose compounds are volatile, are kept in separate plastic bags in a freezer to prevent contamination of other standards; the Au standard, which will slowly amalgamate with atmospheric Hg, is kept in a desiccator. The shape standards are acquired for sufficiently long times to provide a large number of counts in the peaks of interest. It is these elemental shapes spectra that are fitted to the peaks in an unknown sample during spectral processing.

**11.5** The spectra from the calibration standards are deconvoluted to get elemental intensities as described in Section 9.2. Using these intensities and the elemental concentration in the standards the sensitivities are determined by a polynomial fit using a model based on the fundamentals of the x-ray physics process as well as measurements on the calibration standards. This approach allows the calculation of sensitivities for elements for which there are poor or no standards such as volatile ones like Se and elemental As well as improving on elements with good standards.

**11.6** The overlap coefficients are determined during calibration and represent the extent of interference that exists between overlapping spectral peaks. During calibration an affecting element (barium, to continue with the example of Section 9.4) is measured both at the analyte line peak for barium and at the titanium peak. The coefficient is expressed as the ratio of the concentration of the affected element (titanium) to the

concentration of the affecting element (barium). All elements requiring overlap coefficient determination are calculated in this manner.

## 12. Detection Limits

The detection limits are determined by propagation of errors. The sources of random error which are considered are: calibration uncertainty (± 5%); long term system stability (± 5%); peak and background counting statistics; uncertainty in attenuation corrections; uncertainty in overlap corrections; uncertainty in flow rate; and uncertainty in coarse fraction due to flow fraction correction (paired samples only). Table 2 outlines typical 1F (68% confidence level) detection limits on a Teflo® blank for fine particles and a Nuclepore® blank for coarse (2.5 µm-10 µm) particles. These detection limits are defined in terms of the uncertainty in the blank. This ignores the effect of other elements which generally is small except for the light elements (potassium and lower) where overlapping spectral lines will increase the detection limit.

*[Note: The difference in the detection limits between the two filters in Table 2 is due more to the difference in sensitivity to fine and coarse particles and less to the difference in filter material.]*

Higher confidence levels may be chosen for the detection limits by multiplying the 1F limits by 2 for a 2F (or 95% level) or by 3 for 3F (or 99.7% level). To convert the detection limits to more useful units one can use the typical deposit areas for 37-mm and 47-mm diameter filters of 6.5 $cm^2$ and 12.0 $cm^2$ respectively.

## 13. Quality Control

**13.1** A comprehensive quality control program is in effect consisting of many measured parameters covering all measurement conditions and automatically produces control charts for all such measurements. All plotted data are normalized to the mean to give a rapid assessment of relative change.

**13.2** Run-time quality control gives an indication of instrument performance at the time of data acquisition by measurements on stable qualitative standards. The parameters which are measured and their significance are: peak areas (monitors change in sensitivity), background areas (monitors contamination or background changes), centroid (monitors gain and zero adjustment to insure that spectra are assigned the correct channel), and FWHM, (monitors degradation of the detector resolution). These four parameters are measured for elements ranging from sodium to lead and include atmospheric argon. An example of plots of run-time QC data are illustrated in Figures 1 through 4 and Table 5, for the target and tolerance values for the parameters measured.

**13.3** In addition to the run-time quality control procedure the analysis results of Standard Reference Materials SRM1833 and SRM1832 are included in the data reports. These results provide an overall check of the spectral processing program for the elements which are certified in the standards. The sole purpose of the SRMs is to provide a quality control measure; the standards are not used for calibration. Typical results of these SRMs are documented in Tables 6 and 7, and plotted in Figure 5.

**13.4** The run-time quality control procedures serve as an indicator of possible emerging problems by flagging deviations greater than 3 tolerance units as defined for each element in Table 5. Persistently increasing trends are investigated to determine their cause(s) before they impact the results of SRM analyses.

**13.5** The acceptance criteria of results for the elements certified in the SRMs is that the uncertainty intervals for the analytical results and those of the certified values should overlap each other. If any element fails this then the run of unknowns is repeated. Repeated failures indicate the need for recalibration.

**13.6** A value for chi-square is calculated and reported with the data to indicate the quality of the fit. Chi-square values that are much larger than 1.0 indicate a problem in the fitting procedure. Changes in detector resolution or gain in the amplifier produce large values for chi-square; however such changes would be detected by the run-time quality control procedure. Also, large chi-square values can accompany results for heavily loaded filters even though the relative errors are typical. In addition, elements analyzed by the titanium and the iron fluorescers may experience large chi-square values due to interferences from overlapping elements. Chi-square is a more useful measure of goodness-of-fit for the other fluorescers for this reason.

**13.7** To acquire more information about fitting problems the fitted spectra can be viewed on the screen or a hard copy printed. Such plots can be compared to the unknown spectra, background spectra, or to the library shape standards to help elucidate the suspected problem. Various statistics such as the correlation coefficient can be calculated on the fitted and measured spectra as a additional measure of the goodness-of-fit. Fitted spectrum superposed on its measured spectrum along with the associated statistics is illustrated in Figure 6.

## 14. Precision and Accuracy

Precision varies with the element and concentration. At high concentrations (greater than 1 µg/cm²) a precision of 7.1% can be expected for elements analyzed by one fluorescer and 5.0% can be expected for those analyzed by two. Refer to Table 1 for a listing of the elements and the fluorescers which analyze them. Based upon the analysis of NIST SRMs the accuracy is ± 10%.

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TABLE 1. EXAMPLE OF FLUORESCER USAGE

| | Fluorescer | | | | | | |
|---|---|---|---|---|---|---|---|
| Element | Al | Ti | Fe | Ge | Ag | Zr | Gd |
| Na | x | | | | | | |
| Mg | x | | | | | | |
| Al | x | | | | | | |
| Si | x | | | | | | |
| P | x | x | | | | | |
| S | x | x | | | | | |
| Cl | x | x | | | | | |
| Ar | x | x | | | | | |
| K | x | x | | | | | |
| Ca | x | x | | | | | |
| Sc | x | x | | | | | |
| Ti | | | x | x | | | |
| V | | | x | x | | | |
| Cr | | | x | x | | | |
| Mn | | | | x | | x | |
| Fe | | | | x | | x | |
| Co | | | | x | | x | |
| Ni | | | | x | | x | |
| Cu | | | | x | | x | |
| Zn | | | | | | x | |
| Ga | | | | | | x | |
| Ge | | | | | | x | |
| As | | | | | | x | |
| Se | | | | | | x | |
| Br | | | | | | x | |
| Rb | | | | | x | x | |
| Sr | | | | | x | | x |
| Y | | | | | x | | |
| Zr | | | | | x | | x |
| Mo | | | | | x | | x |
| Rh | | | | | | | x |
| Pd | | | | | | | x |
| Ag | | | | | | | x |
| Cd | | | | | | | x |
| Sn | | | | | | | x |
| Sb | | | | | | | x |
| Te | | | | | | | x |
| I | | | | | | | x |
| Cs | | | | | | | x |
| Ba | | | | | | | x |
| La | | | | | | | x |
| W | | | | | x | x | |
| Au | | | | | x | x | |
| Hg | | | | | x | x | |
| Pb | | | | | x | x | |

*[Note: The 'x' marks the fluorescers that analyze each element.]*

TABLE 2. METHOD DETECTION LIMITS (MDL) FOR TEFLO® AND NUCLEPORE® BLANK FILTERS (1F)

| Teflo® - fine element Method Detection Limits (MDL) | | | Nuclepore® - coarse element Method Detection Limits (MDL) | | |
|---|---|---|---|---|---|
| | ng/cm$^2$ | ng/m$^3$[1] | | ng/cm$^2$ | ng/m$^3$[2] |
| Na | 5.3 | 1.59 | Na | 17.4 | 47.12 |
| Mg | 3.2 | 0.96 | Mg | 7.9 | 21.34 |
| Al | 17.6 | 5.29 | Al | 46.7 | 126.48 |
| Si | 8.0 | 2.41 | Si | 21.2 | 50.40 |
| P | 2.6 | 0.78 | P | 4.1 | 11.10 |
| S | 2.6 | 0.78 | S | 6.9 | 16.56 |
| Cl | 4.8 | 1.44 | Cl | 5.6 | 13.44 |
| K | 6.3 | 1.89 | K | 5.6 | 15.17 |
| Ca | 9.0 | 2.71 | Ca | 8.7 | 23.56 |
| Sc | 1.5 | 0.45 | Sc | 1.3 | 3.52 |
| Ti | 16.9 | 5.08 | Ti | 18.7 | 42.52 |
| V | 5.3 | 1.59 | V | 5.5 | 14.89 |
| Cr | 3.0 | 0.90 | Cr | 3.0 | 8.12 |
| Mn | .8 | 0.24 | Mn | .8 | 2.17 |
| Fe | .7 | 0.21 | Fe | 1.0 | 2.71 |
| Co | .4 | 0.12 | Co | .4 | 1.08 |
| Ni | .6 | 0.18 | Ni | .7 | 1.89 |
| Cu | .7 | 0.21 | Cu | .8 | 2.17 |
| Zn | 1.0 | 0.30 | Zn | 1.1 | 2.98 |
| Ga | 1.6 | 0.48 | Ga | 1.5 | 4.06 |
| Ge | 1.1 | 0.33 | Ge | 1.0 | 2.71 |
| As | .8 | 0.24 | As | .9 | 2.44 |
| Se | .7 | 0.21 | Se | .6 | 1.62 |
| Br | .6 | 0.18 | Br | .7 | 1.89 |
| Rb | .7 | 0.21 | Rb | .7 | 1.89 |
| Sr | 1.1 | 0.33 | Sr | .9 | 2.44 |
| Y | 1.2 | 0.36 | Y | 1.1 | 2.98 |
| Zr | 1.2 | 0.36 | Zr | 1.1 | 2.98 |
| Mo | 1.6 | 0.48 | Mo | 1.5 | 4.06 |
| Rh | 25.9 | 7.79 | Rh | 26.5 | 71.70 |
| Pd | 22.9 | 6.89 | Pd | 18.7 | 50.65 |
| Ag | 20.2 | 6.02 | Ag | 20.3 | 54.98 |
| Cd | 22.0 | 6.62 | Cd | 19.2 | 52.00 |
| Sn | 30.5 | 9.18 | Sn | 31.5 | 85.31 |
| Sb | 31.4 | 9.45 | Sb | 26.7 | 72.31 |
| Te | 26.3 | 7.91 | Te | 27.6 | 66.62 |
| I | 35.5 | 10.68 | I | 34.4 | 93.17 |
| Cs | 48.9 | 14.62 | Cs | 50.9 | 137.85 |
| Ba | 51.8 | 15.59 | Ba | 58.3 | 157.89 |
| La | 70.6 | 2.12 | La | 68.9 | 186.60 |
| W | 3.4 | 10.23 | W | 3.3 | 8.93 |
| Au | 1.7 | 0.51 | Au | 1.5 | 4.06 |
| Hg | 1.5 | 0.45 | Hg | 1.4 | 3.79 |
| Pb | 1.5 | 0.45 | Pb | 1.5 | 4.06 |

[1]Based upon dichotomous sampling for 24-hrs. using a 37-mm Teflo® filter at a sampling rate of 0.9 m$^3$/hr.
[2]Based upon dichotomous sampling for 24-hrs using a 37-mm Nuclepore® filter at a sampling rate of 0.1 m$^3$/hr.

TABLE 3. DATA REPORT FORMAT FOR A FINE/COARSE PAIRED SAMPLE

KEVEX SUMMARY: ADOBE FLATS URBAN PARTICULATE STUDY

```
SITE           =    ADB
DURATION (MIN) =    714.0       SAMPLE DATE  =  3/20/92 AND 1900 HOURS
FLOW FRAC      = .0869          FLOW (L/MIN) =   37.105 +-  .500
XRF ID         = 999906         XRF ID       = 999956
SAMPLE ID      = T0033          SAMPLE ID    = NU0033
```

| FINE, NG/M³ | | | | COARSE, NG/M³ | | | |
|---|---|---|---|---|---|---|---|
| MASS | 77912. | +- | 1962. | MASS | 11347. | +- | 812. |
| *NA | 211.9 | +- | 71.4 | *NA | 53.3 | +- | 27.1 |
| MG | 564.6 | +- | 89.4 | MG | 443.9 | +- | 40.8 |
| *AL | 162.2 | +- | 74.1 | AL | 539.9 | +- | 173.8 |
| SI | 213.4 | +- | 40.4 | SI | 909.5 | +- | 232.7 |
| * P | 12.1 | +- | 18.5 | * P | -5.5 | +- | 11.3 |
| S | 2653.4 | +- | 183.7 | S | 285.7 | +- | 84.9 |
| CL | 1164.4 | +- | 79.3 | *CL | 34.8 | +- | 24.6 |
| K | 193.6 | +- | 13.8 | K | 63.5 | +- | 8.9 |
| CA | 43.4 | +- | 5.6 | CA | 181.7 | +- | 13.9 |
| *SC | 3.6 | +- | 4.1 | *SC | -1.3 | +- | 2.2 |
| *TI | 17.6 | +- | 6.6 | TI | 54.7 | +- | 9.6 |
| * V | 4.6 | +- | 2.3 | * V | 3.2 | +- | 1.7 |
| *CR | 2.0 | +- | 1.0 | CR | 9.8 | +- | 1.6 |
| MN | 10.0 | +- | 1.4 | MN | 10.1 | +- | 1.3 |
| FE | 243.7 | +- | 21.9 | FE | 783.5 | +- | 78.2 |
| *CO | 2.8 | +- | 1.8 | *CO | 4.8 | +- | 1.7 |
| NI | 3.8 | +- | 1.2 | *NI | .3 | +- | .6 |
| CU | 14.3 | +- | 1.9 | CU | 8.8 | +- | 1.3 |
| ZN | 167.5 | +- | 14.9 | ZN | 27.6 | +- | 4.9 |
| *GA | 2.4 | +- | 1.0 | *GA | -.0 | +- | .4 |
| *GE | 3.3 | +- | 1.3 | *GE | .0 | +- | .6 |
| AS | 24.7 | +- | 3.6 | *AS | 1.8 | +- | 1.2 |
| SE | 4.7 | +- | .8 | *SE | .7 | +- | .4 |
| BR | 29.0 | +- | 2.8 | BR | 7.9 | +- | 1.1 |
| *RB | 1.7 | +- | .8 | *RB | 1.0 | +- | .4 |
| SR | 2.9 | +- | .9 | SR | 2.2 | +- | .5 |
| * Y | 12.4 | +- | 6.1 | * Y | 3.9 | +- | 2.9 |
| *ZR | 2.9 | +- | 4.8 | *ZR | 4.3 | +- | 2.6 |
| *MO | 7.3 | +- | 4.8 | *MO | -3.2 | +- | 2.2 |
| *RH | .0 | +- | 3.2 | *RH | -1.2 | +- | 1.6 |
| *PD | -3.6 | +- | 3.1 | *PD | -1.0 | +- | 1.7 |
| *AG | -6.4 | +- | 3.4 | *AG | 1.2 | +- | 1.9 |
| *CD | 8.5 | +- | 4.5 | *CD | -.7 | +- | 2.2 |
| SN | 54.3 | +- | 9.4 | *SN | 2.3 | +- | 3.9 |
| *SB | -1.6 | +- | 6.4 | *SB | -.6 | +- | 3.3 |
| *TE | 2.5 | +- | 7.5 | *TE | -7.2 | +- | 3.8 |
| * I | 25.0 | +- | 9.6 | * I | 2.4 | +- | 4.7 |
| *CS | -4.0 | +- | 11.2 | *CS | 12.4 | +- | 5.9 |
| *BA | -7.7 | +- | 13.7 | BA | 25.1 | +- | 7.4 |
| *LA | -4.8 | +- | 34.5 | *LA | 22.6 | +- | 17.9 |
| * W | -1.1 | +- | 2.6 | * W | 1.5 | +- | 1.3 |

```
        *AU       -.9 +-     1.8       *AU        .2 +-      .9
        *HG       -.4 +-     1.9       *HG       1.5 +-     1.0
         PB     221.6 +-    19.7        PB      46.0 +-     6.2
* INDICATES THAT THE CONCENTRATION IS BELOW 3 TIMES THE UNCERTAINTY.
  XRF DATE= 04/29/1992  16:35 RBK   (F):  04/29/1992  20:35 RBK   (C)
  SPECTRAL ANALYSIS DATE=  5/20/1992
```

TABLE 4. CALIBRATION STANDARDS AND CONCENTRATIONS

| Standard ID | Element | µg/cm² | Standard ID | Element | µg/cm² | Standard ID | Element | µg/cm² | Standard ID | Element | µg/cm² |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CaF237 | F | 18.00 | CuS1124 | S | 31.90 | Cr 85 | Cr | 85.00 | RbNO311 | Rb | 69.00 |
| CaF2 29 | F | 14.10 | CuS58.6 | S | 16.50 | Cr 84 | Cr | 84.00 | RbNO322 | Rb | 12.90 |
| CaF2 90 | F | 43.80 | CuS57.6 | S | 13.90 | Cr 75 | Cr | 75.00 | RbNO3 a | Rb | 24.90 |
| CaF2 91 | F | 44.30 | CuS58.2 | S | 14.00 | Cr 74 | Cr | 74.00 | RbNO3 b | Rb | 24.90 |
| CaF2102 | F | 49.60 | NaCl 57 | Cl | 34.60 | Cr 122 | Cr | 122.00 | RbNO3 c | Rb | 24.90 |
| CaF2 66 | F | 32.10 | NaCl 87 | Cl | 52.80 | CrCu32a | Cr | 9.19 | SrF2 57 | Sr | 39.80 |
| CaF2 28 | F | 13.60 | NaCl446 | Cl | 27.10 | CrCu26g | Cr | 8.14 | SbSr29z | Sr | 4.97 |
| CaF2 33 | F | 16.10 | NaCl715 | Cl | 43.40 | MnZn24b | Mn | 8.57 | SrF2 50 | Sr | 34.90 |
| CaF2 39 | F | 19.00 | NaCl497 | Cl | 30.20 | Mn 57 | Mn | 57.00 | SbSr31y | Sr | 5.14 |
| CaF2 54 | F | 26.30 | NaCl501 | Cl | 30.40 | Mn 183 | Mn | 183.00 | SrF2137 | Sr | 95.60 |
| CaF2291 | F | 14.10 | NaCl 51 | Cl | 31.00 | MnZn27x | Mn | 9.10 | SrF2184 | Sr | 12.80 |
| CaF2 30 | F | 14.60 | NaCl512 | Cl | 31.10 | Mn 43 | Mn | 43.00 | SrF2 92 | Sr | 64.20 |
| CaF2 52 | F | 25.30 | NaCl519 | Cl | 31.50 | Mn 46.9 | Mn | 46.90 | SrF2103 | Sr | 71.80 |
| CaF2 48 | F | 23.40 | KCl 45 | Cl | 21.40 | Mn 44.5 | Mn | 44.50 | YF3 46 | Y | 28.00 |
| CaF2 45 | F | 21.90 | KCl53.3 | Cl | 25.40 | Mn 46.6 | Mn | 46.60 | ZrCd24c | Zr | 9.85 |
| CaF2 36 | F | 17.50 | KCl 70 | Cl | 33.30 | Mn 43.7 | Mn | 43.70 | ZrCd20w | Zr | 10.77 |
| CaF2134 | F | 65.20 | KCl 49 | Cl | 23.30 | Mn 69 | Mn | 69.00 | MoO3145 | Mo | 96.70 |
| CaF2110 | F | 53.50 | KCl48.7 | Cl | 23.20 | FePb37y | Fe | 7.72 | MoO3106 | Mo | 70.70 |
| NaCl 57 | Na | 22.40 | KCl47.9 | Cl | 22.80 | Fe 107 | Fe | 107.00 | MoO3110 | Mo | 73.30 |
| NaCl 87 | Na | 34.20 | KCl 48 | Cl | 22.80 | Fe 127 | Fe | 127.00 | MoO3 59 | Mo | 39.30 |
| NaCl446 | Na | 17.60 | KCl47.6 | Cl | 22.60 | Fe 46 | Fe | 46.00 | MoO3 54 | Mo | 36.00 |
| NaCl715 | Na | 28.10 | KCl 45 | K | 23.60 | Fe 88 | Fe | 88.00 | Rh 16 | Rh | 16.00 |
| NaCl497 | Na | 19.60 | KCl53.3 | K | 28.00 | FePb38y | Fe | 7.71 | Pd 33 | Pd | 33.00 |
| NaCl501 | Na | 19.70 | KCl 70 | K | 36.70 | Co 45a | Co | 45.00 | Pd 198 | Pd | 198.00 |
| NaCl 51 | Na | 20.10 | KCl 49 | K | 25.70 | Co 45b | Co | 45.00 | Ag 35 | Ag | 35.00 |
| NaCl512 | Na | 20.10 | KCl48.7 | K | 25.50 | RbCo29c | Co | 7.43 | Ag 132 | Ag | 132.00 |
| NaCl519 | Na | 20.40 | KCl47.9 | K | 25.10 | RbCo25b | Co | 7.65 | Cd 83 | Cd | 83.00 |
| Mg 81 | Mg | 81.00 | KCl 48 | K | 25.20 | Ni 54 | Ni | 54.00 | ZrCd20w | Cd | 9.15 |
| Mg 41 | Mg | 41.00 | KCl47.6 | K | 25.00 | Ni 88 | Ni | 88.00 | ZrCd24c | Cd | 8.38 |
| Mg 41.3 | Mg | 41.30 | CaF2 37 | Ca | 19.00 | NiV 21c | Ni | 5.77 | Cd 77 | Cd | 77.00 |
| Mg 43 | Mg | 43.00 | CaF2 29 | Ca | 14.90 | Ni 101 | Ni | 101.00 | Sn 40 | Sn | 40.00 |
| Mg 43.8 | Mg | 43.80 | CaF2 90 | Ca | 46.20 | Cu 96 | Cu | 96.00 | Sn 185 | Sn | 185.00 |
| Mg 60.2 | Mg | 60.20 | CaF2 91 | Ca | 46.70 | Cu 104 | Cu | 104.00 | Sn 97a | Sn | 97.00 |
| Al 57 | Al | 57.00 | CaF2102 | Ca | 52.40 | Cu 128 | Cu | 128.00 | Sn 97b | Sn | 97.00 |
| Al 37.9 | Al | 37.90 | CaF2 66 | Ca | 33.90 | CrCu26g | Cu | 7.65 | Sn 79 | Sn | 79.00 |
| Al 37.4 | Al | 37.40 | CaF2 28 | Ca | 14.40 | CrCu32a | Cu | 8.63 | Sb 194 | Sb | 194.00 |
| Al 29 | Al | 29.00 | CaF2 33 | Ca | 16.90 | Cu 38 | Cu | 38.00 | Sb 47 | Sb | 47.00 |
| Al 43.2 | Al | 43.20 | CaF2 39 | Ca | 20.00 | Zn 51 | Zn | 51.00 | Sb 147 | Sb | 147.00 |
| Al 62 | Al | 62.00 | CaF2 54 | Ca | 27.20 | Zn 125 | Zn | 125.00 | Sb 42 | Sb | 42.00 |
| Al 75 | Al | 75.00 | CaF2291 | Ca | 14.90 | MnZn27x | Zn | 8.46 | SbSr29z | Sb | 5.01 |
| SiO 46 | Si | 29.30 | CaF2 30 | Ca | 15.40 | MnZn24b | Zn | 7.97 | SbSr31y | Sb | 5.18 |
| SiO 47 | Si | 29.90 | CaF2 52 | Ca | 26.70 | GaP 34 | Ga | 23.50 | Te 53 | Te | 53.00 |
| SiO 51a | Si | 32.50 | CaF2 48 | Ca | 24.60 | GaP 40 | Ga | 27.70 | KI 46 | I | 35.20 |
| SiO 51b | Si | 32.50 | CaF2 45 | Ca | 23.10 | GaP 70 | Ga | 48.50 | CsBr 53 | Cs | 33.10 |
| SiO 56 | Si | 35.70 | CaF2 36 | Ca | 18.50 | GaP 105 | Ga | 72.70 | CsBr 54 | Cs | 33.70 |
| SiO 80 | Si | 51.00 | CaF2134 | Ca | 68.60 | Ge 37 | Ge | 37.00 | CsBr 51 | Cs | 31.90 |
| SiO27.6 | Si | 17.60 | CaF2110 | Ca | 56.50 | TiGe33d | Ge | 6.22 | BaF2108 | Ba | 84.60 |
| SiO46.1 | Si | 29.40 | ScF3 57 | Sc | 25.10 | TiGe29x | Ge | 5.94 | BaF2 48 | Ba | 37.60 |
| SiO72.2 | Si | 46.00 | Ti 39 | Ti | 39.00 | Ge 140 | Ge | 140.00 | BaF2 60 | Ba | 47.00 |
| GaP 34 | P | 10.50 | Ti 95 | Ti | 95.00 | BaAs23y | As | 5.60 | BaF2 57 | Ba | 44.70 |
| GaP 40 | P | 12.30 | TiGe33d | Ti | 2.46 | BaAs36w | As | 5.52 | BaF2143 | Ba | 112.00 |
| GaP 70 | P | 21.50 | TiGe29x | Ti | 2.36 | CsBr 53 | Br | 19.90 | BaF2114 | Ba | 89.40 |
| GaP 105 | P | 32.30 | V 45 | V | 45.00 | CsBr 54 | Br | 20.30 | BaAs23y | Ba | 4.98 |

TABLE 4. (continued)

| Standard ID | Element | µg/cm² | Standard ID | Element | µg/cm² | Standard ID | Element | µg/cm² | Standard ID | Element | µg/cm² |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CuS1052 | S | 30.80 | V 53 | V | 53.00 | CsBr 51 | Br | 19.10 | BaAs36w | Ba | 4.91 |
| CuS 48 | S | 13.00 | NiV 21c | V | 6.64 | RbNO346 | Rb | 26.60 | LaF3157 | La | 111.30 |
| CuS 136 | S | 33.00 | Cr 30 | Cr | 30.00 | RbCo25b | Rb | 7.88 | LaF3 62 | La | 44.00 |
| CuS39.6 | S | 10.20 | Cr 53 | Cr | 53.00 | RbCo29c | Rb | 7.65 | | | |

TABLE 5. TARGET AND TOLERANCE VALUES FOR QC RESULTS

(TARGET VALUES)

FILE: 0:QCBEGTGT FILE: 0:QCENDTGT

| STDEL ID | EL | AREA (cts) | CENTROID (keV) | FWHM (ev) | STD ID | EL | AREA (cts) | CENTROID (keV) | FWHM (ev) |
|---|---|---|---|---|---|---|---|---|---|
| 1833 | Pb | 31112.12 | 10.5449 | 207.4653 | 1832 | Cu | 17548.85 | 8.0411 | 174.1389 |
| 1833 | Zn | 31772.52 | 8.6306 | 179.6835 | 1832 | | 5303.84 | 6.9247 | 167.1478 |
| 1833 | Fe | 313475.41 | 6.3935 | 159.4537 | 1832 | Mn | 86202.33 | 5.8891 | 154.6347 |
| 1833 | Ti | 216978.09 | 4.5037 | 142.4946 | 1832 | Ca | 217562.00 | 3.6847 | 135.3520 |
| 1833 | Si | 69021.60 | 1.7322 | 121.7406 | 1832 | V | 99761.96 | 4.9443 | 146.1904 |
| 1833 | K | 220344.80 | 3.3069 | 132.4137 | 1832 | Al | 16562.45 | 1.4779 | 119.5793 |
| BLKt | Sn | 111.52 | 0.0000 | 0.0000 | 1832 | Si | 67688.42 | 1.7319 | 118.4960 |
| BLKt | Pb | 85.82 | 0.0000 | 0.0000 | 1832 | Na | 10332.21 | 1.0256 | 114.4485 |
| BLKt | Cu | 497.06 | 0.0000 | 0.0000 | BLKn | Ba | 183.14 | 0.0000 | 0.0000 |
| BLKt | Sr | 72.92 | 0.0000 | 0.0000 | BLKn | W | 241.42 | 0.0000 | 0.0000 |
| BLKt | Ni | 648.99 | 0.0000 | 0.0000 | BLKn | Zn | 148.48 | 0.0000 | 0.0000 |
| BLKt | Fe | 459.10 | 0.0000 | 0.0000 | BLKn | Sr | 83.00 | 0.0000 | 0.0000 |
| BLKt | S | 266.76 | 0.0000 | 0.0000 | BLKn | Ni | 654.44 | 0.0000 | 0.0000 |
| BLKt | Al | 396.30 | 0.0000 | 0.0000 | BLKn | Fe | 603.55 | 0.0000 | 0.0000 |
| BLKt | Ar | 747.74 | 0.0000 | 0.0000 | BLKn | S | 3047.53 | 0.0000 | 0.0000 |
| BLKt | Na | 120.85 | 0.0000 | 0.0000 | BLKn | Si | 936.48 | 0.0000 | 0.0000 |
| BaNa | Na | 27711.44 | 1.0278 | 107.2698 | BLKn | Ar | 751.18 | 0.0000 | 0.0000 |
| BaNa | Ba | 7369.12 | 32.0701 | 670.6336 | BLKn | Mg | 3622.12 | 0.0000 | 0.0000 |
| | | | | | BaSr | Sr | 210871.20 | 14.1410 | 227.8625 |
| | | | | | BaSr | Ba | 7464.85 | 32.0692 | 671.0372 |

(TOLERANCE UNITS in %)

FILE: 0:QCBEGTOL FILE: 0:QCENDTOL

| STDEL ID | EL | AREA (cts) | CENTROID (keV) | FWHM (ev) | STD ID | EL | AREA (cts) | CENTROID (keV) | FWHM (ev) |
|---|---|---|---|---|---|---|---|---|---|
| 1833 | Pb | 1.66 | 0.0313 | 0.9901 | 1832 | Cu | 1.66 | 0.0104 | 1.9331 |
| 1833 | Zn | 1.66 | 0.0131 | 1.7328 | 1832 | Co | 1.70 | 0.0308 | 2.4345 |
| 1833 | Fe | 1.66 | 0.0224 | 0.9361 | 1832 | Mn | 1.66 | 0.0198 | 1.3536 |
| 1833 | Ti | 1.66 | 0.0259 | 0.9768 | 1832 | Ca | 1.66 | 0.0253 | 1.1311 |
| 1833 | Si | 1.66 | 0.0616 | 1.4120 | 1832 | V | 1.66 | 0.0243 | 1.1031 |
| 1833 | K | 1.66 | 0.0323 | 0.9235 | 1832 | Al | 2.02 | 0.1173 | 3.3722 |
| BLKt | Sn | 12.98 | 0.0000 | 0.0000 | 1832 | Si | 1.66 | 0.0481 | 0.8888 |
| BLKt | Pb | 8.93 | 0.0000 | 0.0000 | 1832 | Na | 1.78 | 0.1560 | 1.5333 |
| BLKt | Cu | 4.95 | 0.0000 | 0.0000 | BLKn | Ba | 9.92 | 0.0000 | 0.0000 |
| BLKt | Sr | 17.61 | 0.0000 | 0.0000 | BLKn | W | 8.20 | 0.0000 | 0.0000 |
| BLKt | Ni | 3.81 | 0.0000 | 0.0000 | BLKn | Zn | 11.45 | 0.0000 | 0.0000 |
| BLKt | Fe | 7.57 | 0.0000 | 0.0000 | BLKn | Sr | 10.88 | 0.0000 | 0.0000 |
| BLKt | S | 8.71 | 0.0000 | 0.0000 | BLKn | Ni | 6.55 | 0.0000 | 0.0000 |
| BLKt | Al | 7.23 | 0.0000 | 0.0000 | BLKn | Fe | 5.63 | 0.0000 | 0.0000 |
| BLKt | Ar | 17.39 | 0.0000 | 0.0000 | BLKn | S | 2.88 | 0.0000 | 0.0000 |
| BLKt | Na | 16.00 | 0.0000 | 0.0000 | BLKn | Si | 6.75 | 0.0000 | 0.0000 |
| BaNa | N | 1.66 | 0.1103 | 1.2599 | BLKn | Ar | 22.14 | 0.0000 | 0.0000 |
| BaNa | Ba | 2.53 | 0.0979 | 3.9782 | BLKn | Mg | 5.64 | 0.0000 | 0.0000 |
| | | | | | BaSr | Sr | 1.66 | 0.0073 | 0.4538 |
| | | | | | BaSr | Ba | 1.86 | 0.0279 | 2.8094 |

TABLE 6. EXAMPLE PRINTOUT OF SRM 1833

KEVEX SUMMARY: TEFLO® BLANKS LOT #457803 (NEW TUBE)

| | | | |
|---|---|---|---|
| SITE | = | | |
| DURATION (MIN) | = .0 | SAMPLE DATE | = 99/99/99 AND 9999 HOURS |
| FLOW FRAC | = .0000 | FLOW (L/MIN) | = .000 +- .200 |
| XRF ID | = 112141 | | |
| SAMPLE ID | = SRM1833 | | |

| | FINE, NG/CM$^2$ | | | | NIST CERTIFIED VALUES | | |
|---|---|---|---|---|---|---|---|
| MASS | 0. | +- | 398. | MASS | 15447 | | |
| *NA | -801.2 | +- | 326.4 | NA | .0 | +- | .0 |
| MG | 161.3 | +- | 18.2 | MG | .0 | +- | .0 |
| AL | 1027.5 | +- | 102.2 | AL | .0 | +- | .0 |
| SI | 34806.8 | +- | 3023.4 | SI | 33366.0 | +- | 2163.0 |
| P | 79.8 | +- | 19.9 | P | .0 | +- | .0 |
| *S | -28.2 | +- | 782.8 | S | .0 | +- | .0 |
| *CL | -68.6 | +- | 113.8 | CL | .0 | +- | .0 |
| K | 16734.7 | +- | 1018.7 | K | 17147.0 | +- | 1699.0 |
| *CA | -3.9 | +- | 61.4 | CA | .0 | +- | .0 |
| *SC | -17.1 | +- | 5.4 | SC | .0 | +- | .0 |
| TI | 12852.9 | +- | 822.1 | TI | 12821.0 | +- | 1854.0 |
| *V | 46.0 | +- | 52.2 | V | .0 | +- | .0 |
| CR | 108.2 | +- | 12.7 | CR | .0 | +- | .0 |
| MN | 13.8 | +- | 2.9 | MN | .0 | +- | .0 |
| FE | 14332.4 | +- | 872.4 | FE | 14212.0 | +- | 463.0 |
| *CO | -2.6 | +- | 2.9 | CO | .0 | +- | .0 |
| NI | 62.5 | +- | 4.6 | NI | .0 | +- | .0 |
| *CU | 3.8 | +- | 1.5 | CU | .0 | +- | .0 |
| ZN | 3800.9 | +- | 327.7 | ZN | 3862.0 | +- | 309.0 |
| *GA | -30.9 | +- | 7.7 | GA | .0 | +- | .0 |
| *GE | 5.9 | +- | 3.6 | GE | .0 | +- | .0 |
| *AS | 5.7 | +- | 14.6 | AS | .0 | +- | .0 |
| *SE | -2.0 | +- | 2.6 | SE | .0 | +- | .0 |
| *BR | -2.3 | +- | 2.5 | BR | .0 | +- | .0 |
| *RB | .5 | +- | 1.4 | RB | .0 | +- | .0 |
| *SR | -5.0 | +- | 2.9 | SR | .0 | +- | .0 |
| * Y | -2.6 | +- | 7.5 | Y | .0 | +- | .0 |
| *ZR | -7.6 | +- | 3.5 | ZR | .0 | +- | .0 |
| MO | 45.4 | +- | 5.6 | MO | .0 | +- | .0 |
| *RH | 156.7 | +- | 69.5 | RH | .0 | +- | .0 |
| *PD | 79.2 | +- | 67.1 | PD | .0 | +- | .0 |
| *AG | 114.0 | +- | 69.7 | AG | .0 | +- | .0 |

TABLE 6. (continued)

| | FINE, NG/CM$^2$ | | | | NIST CERTIFIED VALUES | | |
|---|---|---|---|---|---|---|---|
| *CD | 24.7 | + - | 66.3 | CD | .0 | + - | .0 |
| *SN | -1496.1 | + - | 188.1 | SN | .0 | + - | .0 |
| *SB | 88.2 | + - | 96.2 | SB | .0 | + - | .0 |
| *TE | 240.8 | + - | 93.8 | TE | .0 | + - | .0 |
| * I | 134.8 | + - | 107.5 | I | .0 | + - | .0 |
| *CS | -209.3 | + - | 106.6 | CS | .0 | + - | .0 |
| *BA | -5098.1 | + - | 517.8 | BA | .0 | + - | .0 |
| *LA | -1416.4 | + - | 202.2 | LA | .0 | + - | .0 |
| W | 59.9 | + - | 17.6 | W | .0 | + - | .0 |
| *AU | 8.7 | + - | 6.8 | AU | .0 | + - | .0 |
| *HG | -30.6 | + - | 5.9 | HG | .0 | + - | .0 |
| PB | 16886.2 | + - | 1028.1 | PB | 16374.0 | + - | 772.0 |

* INDICATES THAT THE CONCENTRATION IS BELOW 3 TIMES THE UNCERTAINTY.
XRF DATE = 28-SEP-93 10:58:37 RBK
SPECTRAL ANALYSIS DATE = 12/14/1993

TABLE 7. EXAMPLE PRINTOUT OF SRM 1832

KEVEX SUMMARY: TEFLO® BLANKS LOT #457803 (NEW TUBE)

| | | | |
|---|---|---|---|
| SITE | = | | |
| DURATION (MIN) | = .0 | SAMPLE DATE | = 99/99/99 AND 9999 HOURS |
| FLOW FRAC | = .0000 | FLOW (L/MIN) | = .000 +- .200 |
| XRF ID | = 112191 | | |
| SAMPLE ID | = SRM1832 | | |

| FINE, NG/CM$^2$ | | | | NIST CERTIFIED VALUES | | | |
|---|---|---|---|---|---|---|---|
| MASS | 0. | +- | 398. | MASS | 16431 | | |
| NA | 11891.5 | +- | 1035.0 | NA | 11173.0 | +- | .0 |
| MG | 92.2 | +- | 13.0 | MG | .0 | +- | .0 |
| AL | 15856.5 | +- | 1373.2 | AL | 14953.0 | +- | 986.0 |
| SI | 34398.8 | +- | 2964.2 | SI | 35491.0 | +- | 1150.0 |
| P | 492.0 | +- | 32.1 | P | .0 | +- | .0 |
| S | 402.1 | +- | 27.3 | S | .0 | +- | .0 |
| CL | 156.8 | +- | 15.9 | CL | .0 | +- | .0 |
| * K | 18.5 | +- | 18.0 | K | .0 | +- | .0 |
| CA | 20011.7 | +- | 1218.2 | CA | 19225.0 | +- | 1315.0 |
| *SC | -21.8 | +- | 5.6 | SC | .0 | +- | .0 |
| *TI | -4.7 | +- | 130.6 | TI | .0 | +- | .0 |
| V | 4593.6 | +- | 281.1 | V | 4272.0 | +- | 493.0 |
| *CR | 7.4 | +- | 7.3 | CR | .0 | +- | .0 |
| MN | 4959.3 | +- | 302.4 | MN | 4437.0 | +- | 493.0 |
| FE | 30.5 | +- | 3.9 | FE | .0 | +- | .0 |
| CO | 1055.1 | +- | 64.7 | CO | 970.0 | +- | 66.0 |
| *NI | -6.8 | +- | 1.8 | NI | .0 | +- | .0 |
| CU | 2400.1 | +- | 146.3 | CU | 2300.0 | +- | 164.0 |
| ZN | 9.3 | +- | 2.7 | ZN | .0 | +- | .0 |
| *GA | 2.1 | +- | 2.1 | GA | .0 | +- | .0 |
| *GE | .3 | +- | 2.4 | GE | .0 | +- | .0 |
| *AS | -3.7 | +- | 2.2 | AS | .0 | +- | .0 |
| *SE | 1.0 | +- | 1.2 | SE | .0 | +- | .0 |
| BR | 10.7 | +- | 1.8 | BR | .0 | +- | .0 |
| *RB | -.2 | +- | .9 | RB | .0 | +- | .0 |
| *SR | 2.8 | +- | 2.3 | SR | .0 | +- | .0 |
| * Y | -5.0 | +- | 1.6 | Y | .0 | +- | .0 |
| *ZR | -6.5 | +- | 1.8 | ZR | .0 | +- | .0 |
| MO | 26.8 | +- | 4.2 | MO | .0 | +- | .0 |
| *RH | 25.2 | +- | 58.2 | RH | .0 | +- | .0 |

TABLE 7. (continued)

| | FINE, NG/CM$^2$ | | | | NIST CERTIFIED VALUES | | |
|---|---|---|---|---|---|---|---|
| *PD | -69.0 | + - | 54.7 | PD | .0 | + - | .0 |
| *AG | 151.2 | + - | 63.4 | AG | .0 | + - | .0 |
| *CD | 24.2 | + - | 58.2 | CD | .0 | + - | .0 |
| *SN | -640.8 | + - | 138.6 | SN | .0 | + - | .0 |
| *SB | -73.5 | + - | 81.3 | SB | .0 | + - | .0 |
| *TE | -9.3 | + - | 73.9 | TE | .0 | + - | .0 |
| * I | -46.6 | + - | 91.6 | I | .0 | + - | .0 |
| *CS | 3.6 | + - | 96.7 | CS | .0 | + - | .0 |
| *BA | -2352.9 | + - | 328.6 | BA | .0 | + - | .0 |
| *LA | -509.9 | + - | 156.5 | LA | .0 | + - | .0 |
| W | 40.0 | + - | 12.9 | W | .0 | + - | .0 |
| *AU | -5.6 | + - | 2.5 | AU | .0 | + - | .0 |
| *HG | -5.4 | + - | 3.0 | HG | .0 | + - | .0 |
| *PB | -10.4 | + - | 4.2 | PB | .0 | + - | .0 |

* INDICATES THAT THE CONCENTRATION IS BELOW 3 TIMES THE UNCERTAINTY.
XRF DATE = 29-SEP-93 13:27:55 RBK
SPECTRAL ANALYSIS DATE = 12/14/1993

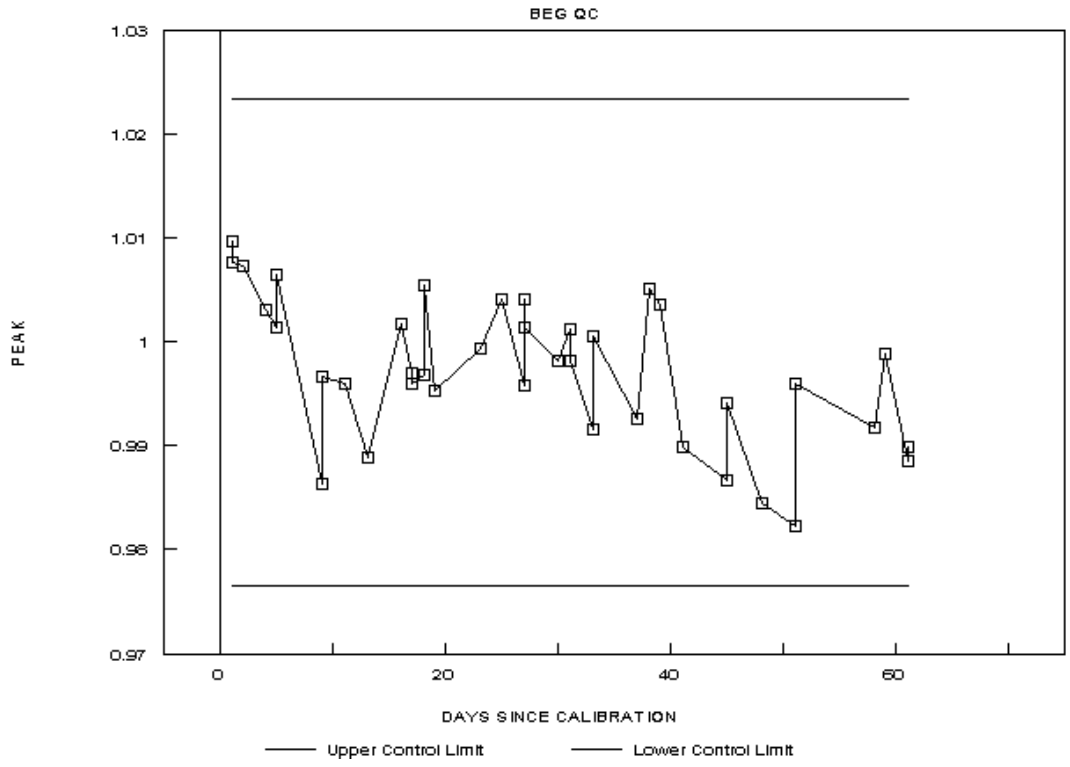


Figure 1. Quality control indicator associated with Fe peak area.

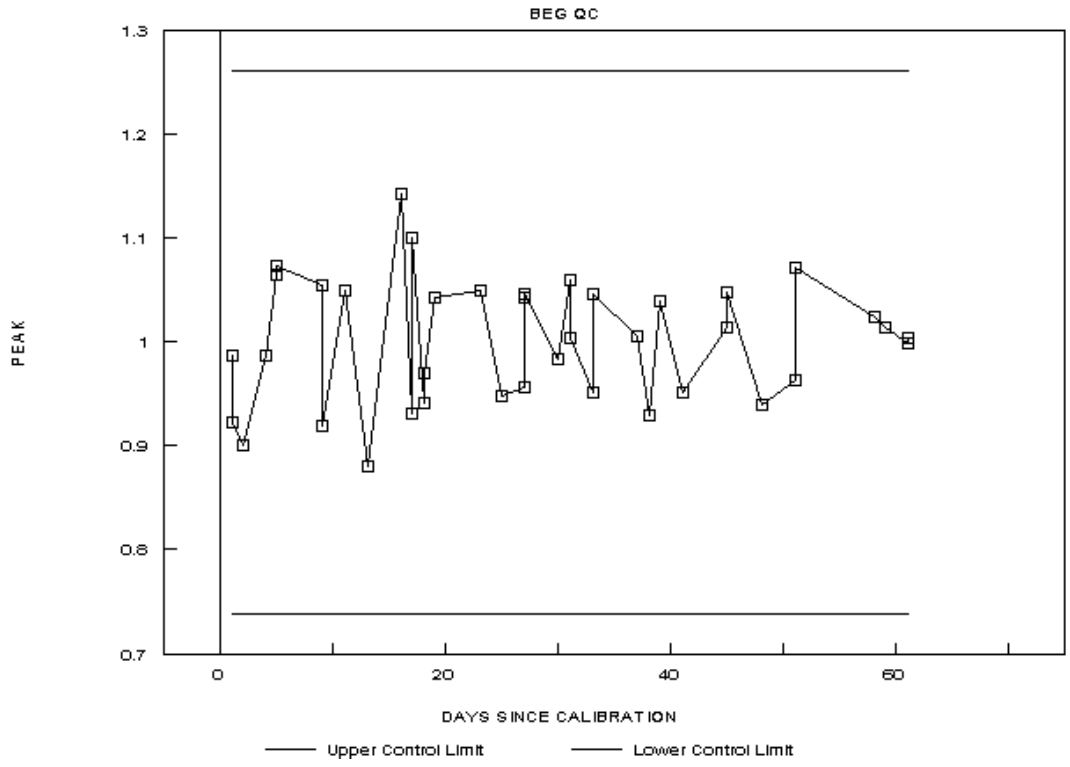


Figure 2. Quality control indicator associated with S background area.

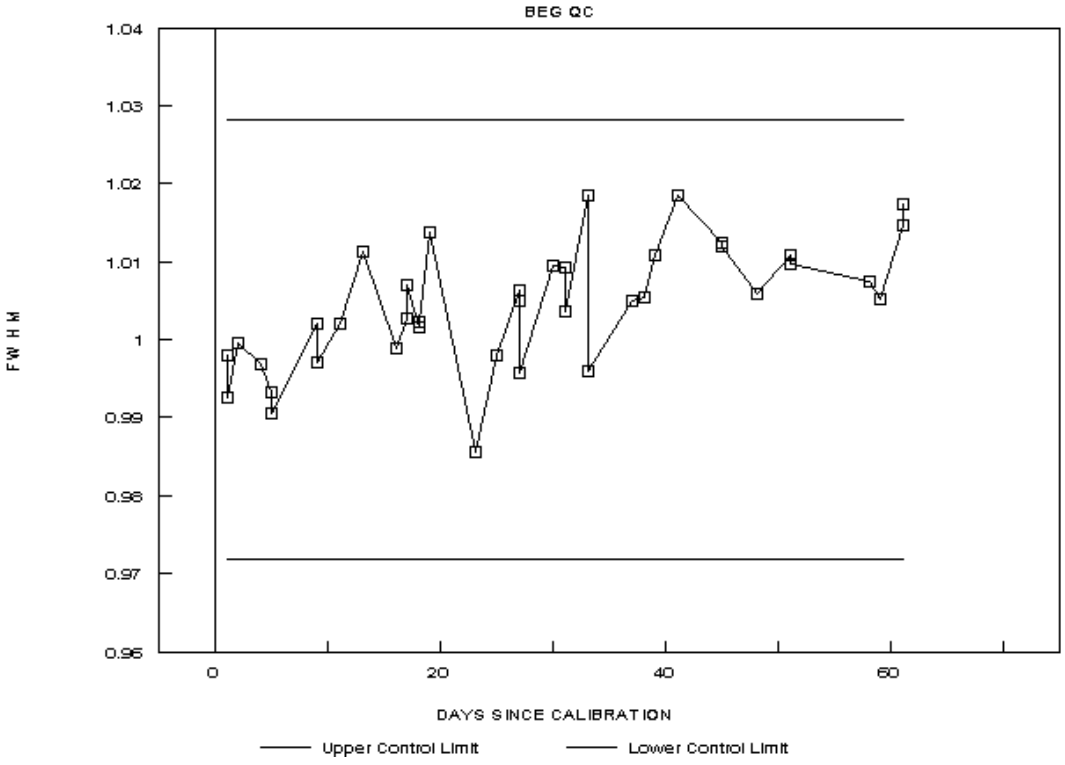


Figure 3. Quality control indicator associated with Fe FWHM.

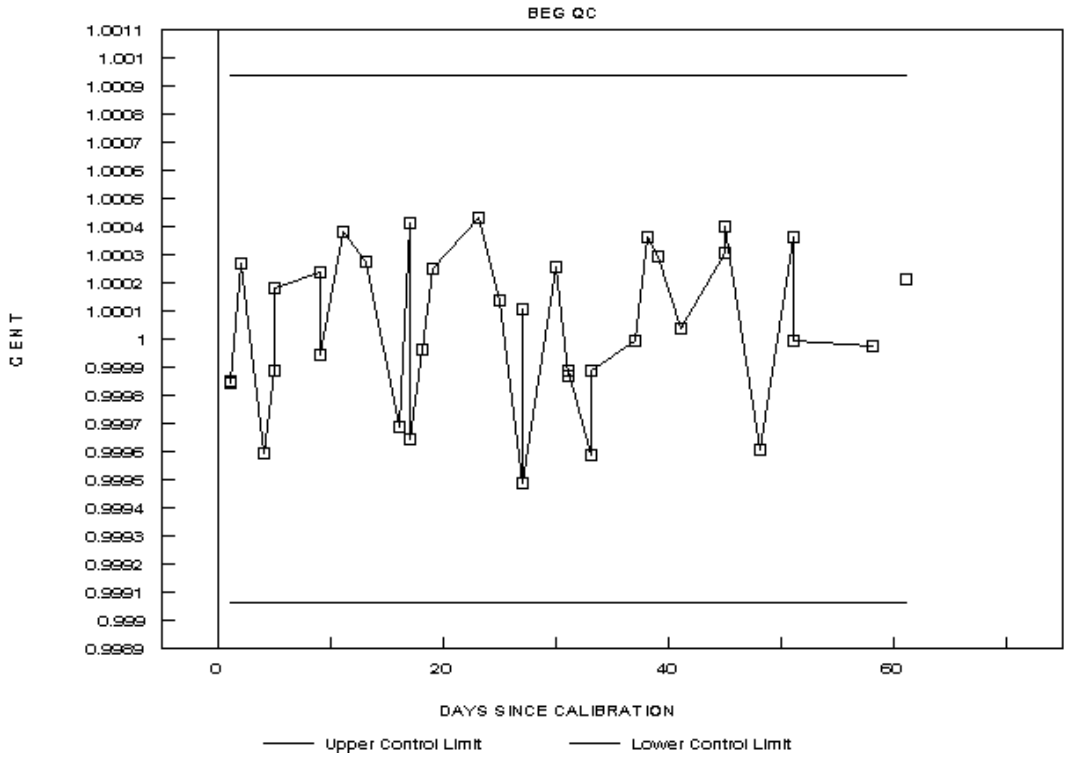


Figure 4. Quality control indicator associated with Pb centroid.

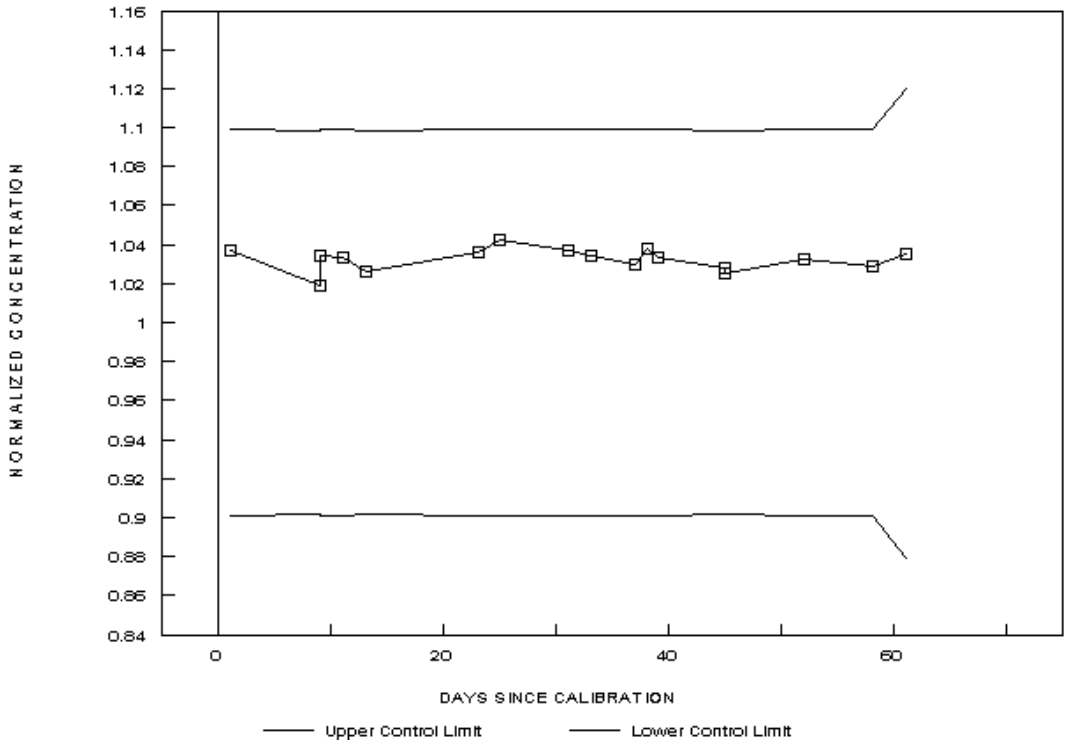


Figure 5. Quality control indicator associated with Pb in SRMs.

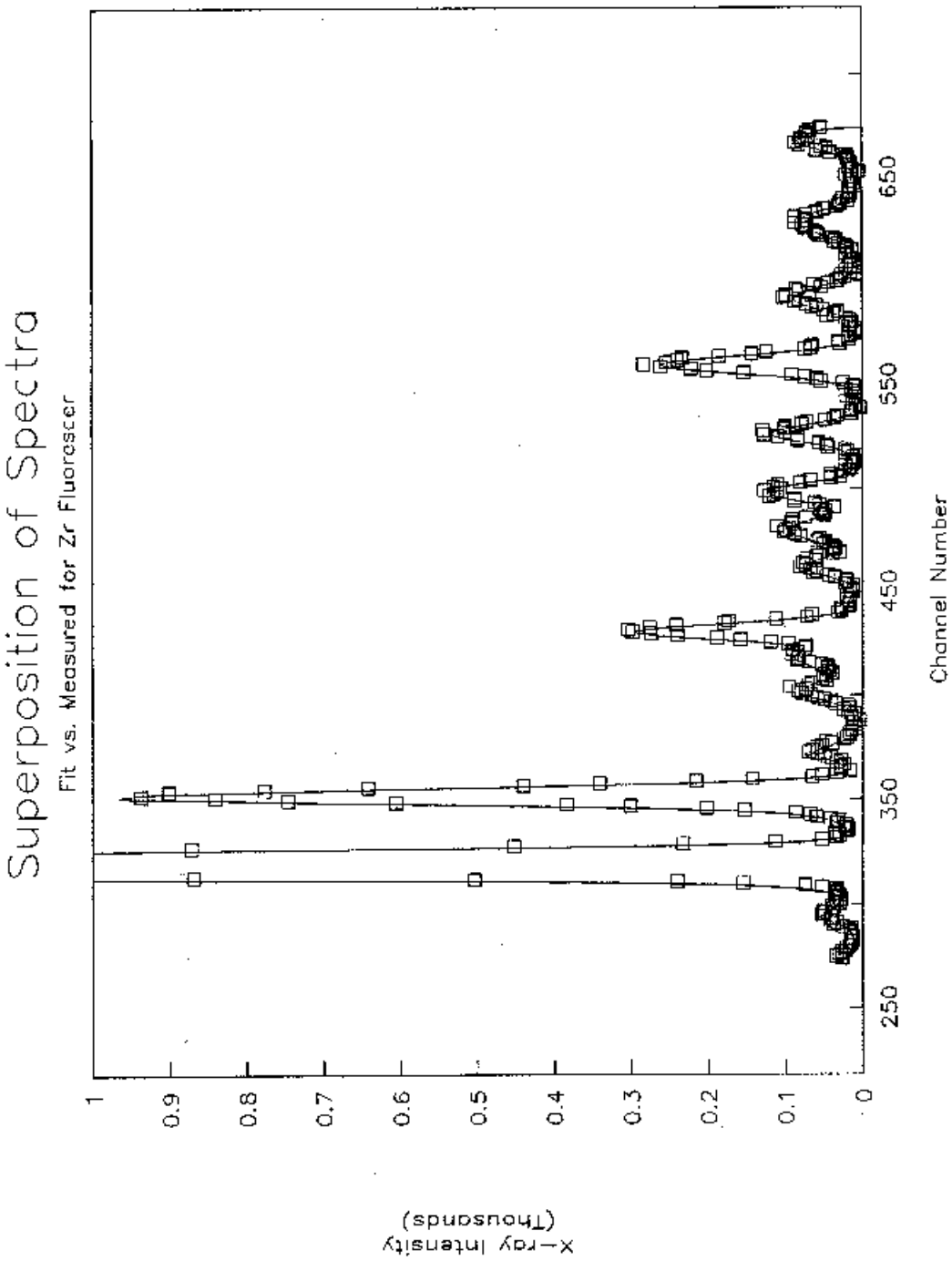


Figure 6. Quality control indicator associated with superposition of fitted and measured spectrum.

# APPENDIX C
# COMPENDIUM METHOD IO-3.4

EPA/625/R-96/010a

# Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air

## Compendium Method IO-3.4

# DETERMINATION OF METALS IN AMBIENT PARTICULATE MATTER USING INDUCTIVELY COUPLED PLASMA (ICP) SPECTROSCOPY

**Center for Environmental Research Information**
**Office of Research and Development**
**U.S. Environmental Protection Agency**
**Cincinnati, OH 45268**

**June 1999**

Method IO-3.4

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This Method is the result of the efforts of many individuals. Gratitude goes to each person involved in the preparation and review of this methodology.

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DISCLAIMER

***This Compendium has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.***

**Method IO-3.4**
**Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma (ICP) Spectroscopy**

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**Chapter IO-3**
**CHEMICAL SPECIES ANALYSIS**
**OF FILTER-COLLECTED SPM**

# Method IO-3.4
# DETERMINATION OF METALS IN AMBIENT PARTICULATE MATTER USING INDUCTIVELY COUPLED PLASMA (ICP) SPECTROSCOPY

## 1. Scope

**1.1** Suspended particulate matter (SPM) in air generally is a complex multi-phase system consisting of all airborne solid and low vapor pressure liquified particles having aerodynamic particle sizes ranging from below 0.01-100 µm and larger. Historically, SPM measurement has concentrated on total suspended particulates (TSP), with no preference to size selection.

**1.2** On July 1, 1987, the U. S. Environmental Protection Agency (EPA) promulgated a new size-specific air quality standard for ambient particulate matter. This new primary standard applies only to particles with aerodynamic diameters $\leq$10 µm ($PM_{10}$) and replaces the original standard for TSP. To measure concentrations of these particles, the EPA also promulgated a new federal reference method (FRM). This method is based on the separation and removal of non-$PM_{10}$ particles from an air sample followed by filtration and gravimetric analysis of $PM_{10}$ mass on the filter substrate. In 1997, the $PM_{10}$ standard was replaced with the national ambient air quality standard (NAAQS) for $PM_{2.5}$.

**1.3** The new primary standard (adopted to protect human health) limits $PM_{2.5}$ concentrations to 50 µg/m$^3$, averaged over a 24-h period. These smaller particles are able to reach the lower regions of the human respiratory tract and, therefore, are responsible for most of the adverse health effects associated with suspended particulate pollution. The secondary standard, used to assess the impact of pollution on public welfare, has also been established at 15 µg/m$^3$ for an annual average.

**1.4** Ambient air SPM measurements are used (among other purposes) to determine whether defined geographical areas are in attainment or non-attainment with the NAAQS for $PM_{2.5}$. These measurements are obtained by the states in their state and local air monitoring station (SLAMS) networks as required under 40CFR Part 58. Further, Appendix C of Part 58 requires that the ambient air monitoring methods used in these EPA-required SLAMS networks must be methods that have been designated by EPA as either reference or equivalent methods.

**1.5** The procedure for analyzing the elemental metal components in ambient air particulate matter collected on high volume filter material is described in this method. The high volume filter material may be associated with either the TSP or $PM_{10}$ sampler, as delineated in Inorganic Compendium Method IO-2.1.

**1.6** Filters are numbered, pre-weighed, field deployed and sampled, returned to the laboratory, extracted using microwave or hot acid, then analyzed by inductively coupled plasma (ICP) spectroscopy. The extraction procedure is accomplished by following Inorganic Compendium Method IO-3.1.

**1.7** This method should be used by analysts experienced in the use of ICP, the interpretation of spectral and matrix interferences and procedures for their correction. A minimum of 6-months experience with commercial instrumentation is required.

**1.8** Those metals and their associated method detection limit (MDL) applicable to this technology are listed in Table 1.

## 2. Applicable Documents

### 2.1 ASTM Standards

- D1356 *Definition of Terms Related to Atmospheric Sampling and Analysis.*
- D1357 *Planning the Sampling of the Ambient Atmosphere*.
- D4096 *Application of the High Volume Sample Method for Collection and Mass Determination of Airborne Particle Matter.*

### 2.2 Other Documents

- U. S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I: A Field Guide for Environmental Quality Assurance*, EPA-600/R-94/038a.
- U. S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Ambient Air Specific Methods (Interim Edition)*, EPA-600/R-94/038b.
- *Reference Method for the Determination of Particulate Matter in the Atmosphere*, 40 CFR 50, Appendix J.
- *Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)*, 40 CFR 50, Appendix B.
- *Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air, Federal Register* 43 (194): 46258-46261.
- U. S. EPA Project Summary Document (1).
- U. S. EPA Laboratory Standard Operating Procedures (2).
- Scientific Publications of Ambient Air Studies (3-7).

## 3. Summary of Method

### 3.1 Instrument Description

**3.1.1** The analytical system is an inductively coupled plasma atomic emission spectrometer, as illustrated in Figure 1. The plasma is produced by a radio frequency generator. The current from the generator is fed to a coil placed around a quartz tube through which argon flows. The oscillatory current flowing in the coil produces an oscillating magnetic field with the lines of force aligned axially along the tube. The argon is seeded with electrons by momentarily connecting a Tesla coil to the tube where the plasma forms inside. The ions in the gas tend to flow in a circular path around the lines of force of the oscillatory magnetic field and the resistance to their flow produces the heat. To avoid melting the silica tube, a flow of argon is introduced tangentially in the tube, which centers the plasma away from the walls of the tube. The plasma is formed in the shape of a toroid or doughnut, and the sample is introduced as an aerosol through the middle of the toroid. The hottest part of the plasma is in the ring around the center of the toroid, where temperatures of about 10,000 K are achieved. Through the center of the toroid where the sample is introduced, the temperature is somewhat lower, and the sample is subjected to temperatures of about 7,000 K. From the very hot region in the plasma and just above it, a continuum is radiated because of the high electron density. Above this

region, the continuum emission is reduced as the temperature falls and the spectral lines of the elements in the sample may be observed. Since this plasma is generated in an inert atmosphere, few chemical interferences exist.

**3.1.2** The spectrum is resolved in a spectrometer. The relative intensities and concentrations of the elements are calculated by a small computer or processor. Samples containing up to 61 preselected elements can be analyzed by ICP simultaneous analysis at a rate of 1 sample per minute. The ICP technique can analyze a large range of concentrations. A single calibration curve can accomodate changes in concentration of 5 orders of magnitude.

### 3.2 Sample Extraction

Two extraction procedures may be performed: hot acid extraction or microwave extraction, as documented in Inorganic Compendium Method IO-3.1. Extraction involving hot acids is hazardous and must be performed in a well-ventilated fume hood.

### 3.3 Sample Analysis

A technique for the simultaneous or sequential multi-element determination of trace elements in an acid solution is described in this Compendium method (see Figure 2). The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio frequency ICP. The spectra are dispersed by a grating spectrometer, and the intensities of the line are monitored by photo multiplier tubes. The photo currents from the photo multiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Data is processed by computer and yields micrograms of metal of interest per cubic meter of air sampled ($\mu g/m^3$).

## 4. Significance

**4.1** The area of toxic air pollutants has been the subject of interest and concern for many years. Recently, the use of receptor models has documented the need for elemental composition of atmospheric aerosol into components as a means of identifying their origins. The assessment of human health impacts, resulting in major control actions by federal, state, and local governments, is based on these data. Accurate measures of toxic air pollutants at trace levels are essential for proper assessments. The advent of inductively coupled plasma spectroscopy has improved the speed and performance of metals analysis in many applications.

**4.2** ICP spectroscopy is capable of quantitatively determining most metals at levels that are required by federal, state, and local regulatory agencies. Sensitivity and detection limits may vary from instrument to instrument.

## 5. Definitions

*[Note: Definitions used in this method are consistent with ASTM methods. All pertinent abbreviations and symbols are defined within this document at point of use.]*

**5.1 Autosampler**. Device that automatically sequences injections of sample solutions into the ICP.

**5.2 Background Correction**. Removing a high or variable background signal, using only the peak height of intensity for calculating concentration. Instruments measure background at one or more points slightly off the emission wavelength and subtract the intensity from the total intensity measured at the analytical wavelength.

**5.3 Channels**. Simultaneous ICPs have an array of photo multiplier tubes positioned to look at a fixed set of elements (wavelengths); each wavelength is a "channel," which varies by instrument.

**5.4 Detection Limits**. Determined by calibrating the ICP and determining the standard deviation of apparent concentrations measured in pure water. The result (F) is multiplied by a factor from 2 to 10 (usually 3) to define a "detection limit." Complex sample matrices result in a higher background noise than pure water, so actual detection limits vary considerably with sample type. It is recommended that an instrument detection limit (IDL) be determined in a standard whose concentration is about three times the expected detection limit.

**5.5 Detectors**. Photomultiplier tubes (PMTs).

**5.6 Fixed Optics**. The most crucial element in the optical design. If the grating moves during measurement, uncertainties in the results are inevitable.

**5.7 Grating**. The optical element that disperses light.

**5.8 Integration Time**. The length of time the signal from the PMT is integrated for an intensity measurement. The most precise measurements are taken at the peak intensity.

**5.9 Inter Element Intereference**. When emission lines from two elements overlap at the exit slit, light measured by the PMT is no longer a simple measure of the concentration of one element. The second element interferes with the measurement of the first at that wavelength. If lines free of interference can't be found, approximate concentrations of the element of interest can be calculated by calibrating that element and the interferent (inter element correction).

**5.10 Linear Dynamic Range**. The light intensity in an ICP source varies linearly with the concentration of atoms over more than 6 orders of magnitude (the linear dynamic range). This variation allows for determination of trace and major elements in a single sample, without dilution. Fewer standards for calibration are needed, often a high standard and a blank suffice.

**5.11 Limit of Quantitation**. The lowest level at which reliable measurements can be made. Defined as ten times the standard deviation of a measurement made in a blank (pure water), which is 3.3 times the "3F" detection limit.

**5.12 Monochromator**. The spectrometer design on a sequential ICP.

**5.13 Nebulizer**. A device creating a fine spray of sample solution to be carried into the plasma for measurement. Its performance is critical for good analyses.

**5.14 Photomultiplier Tubes (PMTs)**. Light detectors in ICP instruments. When struck by light, the PMT generates a current proportional to the intensity.

**5.15 Polychromator**. The spectrometer design of a simultaneous ICP.

## 6. Ranges, Sensitivities, and Detection Limits

**6.1** Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on a particular instrument. All measurements must be within the instrument linear range where correction factors are valid. The analyst must verify that the instrument configuration and operating conditions satisfy the analytical requirements and to maintain quality control data, i.e., confirming instrument performance and analytical results.

**6.2** For comparison, Table 1 provides typical maximum element concentrations obtained on a Thermo Jarrell Ash Model 975 Plasma AtomComp ICP.

**6.3** Calibration sensitivities are dependent upon spectral line intensities. For comparison, Table 1 provides typical sensitivities for the ICP mentioned in Section 6.2 for a Jarrell Ash Model 975 Plasma AtomComp ICP.

**6.4** Detection limits vary for various makes and models. Typical detection limits achievable by the Thermo Jarrell Ash Model 975 ICP are given in Table 1. These are computed as 3.3 times the standard deviation of the distribution of outputs for the repeated measurement of a standard, which contains no metals and is used as the zero point for a two-point instrument standardization described in Section 11.3. The acid concentrations of this standard must match the acid concentrations of blanks and samples.

## 7. Precision and Accuracy

**7.1** Accuracy for this procedure has not been determined. Spiked strips used for audits have been developed by the EPA. The main use of the audit results is to document chronologically the consistency of analytical performance. One multi-element audit sample should be extracted daily with normal ambient air samples. Audit samples can only approximate true atmospheric particulates, which contributes to the overall uncertainty. Attempts should be made to use National Institute of Standards and Technology (NIST) 1648 (urban particulate) to judge recovery. This material is not ideal because (1) there is no filter substrate; (2) relatively large amounts (100 mg) are required to overcome problems of apparent inhomogeneity, which in turn necessitates dilutions not required in normal application of this method; and (3) element ratios differ somewhat from those found in real samples. Typical recoveries experienced with the spiked strips and NIST 1648 are presented in Table 2.

**7.2** Typical precision, bias, and correlation coefficients calculated from audit samples vs. blind replicate analyses are shown in Table 3. Treatment of the glass fibers during filter manufacture affects both recovery and precision of sample replicate pairs. This fact should be considered when studies are designed.

**7.3** Good precision data does not imply accuracy; bias is still possible. Bias is nearly impossible to detect when a given type of sample is always analyzed by the same method using the same instrumentation. In this method, bias, if any, is most likely to arise during the sampling and sample preparation steps.

**7.4** Quality assurance (QA) activities are discussed in Section 13 of this method. QA data for the method are composed of QA data for the instrument and for the sampling and sample preparation steps. The former are relatively easy to obtain by the analysis of known solutions and are usually quite good because of the inherent stability and linearity of the plasma and associated electronics. QA data for the sampling and sample preparation steps are nearly always poorer than for the instrument and thus dictate the QA data for the method as a whole. Consequently, a good instrumental calibration does not guarantee that the data produced are accurate. For instance, independent analysis (by neutron activation analysis) of real samples and of NIST SRM 1648 has revealed that Cr and Ti extractions are 25-75% efficient using the method described herein, yet both elements in solution are recovered very well by the plasma instrument.

## 8. Interferences

### 8.1 Spectral Interferences

Spectral interferences result when spectrally pure solutions of one element produce a finite output on channels assigned to other elements. Table 4 provides recommended wavelengths to monitor selected metals using ICP in order to minimize spectral interferences. When the quantitative correction is made, the order of correction is arranged so that only "true" (that is, interference-free or previously corrected) values are used in any quantitative correction of another element for comparison. The quantitative correction factors are listed in Table 10 in the order in which they are applied in the data-processing step for the analysis of ambient air using the Thermo Jarrell Ash Model 975 ICP. The correction relation for any affected element is:

$$\text{"true" concentration} = \frac{\text{(apparent conc.)} \times \text{(correction factor "true")}}{\text{(concentration of the affecting element)}}$$

*[Note: The information in Table 10 was generated using a specific instrument and is presented only to provide an indication of potential interferences. Specific correction factors must be generated for each instrument during each analysis.]*

### 8.2 Matrix Interference

Matrix interferences do exist. This problem has been minimized by matrix matching of standards and samples. Matrix interferences depend on the types and quantities of acids used; element emission lines may be enhanced or depressed. These interferences may be circumvented by careful matrix matching of standards, QC solutions, and samples. Careful matches were made in the development of this procedure.

## 9. Apparatus

*[Note: This method was developed using the Thermo Jarrell Ash Model 975 Plasma AtomComp, 27 Forge Parkway, Franklin, MA 02038, (508) 520-1880, as a guideline. EPA has experience in use of this equipment during various field monitoring programs over the last several years. Other manufacturers' equipment should work as well. However, modifications to these procedures may be necessary if another commercially available sampler is selected.]*

**9.1 Desiccator.** For cooling oven-dried chemicals.

**9.2 Gravity Convection Type Drying Oven**. Drying chemicals and glassware, Precision Scientific 31281 or equivalent.

**9.3 Mechanical Convection Type Drying Oven**. For drying plastic ware (Blue Island Electric OV 510A-2 or equivalent).

**9.4 Inductively Coupled Plasma Emission Spectrometer**. The ICP described in this method is the Thermo Jarrell Ash Model 975 Plasma AtomComp, 27 Forge Parkway, Franklin, MA 02038, (508) 520-1880. EPA has experience in use of this equipment during various field monitoring programs. Other manufacturers' equipment should work as well. The instrument uses a Plasma Therm HFS 2000D R.F. generator as the power supply for the plasma. The excitation source is a three-turn inductively coupled plasma torch with a cross-flow pneumatic nebulizer for sample introduction. Samples are pumped to the nebulizer with a Gilson Minipuls II single channel peristaltic pump. The instrument is equipped to read 48 elements as identified in Table 4. A dedicated PDP-8E (Digital Equipment Corporation) minicomputer controls the instrument and yields a concentration printout. To achieve data storage capability, the PDP-8E has been interfaced with a PDP11/34.

**9.5 Bottles**. Linear polyethylene or polypropylene with leakproof caps for storage of samples. (500 mL, 125 mL, and 30 mL). Teflon bottles for storing multi-element standards.

**9.6 Pipettes**. Volumetric 50 mL, 25 mL, 20 mL, 15 mL, 10 mL, 9 mL, 8 mL, 7 mL, 6 mL, 5 mL, 4 mL, 3 mL, 2 mL, Class A borosilicate glass.

**9.7 Pipettes**. Graduated 10 mL, Class A Borosilicate glass.

**9.8 Pipette**. Automatic dispensing with accuracy of 0.1 mL or better and repeatability of 20 FL (Grumman Automatic Dispensing Pipet, model ADP-30DT, or equivalent).

## 10. Reagents

**10.1 Hydrochloric Acid**. Ultrex grade, 12.3 M (Baker 1-4800) for preparing standards.

**10.2 Nitric Acid**. ACS reagent grade, concentrated (16 M) for preparing 10% v/v nitric acid, to clean labware only (Fisher A-200). Add 100 mL of concentrated $HNO_3$ to ~ 500 mL of ASTM Type II water and dilute to 1 L.

*[Note: This acid is not for sample preparation; it contains excessive metals].*

**10.3 Nitric Acid**. Ultrex grade, 16 M (Baker 1-4801) for preparing standards.

**10.4 Stock Calibration Standards**. Multi-element and single-element plasma-grade stocks are used for the analysis. The stocks are purchased from Spex Industries, Inc., Inorganic Ventures, Inc., or equivalent. Working calibration standards are prepared by dilution of the concentrated calibration stocks. The calibration standard stocks used for instrument calibration and initial calibration verification (ICV) are purchased from different suppliers. The source (manufacturer and lot), concentration, expiration date, and acid matrix are recorded for all calibration standards used for the analysis. Stock solutions should be stored in Teflon bottles. The final concentration of nitric and hydrochloric acid in the calibration standards should be the same as those in the prepared samples.

**10.5 Compressed Argon in Cylinders and Liquid Argon in Tanks, Purity 99.95%**. Best source.

**10.6 ASTM Type I water (ASTM D1193)**. Best source. The Type I water should have a minimum resistance of 16.67 milli-ohms, as evidenced by the reading of the resistivity meter during water flow.

## 11. Analysis

### 11.1 Standard Stock Solutions

**11.1.1** All labware should be scrupulously cleaned. The following procedure is recommended: Wash with laboratory detergent or ultrasonic for 30 min with laboratory detergent. Rinse and soak a minimum of 4 hr in 10% V/V nitric acid. Rinse 3 times with deionized, distilled water, and oven dry.

*[Note: Nitric and hydrochloric acid fumes are toxic. Prepare in a well-ventilated fume hood. Mixing results in an exothermic reaction. Stir slowly.]*

**11.1.2** Preparing Calibration Curve Standards. Mixed calibration curve standards are prepared by diluting appropriate volumes of the stock calibration standards in Class A volumetric flasks. Table 1 provides examples of typical concentrations used for calibration for several elements. Each working standard solution should be labeled with a name, an expiration date, and the initials of the preparer.

**11.1.3** Prepare Initial Calibration Verification Standard (ICV). The ICV standards are analyzed immediately following initial calibration. The ICV standards are prepared at the midpoints of the calibration curves. These standards are prepared from certified stocks having a different manufacturer than the calibration standards. The final concentration of the ICV should be in the range of 25 µg/mL for Al, Ca, Fe, Mg, K and Na. All other analytes should be in the range of 2 µg/mL.

**11.1.4** Prepare Interference Check Standard (ICS). The interference check standards are analyzed at the beginning and end of the sample run and for every 8 hours of continuous operation. The ICS should contain approximately 200 µg/mL of Al, Ca, Fe, and Mg. In addition, the ICS should contain approximately 1 µg/mL of all other analytes, including Ag, Be, Ca, Cd, Co, Cr, Cu, Fe, Pb, Se T, Y, Zn, and Bi.

**11.1.5** Laboratory Control Spike (LCS). An LCS is prepared and analyzed with each sample batch (or 1 per 20 samples). The LCS is prepared for all analytes at the 2 µg/mL level and when analyzed, should be within 80% to 120% of actual concentration. If the results are not within this criterion, then the results must be qualified.

**11.1.6** Matrix Spike (MS). A MS sample is prepared and analyzed with each sample batch (or 1 per 20 samples). These samples are used to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion, (i.e., prior to the addition of other reagents). The MS should be at the 25 µg/strip level. The percent recovery for the analyte as part of the MS should be between 75% and 125% for all analytes.

**11.1.7** Prepare a Reagent Blank (RB). Prepare a reagent blank that contains all the reagents in the same volumes used in processing the routine samples. The reagent blank must be carried through the entire preparation procedure and analysis scheme. The final solution should contain the same acid concentration as sample solutions for analysis. The running frequency of analysis of a reagent blank is about 1 for every 40 real samples.

### 11.2 ICP Operating Parameters

A daily log of the operating parameters should be maintained for reference. Entries are made by the analyst of periodic intervals throughout the run. The following list of parameters are examples from the Thermo Jarrell Ash Model 975 Plasma AtomComp. Specific manufacturer's guidelines should be followed.

| ICP HARDWARE | SPECIFICATIONS |
|---|---|
| • Plasma power | 1.1 kW forward automatic control<br>11 W reflected (minimum possible) |
| • Argon coolant flow | 18 1/min liquid argon source |
| • Argon nebulizer flow | 16 psi (approx. 700 mL/min) |
| • Sample uptake | Avg. 1.85 mL/min |
| • Observation Zone | Centered 16 mm above the load coil |
| • Sample preflush time | 45 s; preburn, 1 s |
| • Exposure | 10 s |
| • $H_2O$ Post Flush | 10 s then proceed to next sample |
| • Slits | 25-µm entrance slit; 75-µm exit slit |
| • Photomultiplier tube voltage | 900 V |

### 11.3 Instrumental Preparations

**11.3.1 Calibration Curve Linearity**. ICP spectrometers generally are considered to yield a linear response over wide concentration ranges; however, investigation for linearity for elements expected to exceed concentrations of about 25 µg/mL may be necessary. Linearity may vary among manufacturers and according to operating parameters. The method and conditions described in this procedure have imposed the following limitations:

- Ca response is linear to 40 µg/mL, becoming non-linear.
- Cr saturates the electronics at 50 µg/mL.
- Cu saturates the electronics at 40 µg/mL.
- Fe saturates the electronics at 230 µg/mL.

- Mg response is curvilinear to 40 µg/mL, becoming unuseable.
- Na response is curvilinear to 80 µg/mL, becoming unuseable.

The curvilinear nature of Mg and Na responses below the levels specified were made acceptable by programming the ICP computer with segmented calibration curves as described in the manufacturer's instructions.

**11.3.2 Spectral Interferences**. Section 8 described briefly spectral interferences. A thorough determination of spectral interferences is a lengthy, time-consuming study in itself. The following are some of the factors influencing the presence or absence and magnitude of interferences:

- Wavelength of lines being read;
- Expected concentrations of the elements involved;
- Quality and the stability of the system optics (i.e., minimal deterioration with time);
- Quality and stability of photo multiplier tubes and electronics; and
- Purity of chemicals in use.

A thorough study of interferences has been conducted by EPA in the development of this method and have been addressed in the data processing program listed in Table 5.

*[Note: The spectral interference factors listed in Table 5 were determined by analyzing single element solutions of each interfering element. The concentration of each single element solution was within the linear dynamic range (LDR) of the analysis, usually 100 µg/mL. The criteria for listing a spectral interference was an apparent analyte concentration from the interfering single element solution that was outside the 95% confidence interval estimates for the determined method detection limit (MDL) of the analyte. The factors are presented as a guide for users of this method for determining interrelement interference effects. The user is cautioned that other analytical systems other than the Thermo Jarrell Ash Model 975 Plasma AtomComp described in this method may exhibit somewhat different levels of interference than those listed in Table 5 and that the interference effects must be evaluated for each individual system.]*

**11.3.3 Matrix Interferences**. Matrix interferences depend on the types and quantities of acids used; element emission lines may be enhanced or depressed. These interferences may be circumvented by careful matrix matching of standards, QC solutions, and samples. Careful matches should be made in the use of this procedure.

### 11.4 Sample Receipt in the Laboratory

**11.4.1** The sample should be received from the extraction laboratory in a centrifuge tube, as documented in Inorganic Compendium Method IO-3.1.

**11.4.2** No additional preservation is needed at this time. Sample is ready for ICP analysis.

### 11.5 ICP Operation

*[Note: This method was developed using the Thermo Jarrell Ash 975 Plasma AtomComp spectrometer. EPA has experience in the use of the Model 975 spectrometer associated with various field monitoring programs involving analysis of filterable particulate matter for metals using ICP over the last several years. The use of other manufacturers of ICP spectrometers should work as well as long as the quality assurance and quality control specifications identified in Sections 13, Quality Control, are met. However, modifications to Compendium Method 10-3.4 procedures may be necessary if another commercial ICP spectrometer is used.]*

**11.5.1** Start and allow the instrument at least 45 min for warmup.

**11.5.2** Profile following manufacturer's directions. Run 12 warmup burns of old high QC solution to exercise the photomultiplier tubes.

**11.5.3** Standardize by opening the standardization buffers with a J command on the CRT operating off-line from the PDP-11/34. Flush for 2 min with the first working standard. Make two exposures, print the average ratio on the teletype, and identify the standard when queried. Repeat for all five working standards. Complete with an S command and answer the query "Enter LCN" with a carriage return (RTN). Calibration data are not stored in the PDP-ll.

**11.5.4** Go on-line to the PDP-ll by typing "RUN JA" and answer PDP-ll queries to identify the operator, data storage, and operating condition codes.

**11.5.5** The PDP-ll will automatically acquire gains and offsets (slopes and X-intercepts of the calibration curve) determined by the ICP standardization. Values falling outside a previously determined bandwidth will be reported by the computer. When this occurs, corrective action must be taken. Gain and offset values are element-specific.

**11.5.6** Measure the sample-pump uptake rate which should be approximately 1.8 mL/min.

**11.5.7** Select a QC solution for analysis. On the CRT, enter RTN "QC" RTN "21", RTN for high QC, or "QC" RTN "22", RTN for low QC. When "DSC" appears on CRT, type "HIQC" or "LOQC", as applicable, followed by its prep date and RTN. The number "1.0" will appear twice, indicating the multiplication and dilution factors have been set to 1.0. This step is followed by the query "OK?"

**11.5.8** Begin pumping the QC solution selected in Section 11.5.7 from an aliquot. Start the stopwatch when the leading edge of the solution has just entered the nebulizer. Time for 45 s and press RTN on the CRT to begin the exposure. The end is signaled by the CRT bell. Transfer the pickup tube to deionized distilled water.

**11.5.9** When the PDP-ll has acquired the data, it will query "QC SMP:." Type RTN, "STD," RTN "21," RTN to identify the zero standard (Working Standard No. 1; see Section 11.1). After "DCS:" As in Section 11.5.7, the multiplication and dilution factors will default to 1.0, and the query "OK?" will appear.

**11.5.10** Begin pumping from an aliquot of the zero standard and time for 45 s, as in Section 11.5.8. Start the exposure with RTN on the CRT. At the bell, return the pickup to deionized, distilled water.

**11.5.11** When the PDP-ll has acquired the data, it will query "STD SMP:." Type "1," RTN, RTN, and it will query "OK?" Type "NO," RTN and the cursor will move to the left end of the line.

**11.5.12** Select the first sample. On the CRT, enter the Project I.D. from the label. Press RTN. Type numerical sample number and RTN. After "DCS:," type the four letter I.D. code and RTN. The computer next queries "MLT:" (for multiplication factor); enter "360", RTN. After "DIL:" (for dilution factor), enter "1," RTN. The computer then asks "OK?"

**11.5.13** Begin pumping the sample from the sample bottle and time for 45 s before pressing RTN. At the bell, return the pickup to deionized, distilled water and select the next sample.

**11.5.14** Enter second sample by typing the sample number, RTN, 4-letter I.D., RTN, and another RTN to begin the exposure.

**11.5.15** Present 8 samples to the instrument.

**11.5.16** Challenge the instrument with the QC solution that was not selected in Section 11.3.7. Repeat CRT entries and procedure in Sections 11.5.7 and 11.5.8.

**11.5.17** Resume sample analysis. Repeat Sections 11.5.11 through 11.5.13.

**11.5.18** Analyze nine samples.

**11.5.19** Return to Section 11.5.6 and repeat through Section 11.5.17.

**11.5.20** End the analytical session after about 3 to 3.5 h. Type "-1," RTN. The computer will query "DO YOU WISH TO SAVE THIS SESSION'S DATA?" Type "YES," RTN. The computer will back up the data and issue instructions. This terminates the RUN JA program.

**11.5.21** Usually two sessions per day are attempted. Repeat Sections 11.5.2 through 11.5.20 for the second session.

**11.5.22** Instrument operating parameters are recorded before and after every 20 burns. A typical day's record is shown in Figure 3.

**11.5.23** With minimal experience, the instrument operator will be able to compress the above steps (i.e., process more than one sample at a time by overlapping the steps required for the different samples).

## 12. Data Processing

### 12.1 Filter Blanks and Discrimination Limit

Since individual blanks are not available from each filter used for sampling, the mean unexposed filter value is subtracted from the result for each exposed sample to obtain the best estimate of each element in the filter particulate material. A discrimination limit must be defined so that possible contributions from an individual filter are not falsely reported as being from the particulate material. Calculate the filter batch mean, $F_m$ (see

Method IO-3.2), and the standard deviation of the $F_m$ values for each filter. If $F_m$ is greater than the instrumental detection limit, then $F_m$ must be subtracted from the total elemental content for each particulate bearing filter when the net metal in the particulate material is calculated. Determine the smallest atmospheric concentration of the element that can be reliably distinguished from the filter's contribution by multiplying the standard deviation for the filter batch by 3.3 and dividing by the average volume of air sampled, usually 1700 $m^3$. The resulting value will be the discrimination limit for that element.

### 12.2 Metal Concentration in Filter

**12.2.1** Calculate the air volume sampled, corrected to EPA-reference conditions:

$$V_{std} = V_s \left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}}{P_{std}}\right)$$

where:

$V_{std}$ = volume of ambient air sampled at EPA-reference conditions, $m^3$.
$V_s$ = volume of ambient air pulled through the sampler, $m^3$.
$T_{std}$ = absolute EPA-reference temperature, 298EK.
$T_m$ = average ambient temperature, EK.
$P_{bar}$ = barometric pressure during sampling measurement condition, mmHg.
$P_{std}$ = EPA-reference barometric pressure, 760 mmHg.

**12.2.2** Metal concentration in the air sample can then be calculated as follows:

$$C = [(\mu g \text{ metal/mL})(\text{final extraction volume (i.e., 20 mL)/strip})(9) - F_m]/V_{std}$$

where:

C = concentration, µg metal/std. $m^3$
µg metal/mL = metal concentration determined from Section 11.5.
Final extraction volume, mL/strip = total sample extraction volume, mL, from extraction procedure (i.e., 20 mL).

$$9 = \frac{\text{Useable filter area [20 cm x 23 cm (8" x 9")]}}{\text{Exposed area of one strip [2.5 cm x 20 cm (1" x 8")]}}$$

$F_m$ = average concentration of blank filters, µg.
$V_{std}$ = standard air volume pulled through filter, std $m^3$, (25EC and 760 mmHg).

## 13. Quality Assurance (QA)

### 13.1 Instrumental Tuning and Standardization

**13.1.1** The instrument must be tuned by the manufacturer at installation. However, the element lines should be checked periodically to determine if they have maintained their positions relative to the mercury profile line. Follow the manufacturer's instructions.

**13.1.2** The Thermo Jarrell Ash Company published directions for performing instrument diagnostic checks and pertinent acceptable data limits (Ward, 1978, 1979 a, b, 1980 a, b). Diagnostic checks should be run periodically at a frequency dictated by the "goodness" of instrumental QC checks.

### 13.2 Calibration For Quantitative Analysis

See Section 13.3.2.1.

### 13.3 Daily QA Check and Analytical Run Sequence

Data validation steps described in this section are primarily instrumental and do not guarantee extraction efficiency.

**13.3.1 Real-Time Judgments: Standards, Gains, Offsets**. This system requires virtually no data computations by the operator. However, the operator is required at several points to judge, based on historical experience, the validity of numbers generated and to decide whether to continue or stop. During the standardization, the operator must observe element response to determine if values are normal. The operator must watch for computer-generated messages reporting gains or offsets that exceed the tolerance limits. Proper corrective action is based on operator experience and is discussed in Section 14.5.

**13.3.2 General Quality Control**. The required general quality control requirements for ICP analysis are discussed below and summarized in Table 6.

**13.3.2.1** Initial Calibration. At least two calibration standards and a calibration blank are analyzed at the beginning of an analysis run. The standards used to calibration are diluted from certified stock standards (see Section 11.1) and are used within the expiration dates. The calibration standards and blanks are prepared in the same nitric and hydrochloric acid matrix as the samples.

**13.3.2.2** Initial Calibration Verification (ICV). The ICV standards are analyzed immediately following initial calibration. The ICV standards are prepared from certified stocks having a different manufacturer than the calibration standards. The measured concentration should be within 90% to 110% of the actual concentration.

**13.3.2.3** Initial Calibration Blank (ICB). The ICB is analyzed immediately following ICV and prior to the high standard verification. The acceptance criteria for the ICB is the same as for continuing calibration blank (CCB) verification.

**13.3.2.4** High Standard Verification (HSV). Immediately after the analysis of the ICB, and prior to the analysis of samples, the HSVs are reanalyzed. The measured concentration should be within 95% to 105% of actual concentration.

**13.3.2.5** Interference Check Standards (ICSs). The ICSs are analyzed at the beginning and end of the run and for every 8 hours of continuous operation. The results for the analytes should be within 80% and 120% of the actual concentration. Samples containing levels of interferences above the levels in the ICS should be considered for dilution.

**13.3.2.6** Continuing Calibration Verification (CCV). CCV standards are prepared from the calibration standard stocks at the midpoint of the calibration curve. The CCV standards are analyzed at the beginning of the run prior to samples, after every 10 samples, and at the end of the run prior to the last continuing calibration blank (CCB) analysis. The measured concentration should be within 90% and 110% of the actual concentration.

**13.3.2.7** Continuing Calibration Blanks (CCBs). The CCBs are analyzed following each CCV. The results of the CCBs are evaluated as follows:

- The CCBs are compared to the method detection limits.
- The absolute value of the instrument response must be less than the method detection limits.-

- If not, then sample results for analytes < 5 times the amount in the blank must be flagged or analysis must be repeated.

**13.3.2.8** Reagent Blank (RB). A RB sample is prepared and analyzed with each sample batch. This analysis is used to determine if concentrations reflect background levels from sample digestion. If the instrument measured response is greater than the method detection limits, then the sample results for the affected analyte(s) must be flagged. Samples may be considered candidates for redigestion and reanalysis for that analyte.

**13.3.2.9** Laboratory Control Spike (LCS). An LCS is prepared and analyzed with each sample batch (or 1 per 20 samples). The results for the analytes should be within 80% to 120% of actual concentration. If the results are not within this criterion, then strips of the LCS and all samples should be redigested and reanalyzed.

**13.3.2.10** Matrix Spike (MS). A MS sample is prepared and analyzed with each sample batch (or 1 per 20 samples). These samples are used to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion, (i.e., prior to the addition of other reagents). The percent recovery for the analyte as part of the MS should be between 75% and 125% for all analytes.

**13.3.2.11** Duplicate and/or Spike Duplicate. Duplicate samples and/or matrix spike duplicates are prepared and analyzed with each sample batch. These samples are used to estimate method precision, expressed as relative percent difference (RPD). The RPD between the duplicate and/or matrix spike duplicate final concentrations should be < 20%.

**13.3.2.12** Serial Dilution. The ICP serial dilution analysis must be performed on one sample per batch. After a fivefold serial dilution, the analyte concentration must be within 90% and 110% of the undiluted sample results.

**13.3.2.13** Sample Dilution. Dilute and reanalyze samples that are more concentrated than the linear calibration limit.

### 13.4 Corrective Actions

**13.4.1** The plasma must operate in a stable mode with a uniform sample feed rate. Failure to reproduce standards' responses or QC values usually is caused by a partially or totally plugged nebulizer. This condition may be verified by observing a decrease in the pump rate or the absence of a fog in the nebulizer spray chamber. A similar effect will be observed if the argon supply pressure or the RF power should change. Experience with the sample pump and the RF power supply has been excellent, and both appear to be very stable electronically.

**13.4.2** Intermittent failure of QC solutions to fall within the tolerance band may be due to an intermittent failure in a spectrometer circuit or to a broken nebulizer needle. Both are difficult to detect without extensive testing or dismantling of equipment. Leaks in the argon supply lines are also likely causes of such problems. Leaks in the ground-glass joints of the torch-spray chamber can be eliminated by the light use of a good grade stopcock grease (not silicone-base) (see Section 13.5).

**13.4.3** One intended purpose of the repeated analysis of QC solutions was to detect and correct instrument drift occurring within any 1 day. Experience has shown that drift is not a problem when the instrument is standardized twice daily. When drift has been detected, it has been attributed to thermal drift and corrected by repro filing (i.e., adjusting the optical alignment). The instrument must be restandardized after profiling.

**13.4.4** Long-term drift is more difficult to detect. A gradual increase in the gains of short-wavelength elements over a period of weeks or months is probably due to degradation of mirror coatings. Washing the mirrors may help in the short term, but usually they must be replaced. Mirrors may be ruined if washed

improperly; manufacturer-approved procedures should be followed. Gradual degradation of electronic circuits will also cause long-term drift.

### 13.5 Routine Maintenance

**13.5.1** The torch and spray chambers occasionally must be cleaned. Frequency of cleaning must be determined through experience, as a schedule and criteria have not been established. Ultrasonic the chambers in a hot detergent for at least 30 min, soak in aqua regia overnight, and rinse in deionized, distilled water.

*[Note: Aqua regia is a strong oxidizing agent. Wear protective clothing and a face shield.]*

**13.5.2** The ground-glass joints of the torch-spray chamber should be greased with a good grade of non-silicone base stopcock grease. After reassembly, the torch must be optimized for maximum flux throughput according to manufacturer's instructions.

**13.5.3** Should the plasma be extinguished during an analysis session, the session must be ended. Restandardization is necessary after the plasma is reignited. Restandardization must be delayed until the reflected power has been at a minimum for approximately 10 min.

## 14. Method Safety

The toxicity or carcinogenicity of each reagent used in this method has not been defined precisely; however, each chemical compound should be treated as a potential health hazard. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material handling data sheets should be made available to all personnel involved in the chemical analysis.

## 15. References

1. "Standard Operating Procedures for the ICP-DES Determination of Trace Elements in Suspended Particulate Matter Collected on Glass-Fiber Filters," EMSL/RTP-SOP-EMO-002, Revision, October, 1983.

2. "Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," *Code of Federal Regulations*, Title 40, Part 50, Appendix B, pp. 12-16 (July 1, 1975).

3. "Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air.," *Federal Register* 43 (194): 46262-3, 1978.

4. Rhodes, R. C., 1981, "Special Extractability Study of Whatman and Schleicher and Schuell Hi-Vol Filters," Memo to file, August 5, 1981, Quality Assurance Division, Environmental Monitoring Systems Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, NC.

5. Ward, A. F., *The Jarrell-Ash Plasma Newsletter*, Volumes I, II, and III.

6. Nygaard, D., and Sot, J. J., "Determination Near the Detection Limit: A Comparison of Sequential and Simultaneous Plasma Emission Spectrometers," *Spectroscopy*, Vol. 3(4).

7. "Simplex Optimization of Multielement Ultrasonic Extraction of Atmospheric Particulates," Harper, et. al., *Analytical Chemistry*, Vol. 55(9), August 1983.

TABLE 1. TYPICAL CONCENTRATIONS OF THE MOST CONCENTRATED WORKING STANDARD,[1] TYPICAL ICP CALIBRATING SENSITIVITIES AND TYPICAL METHOD DETECTION LIMITS[2]

| Element | Most Conc. Working Std., mg/L | Calibrating Sensitivity, counts/Fg metal | Detection[3] Limit | |
|---|---|---|---|---|
| | | | mg/L | ng/m$^3$ |
| Al | 50.0 | 4,887 | 0.061 | 13.5 |
| As | 5.0 | 5,063 | 0.025 | 5.5 |
| Au | 5.0 | 11,683 | 0.009 | 1.9 |
| B | 10.0 | 42,892 | 0.030 | 6.6 |
| Ba | 10.0 | 13,430 | 0.003 | 0.7 |
| Be | 2.0 | 57,457 | 0.002 | 0.4 |
| Bi | 10.0 | 467 | 1.030 | 226.6 |
| Ca | 40.0 | 52,787 | 0.103 | 22.7 |
| Cd | 4.0 | 37,438 | 0.005 | 1.1 |
| Ce | 5.0 | 13,859 | 0.048 | 10.6 |
| Co | 5.0 | 2,787 | 0.015 | 3.3 |
| Cr | 4.0 | 76,772 | 0.012 | 2.6 |
| Cu | 20.0 | 159,213 | 0.010 | 2.2 |
| Fe | 50.0 | 16,985 | 0.034 | 7.5 |
| Ge | 5.0 | 1,645 | 0.079 | 17.5 |
| Hg | 5.0 | 9,031 | 0.055 | 12.1 |
| In | 5.0 | 520 | 0.081 | 18.5 |
| K | 20.0 | 253 | 0.205 | 45.1 |
| La | 2.0 | 44,468 | 0.007 | 1.5 |
| Li | 2.0 | 12,500 | 0.003 | 0.7 |
| Mg | 40.0 | 70,951 | 0.024 | 5.3 |
| Mn | 10.0 | 108,751 | 0.004 | 0.9 |
| Mo | 5.0 | 5,266 | 0.009 | 1.9 |
| Na | 80.0 | 186 | inoperative | inoperative |
| Nb | 2.0 | 59,859 | 0.11 | 2.4 |
| Ni | 5.0 | 4,306 | 0.014 | 3.1 |
| P | 20.0 | 2,941 | 0.104 | 22.9 |
| Pb | 25.0 | 10,324 | 0.032 | 7.0 |
| Pd | 5.0 | 7,996 | 0.130 | 7.0 |
| Pt | 5.0 | 847 | 0.107 | 23.5 |
| Re | 10.0 | 288 | 0.150 | 33.0 |
| Rh | 5.0 | 32,421 | 2.000 | 440.0 |
| Ru | 10.0 | 5,227 | 0.187 | 41.1 |
| Sb | 5.0 | 4,246 | 0.025 | 5.5 |
| Se | 5.0 | 930 | 0.156 | 34.3 |
| Si | 50.0 | 9,152 | 0.172 | 37.8 |
| Sm | 5.0 | 52,532 | 0.024 | 5.4 |
| Sn | 5.0 | 469 | 0.042 | 9.2 |
| Sr | 5.0 | 55,091 | 0.001 | 0.2 |
| Ta | 5.0 | 21,030 | 0.145 | 52.1 |
| Te | 5.0 | 4,676 | 0.021 | 4.6 |
| Ti | 5.0 | 58,777 | 0.003 | 0.7 |
| Tl | 5.0 | 3,063 | 0.152 | 33.4 |
| V | 5.0 | 107,250 | 0.007 | 1.5 |
| W | 5.0 | 1,170 | 0.057 | 12.5 |
| Y | 5.0 | 35,800 | 0.004 | 0.9 |
| Zn | 20.0 | 478 | 0.120 | 26.4 |
| Zr | 5.0 | 18,010 | 0.008 | 1.8 |

[1]The least concentrated working standard contains no metals.
[2]Data source is 48 determinations of standard No.1 made from 01/26/83--03/22/83 during analysis of 1982 NAMS filters.
[3]Based upon sampling rate of 1.13 m$^3$/min for 24-hr for a total sample volume of 1627.2 m$^3$; factor of 9 for partial filter analysis; digestion of 0.020 L/filter.

TABLE 2. RECOVERIES FROM SPIKED STRIPS[1] AND FROM NIST SRM 1648

| Element | % Recovery | %RSD |
|---|---|---|
| Spiked Strips[1] | | |
| As | 96.5 | 2.7 |
| Co | 95.5 | 3.4 |
| Cu | 76.1 | 4.3 |
| Fe | 98.3 | 3.7 |
| Mn | 96.9 | 4.0 |
| Ni | 96.4 | 3.9 |
| Pb | 99.1 | 1.9 |
| Sr | 96.4 | 4.4 |
| V | 94.0 | 2.1 |
| Zn | 89.4 | 6.2 |
| NIST SRM 1648 | | |
| Ba | 80 | 0.8 |
| Be | not listed by NIST | |
| Cd | 114 | 8.5 |
| Cu | 100 | 1.4 |
| Fe | 68 | 1.4 |
| Mn | 88 | 1.6 |
| Mo | not listed by NIST | |
| Ni | 90 | 9.0 |
| Pb | 95 | 1.1 |
| V | 79 | 1.9 |
| Zn | 97 | 3.8 |

[1]Recovery values based on X-ray fluorescence analytical values taken as "true".

TABLE 3. TYPICAL PRECISION, BIAS, AND CORRELATION COEFFICIENTS OBTAINED BY SAMPLE/REPLICATE PAIR ANALYSIS[1]

| Element | Pairs Found | Coefficient Variation (%) | Coefficient Bias (%) | Coefficient |
|---|---|---|---|---|
| B | 32 | 10 | 1.0 | 0.95 |
| Ba | 32 | 9 | 0 | 1.0 |
| Cd | 17 | 11 | 0 | 1.0 |
| Cu | 32 | 4 | -1.0 | 1.0 |
| Fe | 32 | 8 | 1.0 | 0.99 |
| Mn | 32 | 21 | 5.0 | 0.99 |
| Ni | 14 | 10 | -2.0 | 1.0 |
| Pb | 31 | 3 | 0.0 | 1.0 |
| Sb | 4 | 5 | 3.0 | 0.99 |
| Sr | 32 | 7 | 1.0 | 1.0 |
| V | 25 | 6 | -1.0 | 1.0 |
| Zn | 31 | 16 | -3.0 | 0.94 |

[1]Based on the analysis of 32 sample/replicate pairs of 1982 NAMS filters from 01/26/83 - 03/22/83. Because these data were obtained from real samples, there was no control over the actual concentrations. Elements displaying a large coefficient of variation tended to have mean concentrations in the lower end of the quantifiable range.

TABLE 4. ICP SPECTROMETER ELEMENTS WITH WAVELENGTHS

| Element | Wavelength | Element | Wavelength |
|---|---|---|---|
| Al | 308.22 | Nb | 316.34 |
| As | 193.76 | Ni | 231.60 |
| Au | 242.80 | P | 214.91 |
| B | 249.77 | Pb | 220.35 |
| Ba | 493.41 | Pd | 363.47 |
| Be | 313.04 | Pt | 265.95 |
| Bi | 195.33 | Re | 209.24 |
| Ca | 396.85 | Rh | 343.49 |
| Cd | 226.50 | Ru | 297.66 |
| Ce | 446.02 | Sb | 206.84 |
| Co | 228.62 | Se | 196.09 |
| Cr | 357.87 | Si | 288.16 |
| Cu | 324.75 | Sm | 442.43 |
| Fe | 259.94 | Sn | 189.99 |
| Ge | 199.82 | Sr | 407.77 |
| Hg | 253.65 | Ta | 240.06 |
| In | 230.69 | Te | 214.28 |
| K | 766.49 | Ti | 334.90 |
| La | 379.48 | Tl | 351.92 |
| Li | 670.78 | V | 292.40 |
| Mg | 279.55 | W | 202.99 |
| Mn | 257.61 | Y | 371.03 |
| Mo | 202.03 | Zn | 206.19 |
| Na | 589.00 | Zr | 339.20 |

TABLE 5. CORRECTION FACTORS FOR SPECTRAL INTERFERENCES

| Affecting Element | Affecting Factor | Affected Element | Affecting Element | Affecting Factor | Affected Element |
|---|---|---|---|---|---|
| Ta | 0.0166 | Co | Bi | 0.0268 | Rh |
| Ta | 0.0026 | Fe | Bi | 0.0116 | Se |
| Al | 0.0141 | Ta | Bi | 0.0041 | Si |
| Al | 0.0375 | V | Bi | 0.0125 | Sr |
| B | 0.0181 | Zr | Ge | 0.0071 | Al |
| Be | 0.0020 | Nb | Ge | 0.0015 | Be |
| Be | 0.0025 | V | Ge | 0.0085 | Mo |
| Ce | 0.2313 | V | Ge | 0.0293 | Nb |
| Hg | 0.0574 | Co | Ge | 0.1489 | Ta |
| Hg | 0.0151 | Fe | P | 0.0017 | Al |
| La | 0.0028 | Fe | P | 0.0265 | Cu |
| La | 0.0122 | V | P | 0.0016 | Fe |
| Pb | 0.1104 | Nb | P | 0.0032 | Mg |
| Pd | 0.0247 | Nb | P | 0.0100 | Nb |
| Pd | 0.1649 | Sm | P | 0.0017 | Si |
| Pd | 0.0125 | Ti | P | 0.0010 | Zn |
| Pt | 0.0600 | Cr | Re | 0.0240 | Al |
| Pt | 0.0175 | Nb | Re | 0.0110 | B |
| Pt | 0.1300 | Ta | Re | 0.1609 | Mn |
| Pt | 0.0210 | V | Re | 1.2400 | Mo |
| Si | 0.0281 | Nb | Re | 0.0556 | Pd |
| Si | 0.1300 | Ta | Re | 0.0044 | Si |
| Si | 0.2495 | Zr | Re | 0.2146 | V |
| Te | 0.0254 | V | Ru | 0.0141 | Fe |
| Tl | 0.0607 | Ce | Ru | 0.0843 | Mn |
| Tl | 0.0229 | Zr | Ru | 0.0233 | Mo |
| Zn | 0.0132 | Ta | Ru | 0.0827 | Nb |
| As | 0.0119 | A1 | Ru | 0.2531 | Ta |
| As | 0.1736 | Pt | Ru | 0.0364 | Ti |
| As | 0.0125 | V | Ru | 5.5170 | V |
| Bi | 0.0083 | A1 | Ru | 0.4996 | Zr |
| Bi | 0.0212 | Cr | W | 0.0021 | Al |
| Bi | 0.0065 | Fe | W | 0.0039 | Mg |
| Bi | 0.0326 | La | W | 0.0027 | Zn |
| Bi | 0.0155 | Mg | As | 0.0218 | Ge |
| Bi | 0.0312 | Mn | | | |

TABLE 6. EXAMPLE REQUIRED QUALITY CONTROL REQUIREMENTS FOR ICP ANALYSIS

| QC procedure | Typical frequency | Criteria |
|---|---|---|
| Initial calibration (IC) | At the beginning of the analysis | None |
| Initial calibration verification (ICV) | Immediately after initial calibrations | 90-110% of the actual concentration |
| Initial calibration blank (ICB) | Immediately after initial calibration verification | Must be less than project detection limits |
| High standard verification (HSV ) | Following the initial calibration blank analysis | 95-105% of the actual concentration |
| Interference check standard (ICS) | Following the high standard verification, every 8 hours, and at the end of a run | 80-120% of the actual concentration |
| Continuing calibration verification (CCV) | Analyzed before the first sample, after every 10 samples, and at the end of the run | 90-110% of the actual concentration |
| Continuing calibration blanks (CCBs) | Analyzed following each continuing calibration verification | Must be less than project detection limits (MDLs) |
| Reagent blank (RB) | 1 per 40 samples, a minimum of 1 per batch | Must be less than project detection limits |
| Laboratory control spike (LCS) | 1 per 20 samples, a minimum of 1 per batch | 80-120% recovery, with the exception of Ag and Sb |
| Duplicate and/or spike duplicate | 1 per sample batch | RPD # 20% |
| Matrix spike (MS) | 1 per 20 samples per sample batch | Percent recovery of 75-125% |
| Serial dilution | 1 per sample batch | 90-110% of undiluted sample |
| Sample dilution | Dilute sample beneath the upper calibration limit and at least 5X the MDL | As needed |

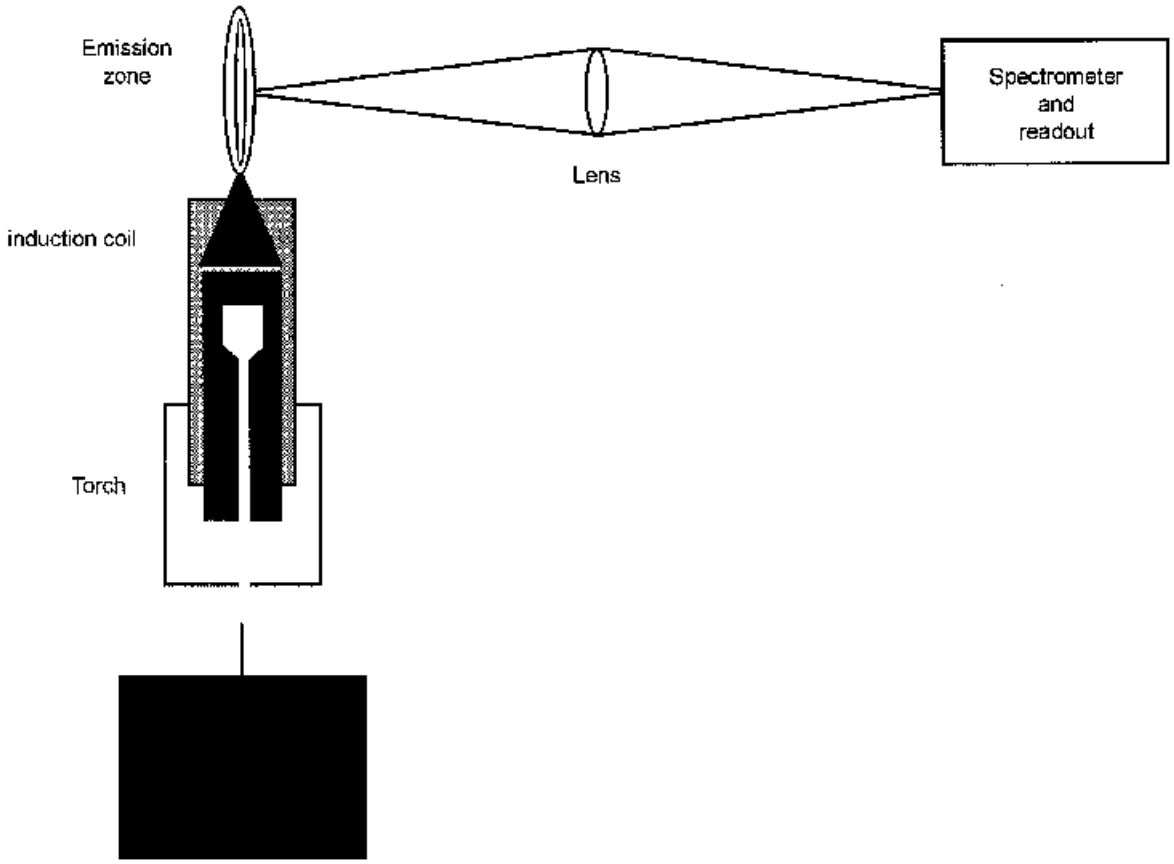


Figure 1. Schematic diagram of a typical inductively coupled plasma-optical emission spectroscopy instrument featuring parts of the instrument most important to the user.

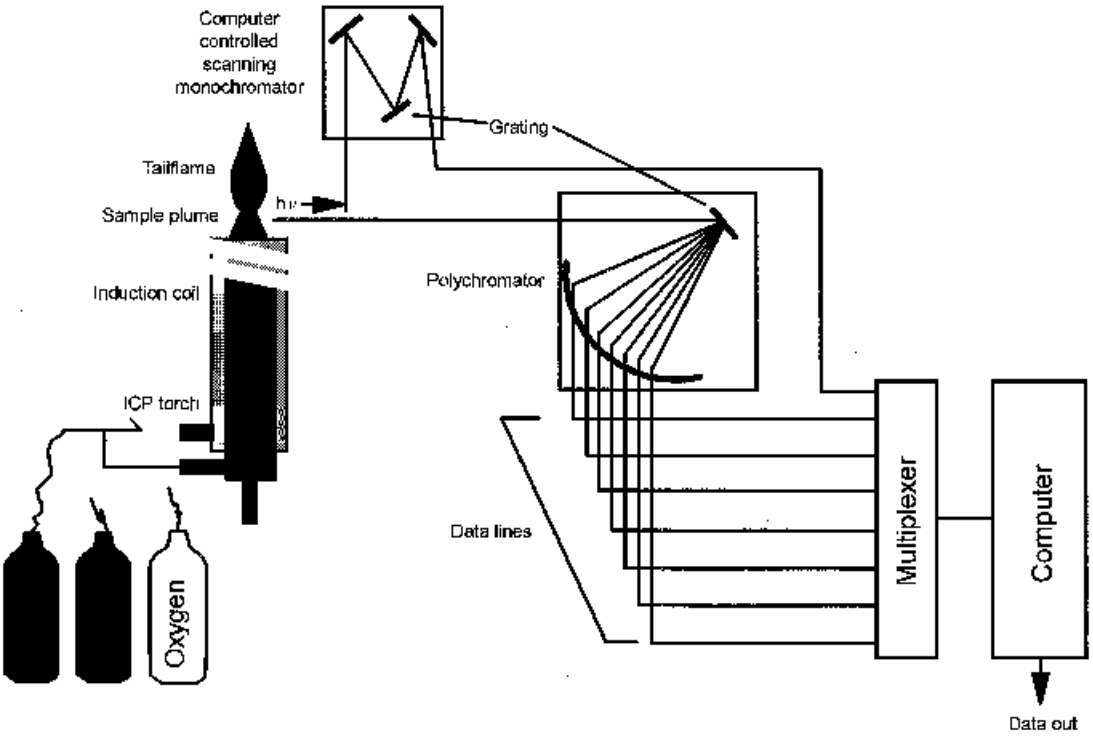


Figure 2. Simultaneous or sequential multi-element determination of trace elements by ICP.

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# APPENDIX D
# FIELD MONITORING / SAMPLING FORM

# FIELD DATA SHEET

Dona Park Neighborhood Air Monitoring Program

Operator Name / Company: _____ Date: _____

**Comments:**

**Formulas:**

Average Flow (L/min) = (Pre cal + Post Cal)/2

Sample Volume(Liters = Avg Flow (L/min) X Duration (min)

*Please Send Copy of this form to Chester LabNet with the COC.*

**Labeling for COC:**

**DP-TCEQ-YYMMDD-LOC-LOC2-XX[-QQ]**

| | |
|---|---|
| ***DP_TCEQ*** | Project |
| ***YYMMDD*** | Date (year, month, day: 20110415) |
| ***LOC*** | Location (UP and DW) |
| ***LOC2*** | Sample Location (DP-1, etc) |
| ***XX*** | Lab Analysis (ML = Metals; ASB = Asbestos) |
| ***QQ*** | Optional QA Flag (TB = trip blank, FB = field blank; SC = duplicate) |

## Upwind

***SAMPLE COLLECTION DATA***

| | | | |
|---|---|---|---|
| PQ200# | | PQ200# | |
| Avg Flow (L/min) | | Avg Flow (L/min) | |
| Start time | | Start time | |
| End Time | | End Time | |
| Duration in minutes | | Duration in minutes | |
| Sample Volume (Liters) | | Sample Volume (Liters) | |
| GPS Location | | GPS Location | |
| **ID #** | | **ID #** | |
| **Filter #** | | **Filter #** | |

### Upwind E-BAM PM10

E-BAM SN M2404

DATALOGGER 16708

EBAM LEAK CHECK PASS / FAIL

START TIME: _____

END TIME: _____

## Downwind

***SAMPLE COLLECTION DATA***

| | | | |
|---|---|---|---|
| PQ200# | | PQ200# | |
| Avg Flow (L/min) | | Avg Flow (L/min) | |
| Start time | | Start time | |
| End Time | | End Time | |
| Duration in minutes | | Duration in minutes | |
| Sample Volume (Liters) | | Sample Volume (Liters) | |
| GPS Location | | GPS Location | |
| **ID #** | | **ID #** | |
| **Filter #** | | **Filter #** | |

### Downwind E-BAM PM2.5 (w/cyclone)

E-BAM SN M2406

DATALOGGER 16709

EBAM LEAK CHECK PASS / FAIL

LOCATION 1: _____

Start time: _____

End time: _____

LOCATION 2: _____

Start time: _____

End time: _____

# APPENDIX E
# APPLICABLE TCEQ STANDARD OPERATING PROCEDURES

# STANDARD OPERATING PROCEDURE NO. 14.1
# AIR SAMPLING AND MONITORING DESIGN

## 1.0 METHOD SUMMARY

This standard operating procedure (SOP) provides guidance in developing and implementing sampling plans to assess the impact of hazardous waste sites on ambient air. It is not within the scope of this SOP to provide a generic air sampling plan. Experience, objectives, site characteristics, and chemical characteristics will dictate sampling strategy. This SOP does not address indoor air sampling.

## 2.0 EQUIPMENT/APPARATUS/REAGENTS

### 2.1 Tools/Material and Equipment List

- Camera
- Clipboard
- Laptop computer
- Site logbook

## 3.0 PROCEDURES

### 3.1 Air Monitoring Design

#### 3.1.1 Initial Surveys

In general, the initial survey is considered to be a relatively rapid screening process for collecting preliminary data at hazardous waste sites. However, initial surveys may require many hours to complete and may consist of more than one entry.

Some information is generally known about the site; therefore, real-time instrumentation for specific compounds (i.e., detector tubes and electrochemical sensors) can be used to identify hot spots. Sufficient data should be obtained with real-time instruments during the initial entry to screen the site for various contaminants. When warranted, intrinsically safe or explosion-proof instruments should be used. An organic vapor analyzer (OVA) is typically used during this survey. These gross measurements may be used on a preliminary basis to (1) determine levels of personal protection, (2) establish site work zones, and (3) map candidate areas for more thorough qualitative and quantitative studies involving air sampling.

In some situations, the information obtained may be sufficient to preclude additional monitoring.

Materials detected during the initial survey may call for a more comprehensive evaluation of hazards and analyses for specific compounds. Since site activities and weather conditions change, a continuous program to monitor the ambient atmosphere must be established.

#### 3.1.2 Off-Site Monitoring

Typically, perimeter monitoring with the same instruments employed for on-site monitoring is utilized to determine site boundaries. Because air is a dynamic matrix, physical boundaries like property lines and fences do not necessarily delineate the site boundary or area influenced by a release. Whenever possible, atmospheric hazards in the areas adjacent to the on-site zone should be monitored with direct- reading instruments. Monitoring at the fenceline or at varying locations off site provides useful information regarding pollutant migration. Three to four locations downwind of the source (i.e., plume) at breathing-zone height, provide a basic fingerprint of the plume. Negative instrument readings off site should not be interpreted as the complete

absence of airborne toxic substances; rather, they should be considered another piece of information to assist in the preliminary evaluation. The interpretation of negative readings is instrument-dependent. The lack of instrument readings off site should not be interpreted as the complete absence of all airborne toxic substances; rather, it is possible that the particular compound or class of compounds to which the monitoring instrument responds is not present or that the concentration of the compound(s) is below the instrument's detection limit.

### 3.2 Air Sampling Design

#### 3.2.1 Sampling Plan Design

The goal of air sampling is to accurately assess the impact of a contaminant source(s) on ambient air quality. This impact is expressed in terms of overall average and/or maximum air concentrations for the time period of concern and may be affected by the transport and release of pollutants from both on- and off-site sources. The location of these sources must be taken into account as they impact the selection of sampling locations. Unlike soil and groundwater concentrations, air concentrations at points of interest can easily vary by orders of magnitude over the period of concern. This variability plays a major role in designing an air sampling plan.

Downwind air concentration is determined by the amount of material being released from the site into the air (the emission rate) and by the degree that the contamination is diluted as it is transported. Local meteorology and topography govern downwind dilution. Contaminant emission rates can also be heavily influenced by on-site meteorology and on-site activities. All of these concerns must be incorporated into an air sampling plan.

A sampling strategy can be simple or complex, depending on the sampling program objectives. Programs involving characterization of the pollutant contribution from a single point source tend to be simple, whereas sampling programs investigating fate and transport characteristics of components from diverse sources require a more complex sampling strategy. In addition, resource constraints may affect the complexity of the sampling design.

An optimal sampling strategy accounts for the following site parameters:

- Location of stationary as well as mobile sources
- Access to the sampling location
- Analytes of concern
- Analytical detection limit to be achieved
- Rate of release and transport of pollutants from sources
- Availability of space and utilities for operating sampling equipment
- Meteorological monitoring data
- Meteorological conditions in which sampling is to be conducted

The sampling strategy typically requires that the concentration of contaminants at the source or area of concern as well as background contributions be quantified. It is important to establish background levels of

contaminants in order to develop a reference point from which to evaluate the source data. Field blanks and lot blanks, as well as various other types of QA/QC samples, can be utilized to determine other sources. The impact of extraneous sources on sampling results can frequently be accounted for by placing samplers upwind, downwind and crosswind from the subject source. The analytical data from these different sampling locations may be compared to determine statistical differences.

### 3.2.2 Sampling Objectives

The objectives of the sampling must be determined prior to developing the sampling plan. Does the sampling plan verify adequate levels of protection for on-site personnel, or address potential off-site impacts associated with the site or with site activities? In addition, the assumptions associated with the sampling program must be defined. These assumptions include whether the sampling is to take place under "typical," "worst case," or "one-time" sampling conditions. If the conditions present at the time of sampling are different from those assumed during the development of the sampling plan, then quality of the data collected may be affected. The following definitions have been established:

- Typical: routine daily sampling or routine scheduled sampling at pre-established locations.
- Worst case: sampling conducted under the worst meteorological and/or site conditions which would result in elevated ambient concentrations.
- One-time: only one chance is given to collect a sample without regard to time or conditions.

Qualitative data acquired under these conditions are usually applicable only to the time period during which the data were collected and may not provide accurate information to be used in estimating the magnitude of an air impact during other periods or over a long time interval.

The sampling objectives also dictate the detection limits. Sampling methods for airborne contaminants will depend upon the nature and state (solid, liquid or gas) of the contaminant. Gases and vapors may be collected in aqueous media or adsorbents, in molecular sieves, or in suitable containers. Particulates are collected by filters or impactors. The volume of sample to be collected is dependent upon an estimate of the contaminant concentration in the air, the sensitivity of the analytical method, and the standard or desired detection limit. A sufficient amount of sample must be collected to achieve the desired detection limit without interference from other contaminants. In addition, the selected method must be able to detect the target compound(s).

### 3.2.3 Location and Number of Individual Sampling Points

Choose the number and location of sampling points according to the variability, or sensitivity, of the sampling and analytical methods being utilized, the variability of contaminant concentration over time at the site, the level of precision required and cost limitations. In addition, determine the number of locations and placement of samplers by considering the nature of the response, local terrain, meteorological conditions, location of the site (with respect to other conflicting background sources), size of the site, and the number, size, and relative proximity of separate on-site emission sources and upwind sources. The following are several considerations for sampler placement:

- Location of potential on-site emission sources, as identified from the review of site background information or from preliminary on-site inspections.
- Location of potential off-site emission sources upwind of the sampling location(s). Review local wind patterns to determine the location of off-site sources relative to wind direction.
- Topographic features that affect the dispersion and transport of airborne toxic constituents.

Avoid natural obstructions when choosing air sampling station locations, and account for channelization around those obstructions.

- Large water bodies, which affect atmospheric stability and the dispersion of air contaminants.
- Roadways (dirt or paved), which may generate dust that could mask site contaminants.
- Vegetation, such as trees and shrubs, which stabilizes soil and retards subsurface contaminants from becoming airborne. It also affects air flow and scrubs some contaminants from the air. Sometimes thick vegetation can make an otherwise ideal air monitoring location inaccessible.

Consider the duration of sampling activities when choosing the location and number of samples to be collected. For example, if the sampling period is limited to a few hours, one or two upwind and several downwind samples would typically be adequate, especially around major emission sources.

A short-term monitoring program ranges from several days to a few weeks and generally includes gathering data for site assessments, removal actions, and source determination data (for further modeling). Activities involved in a short-term sampling strategy must make the most of the limited possibilities for data collection. Consider moving upwind/downwind locations daily based on National Oceanic and Atmospheric Administration (NOAA) weather forecasts. Weather monitoring becomes critical where complex terrain and local meteorological effects frequently change wind direction. Often, a number of alternatives can fulfill the same objective.

Prevailing winds running the length of a valley usually require a minimum number of sampler locations; however, a complex valley may require more sampler locations to account for the wide variety of winds. Ocean/lake effects may require a radical plan to collect enough samples to reach a low detection limit.

Two sets of samplers may be placed next to each other: one set would be activated during the sea breeze while the other set is turned off, and vice versa when there is no sea breeze. After the sampling event, the respective upwind and downwind samples would be combined. Another alternative for sampling near a large body of water may be to use automatic, wind- vector-operated samplers, which turn the sampler on only when the wind comes from a specified vector. At sites located on hillsides, wind will move down a valley and produce an upward fetch at the same time. Sampling locations may have to ring the site to measure the wind's impact.

Off-site sources may affect on-site monitoring. In this case, on-site meteorological data, concurrent with sampling data, is essential to interpreting the acquired data. Also, additional upwind sampling sites may be

needed to fully characterize ambient background contaminant levels. Multiple off-site sources may require several monitoring locations, but if the sources are at a sufficient distance, only one monitoring location is needed.

Topography and weather are not the only factors in sampler location; the sampling sites must be secure from vandals and mishap. Secure all sampling locations to maintain chain of custody, and to prevent tampering with samples or loss of sampling units. High-volume sampling methods often require the use of 110 VAC electric power. When portable generators are used, the power quality may affect sampler operation. Also, be aware that the generators themselves could be a potential pollution source if their placement is not carefully considered.

Air quality dispersion models can be used to place samplers. The models incorporate source information, surrounding topography, and meteorological data to predict the general distance and directions of maximum ambient concentrations. Modeling results should be used to select sampling locations in areas of maximum pollutant concentrations.

### 3.2.4 Time, Duration and Frequency of Sampling Events

After choosing appropriate sampling or monitoring locations, determine the sampling frequency and the number of samples to be collected. The time of day, duration and frequency of sampling events is governed by:

- The effects of site activities and meteorology on emission rates
- The diurnal effect of the meteorology on downwind dispersion
- The time period(s) of concern as defined by the objective
- The variability in the impact from other off-site sources
- If defined, the degree of confidence needed for either the mean or maximum downwind concentrations observed
- The precision requirements for single measurements
- Cost and other logistical considerations

The duration of the removal action and the number of hours per day that site work is conducted determine the time, duration, and frequency of samples. Short-term sampling programs may require daily sampling, while long-term programs may require 24-hour sampling every sixth or twelfth day. If the site will be undergoing removal activities 24 hours a day, continuous air sampling may be warranted. However, if the site activities will be conducted for only eight hours a day, and there are no emissions likely to occur during the remaining 16 hours, then sampling would be appropriate prior to the start of daily activities, would continue during operations, and end at the conclusion of the daily activities. An off-peak sample collection can ensure that emissions are not persisting after the conclusion of daily cleanup activities. For some sites, emissions are still a factor several hours after daily site activities have been completed. Because of the typically decreased downwind dispersion in the evening, higher downwind concentrations than were present during daytime site activities may be detected. For sites where this is possible, the sampling duration needs to be lengthened accordingly.

Sampling duration and flow rate dictate the volume of air collected, and to a major degree, the detection limit. The analytical method selected will provide a reference to flow rate and volume. Flow rates are limited to the

capacity of the pumps being employed and the contact time required by the collection media.

The duration or period of air sampling is commonly divided into two categories (1) samples collected over a brief time period are referred to as "instantaneous" or "grab" samples and are usually collected in less than five minutes and (2) average or integrated samples are collected over a significantly longer period of time. Integrated samples provide an average concentration over the entire sampling period. Integrated samples are not suited to determining cyclical releases of contaminants because periodic or cyclical events are averaged out by the proportionally long sampling duration.

Air quality dispersion models can predict the maximum air contaminant concentration expected from a source. The meteorological and site conditions expected to cause the highest concentration are known as worst-case conditions and can be identified by analyzing the modeling results. Depending upon the objective, one may sample when the model predicts worst-case conditions will exist.

## 4.0 CAUTIONS AND INTERFERENCES

### 4.1 Meteorological Cautions and Interferences

A meteorological monitoring program is an integral part of site monitoring activities. Meteorological data, which define local terrain impacts on air flow paths, are needed to interpret air concentration data.

Meteorological data may be available from an existing station located near the site (i.e., at a local airport), otherwise a station should be set up at the site. This data will document the degree that samples actually were downwind and verify whether other worst-case assumptions were met. Meteorological parameters to be monitored are, at a minimum, wind speed, wind direction, and sigma theta (which is the horizontal wind direction standard deviation and an indicator of atmospheric stability). The remaining parameters primarily affect the amount of a contaminant available in the air.

#### 4.1.1 Wind Speed

When the contaminant of concern is a particulate, wind speed is critical in determining whether the particulate will become airborne, the quantity of the particulate that becomes airborne, and the distance the particulate will travel from the source. Wind speed also contributes to the volatilization of contaminants from liquid sources. Also, under stagnant wind conditions, exhaust air can be re-sampled.

#### 4.1.2 Wind Direction

Wind direction highly influences the path of airborne contaminants. In addition, variations in wind direction increase the dispersion of pollutants from a given source. Upwind sources can contribute to sample concentration. During periods when the sampler is inoperative, particulate matter may be deposited on the filter by wind.

#### 4.1.3 Atmospheric Stability

Atmospheric stability refers to the degree to which the atmosphere tends to dampen vertical and horizontal motion. Stable atmospheric conditions (i.e., evenings) result in low dispersion, and unstable atmospheric

conditions (i.e., hot sunny days) result in higher dispersion.

#### 4.1.4 Temperature

Higher temperatures increase the rate of volatilization of organic and some inorganic compounds and affect the initial rise of gaseous or vapor contaminants. Therefore, worst-case emission of volatiles and semivolatiles occurs at the hottest time of day, or on the hottest day.

#### 4.1.5 Humidity

High humidity affects water-soluble chemicals and particulates. Humid conditions may dictate the sampling media used to collect the air sample, or limit the volume of air sampled and thereby increase the detection limit.

#### 4.1.6 Atmospheric Pressure

Migration of landfill gases through the landfill surface and through surrounding soils are governed by changes in atmospheric pressure. Atmospheric pressure will influence upward migration of gaseous contaminants from shallow aquifers into the basements of overlying structures. In many cases, the transport and dispersion of air pollutants is complicated by local meteorology.

#### 4.1.7 Physical/Chemical Considerations

Normal diurnal variations (i.e., temperature inversions) affect dispersion of airborne contaminants. Terrain features can enhance or create air inversions and can also influence the path and speed of air flow, complicating transport and dispersion patterns. The chemical characteristics of a contaminant (i.e., molecular weight, physical state, vapor pressure, aerodynamic size, temperature, reactive compounds, and photodegradation) affect its behavior and can influence the method used to sample and analyze it.

### 4.2 Other Influences

#### 4.2.1 Loss of Volatiles

During subsequent sampling, shipping, or storage of the filter prior to the post-sampling weighing, volatile particles collected on the filter can be lost. Thus, the filter should be re-weighed as soon as practical after sampling.

#### 4.2.2 Artifact Particulate Matter

A higher than true TSP determination can result from artifact particulate matter forming on the surface of alkaline glass fiber filters by oxidation of acid gases in the sample air.

#### 4.2.3 Filter Handling

The filter should be handled carefully between the pre-sampling and post-sampling weighing in order to avoid loss of fibers or particles from the filter. To minimize error from handling, a filter paper cartridge or cassette can be used to protect the filter.

### 4.3 Detection Limits

Detection limits depend on the contaminants being investigated and the particular site situation. It is important to know why the data are needed and how the data will be used. Care should be taken to ensure the detection limits are adequate for the intended use of the final results. Some equipment may be sensitive to humidity and temperature extremes.

# STANDARD OPERATING PROCEDURE NO. 14.2
# AIR SAMPLING USING A HIGH VOLUME SAMPLER

## 1.0 METHOD SUMMARY

This standard operating procedure (SOP) provides guidance for the collection of total suspended particulates (TPS) using high-volume samplers. These guidelines are derived from 40 CFR 50 Chapter I, Appendix B.

## 2.0 EQUIPMENT/APPARATUS/REAGENTS

### 2.1 High-Volume, TSP Samplers

High-volume TSP samplers collect all suspended particles by drawing air across an 8- by 10-inch glass-quartz filter. The sample rate is adjusted to 40 cubic feet per minute (CFM), or 1,134 liters per minute (L/min), and it is held constant by a flow controller over the sample period. The mass of TSPs can be determined by weighing the filter before and after sampling. The composition of the filter varies according to the analytical method and the detection limit required.

### 2.2 Equipment List

- Camera
- Site logbook
- Clipboard
- Chain of custody records
- Custody seals
- Air sampling worksheets
- Filters supplied by the EPA National Filter Distribution Program
- High-volume sampler
- Sampler Shelter
- Flow rate measurement devices
- Manometer
- Thermometer
- Barometer
- Timing/control device
- Flow rate transfer standard, traceable to a primary standard
- Filter conditioning environment
- Analytical balance
- Area light source
- Numbering device (capable of printing identification numbers on the filters before they are placed in the filter conditioning environment)
- Positive displacement standard volume meter
- Stop-watch
- High-Volume air pump
- Large diameter rubber stopper, wide cellophane tape, or other means
- blower motor
- Glassine envelope or manila folder.

## 3.0 PROCEDURES

### 3.1 Calibration

These calibration instructions are based on 40 CFR 50 Chapter I, Appendix B, 9.0. Calibration of the high-volume samplers flow indicating device or control devices is necessary to establish traceability of the field measurement to primary standard via a flow rate transfer standard.

**3.1.1 Certification of the flow indicator.**

1. Get a positive displacement standard volume meter, stop-watch, manometer, thermometer, and barometer.
2. Connect the flow rate transfer standard to the inlet of the standard volume meter.
3. Connect the manometer to measure the pressure at the inlet of the standard volume meter.
4. Connect the orifice manometer to the pressure tap on the transfer standard.
5. Connect the high volume air pump to the outlet side of the standard volume meter.
6. Check for leaks by clamping both manometer lines and blocking the orifice with a large-diameter rubber stopper, wide cellophane tape, or other means. Start the high-volume air pump and note any changes in the standard volume meter reading. The reading should stay constant but if it does not, check for leaks.
7. Un-clamp both manometer lines and zero both manometers.
8. By means of variable flow resistance in the transfer standard or by varying the voltage to the air pump, achieve the appropriate flow rate through the system. The system requires at least five different but constant flow rates with at least three in the specified flow interval of 1.1 to 1.7 $m^3$/min or 39-60 $ft^3$/min.
9. Observe the barometric pressure and record as $P_1$.
10. Read the ambient temperature in the vicinity of the standard volume meter and record it as $T_1$.
11. Start the blower motor, adjust the flow, and allow the system to run for at least 1 min for a constant motor speed to be attained.
12. Observe the standard volume meter reading and simultaneously start a stopwatch. Record the initial meter reading ($V_i$).
13. Maintain this constant flow rate until at least 3 $m^3$ of air have passed through the standard volume meter. Record the standard volume meter inlet pressure manometer reading as ÄP, and the orifice manometer reading as ÄH. Be sure to indicate the correct units of measurement.
14. Observe the standard volume meter reading while simultaneously stopping the stopwatch. Record the final meter reading ($V_f$) and the elapsed time (t).
15. Calculate the volume measured by the standard volume meter at meter conditions of temperature and pressures as $V_m=V_f-V_i$.
16. Correct this volume to standard volume (std $m^3$) as follows:

$V_{std} = V_m((P_1 - D_P)T_{std})/(P_{std}T_1)$

where:

$V_{std}$=standard volume, std $m^3$;

$V_m$=actual volume measured by the standard volume meter;

$P_1$=barometric pressure during calibration, mm Hg or kPa;

ÄP=differential pressure at inlet to volume meter, mm Hg or kPa;

$P_{std}$=760 mm Hg or 101 kPa;

$T_{std}$=298 K;

$T_1$=ambient temperature during calibration, K.

Calculate the standard flow rate (std $m^3$/min) as follows:

$$Q_{std} = V_{std}/t$$

where:

$Q_{std}$=standard volumetric flow rate, std $m^3$/min

t=elapsed time, minutes.

Record Qstd to the nearest 0.01 std $m^3$/min.

17. Repeat steps 12 through 16 for at least four additional constant flow rates, evenly spaced over the approximate range of 1.0 to 1.8 std $m^3$/min (35-64 $ft^3$/min).

18. For each flow, compute

- (ÄÄH $(P_1/P_{std})(298/T_1)$)

and plot these value against Qstd. Be sure to use consistent units (mm Hg or kPa) for barometric pressure. Draw the orifice transfer standard certification curve or calculate the linear least squares slope (m) and intercept (b) of the certification curve:

- (ÄÄH $(P_1/P_{std})(298/T_1)$)=$mQ_{std}$+b

A certification graph should be readable to 0.02 std $m^3$/min.

19. Recalibrate the transfer standard annually or as required by applicable quality control procedures.

### 3.1.2 Calibration of Sampler Flow Indicator

Note: For samplers equipped with a flow controlling device, the flow controller must be disabled to allow flow changes during calibration of the sampler's flow indicator, or the alternate calibration of the flow controller given in 3.1.3 may be used. For samplers using an orifice-type flow indicator

downstream of the motor, do not vary the flow rate by adjusting the voltage or power supplied to the sampler.

1. A form should be used to record the calibration data.

2. Connect the transfer standard to the inlet of the sampler. Connect the orifice manometer to the orifice pressure tap. Make sure there are no leaks between the orifice unit and the sampler.

3. Operate the sampler for at least 5 minutes to establish thermal equilibrium prior to the calibration.

4. Measure and record the ambient temperature, $T_2$, and the barometric pressure, $P_2$, during calibration.

5. Adjust the variable resistance or, if applicable, insert the appropriate resistance plate (or no plate) to achieve the desired flow rate.

6. Let the sampler run for at least 2 min to re-establish the run-temperature conditions. Read and record the pressure drop across the orifice (ÄH) and the sampler flow rate indication (I).

7. Calculate • (ÄÄH $(P_2/P_{std})(298/T_2)$) and determine the flow rate at standard conditions ($Q_{std}$) either graphically from the certification curve or by calculating $Q_{std}$ from the least square slope and intercept of the transfer standard's transposed certification curve:

   $Q_{std}$=1/m • (ÄH $(P_2/P_{std})(298/T_2)$-b)

   Record the value of $Q_{std}$.

8. Repeat steps 5-7 for several additional flow rates distributed over a range that includes 1.1 to 1.7 std $m^3$/min.

9. Determine the calibration curve by plotting values of the appropriate expression involving I, selected from Table 1, against $Q_{std}$.

10. Draw the sampler calibration curve or calculate the linear least squares slope (m), intercept (b), and correlation coefficient of the calibration curve: [Expression from Table 1]= m $Q_{std}$+b. Calibration curves should be readable to 0.02 std $m^3$/min.

11. For a sampler equipped with a flow controller, the flow controlling mechanism should be re-enabled and set to a flow near the lower flow limit to allow maximum control range. The sample flow rate should be verified at this time with a clean filter installed. Then add two or more filters to the sampler to see if the flow controller maintains a constant flow; this is particularly important at high altitudes where the range of the flow controller may be reduced.

### 3.1.3 Alternate Calibration of Flow-Controlled Samplers

A flow-controlled sampler may be calibrated solely at its controlled flow rate, provided that previous operating history of the sampler demonstrates that the flow rate is stable and reliable. In this case, the flow indicator may remain uncalibrated but should be used to indicate any relative change between initial and final flows, and the sampler should be recalibrated more often to minimize potential loss of

samples because of controller malfunction.

1. Set the flow controller for a flow near the lower limit of the flow range to allow maximum control range.
2. Install a clean filter in the sampler and carry out steps 2, 3, 4, 6, and 7 from 3.1.2.
3. Following calibration, add one or two additional clean filters to the sampler, reconnect the transfer standard, and operate the sampler to verify that the controller maintains the same calibrated flow rate; this is particularly important at high altitudes where the flow control range may be reduced.

### 3.2 Procedures

These procedures are based on 40 CFR 50 Chapter I, Appendix B, 8.0.

1. Number each filter, if not already numbered, near its edge with a unique identification number.
2. Back light each filter and inspect for pinholes, particles, and other imperfections; filters with visible imperfections must not be used.
3. Equilibrate each filter in the conditioning environment for at least 24-hr.
4. Following equilibration, weigh each filter to the nearest milligram and record this tare weight ($W_i$) with the filter identification number.
5. Do not bend or fold the filter before collection of the sample.
6. Open the shelter and install a numbered, pre-weighed filter in the sampler, following the sampler manufacturer's instructions. During inclement weather, precautions must be taken while changing filters to prevent damage to the clean filter and loss of sample from or damage to the exposed filter. Filter cassettes that can be loaded and unloaded in the laboratory may be used to minimize this problem.
7. Close the shelter and run the sampler for at least 5 min to establish run-temperature conditions.
8. Record the flow indicator reading, the barometric pressure ($P_3$), and the ambient temperature ($T_3$) ( see NOTE following step12). Stop the sampler and determine the sampler flow rate (see Section 3.3). If the sample flow rate is outside the acceptable range (1.1 to 1.7 $m^3$/min or 39-60 $ft^3$/min), use a different filter, or adjust the sampler flow rate. Substantial flow adjustments may affect the calibration of the orifice-type flow indicators and may necessitate re-calibration.
9. Record the sampler identification information (filter number, site location or identification number, sample date, and starting time).
10. Set the timer to start and stop the sampler such that the sampler runs 24-hrs, from midnight to midnight (local time).
11. As soon as practical following the sampling period, run the sampler for at least 5 min to again establish run-temperature conditions.
12. Record the flow indicator reading, the barometric pressure ($P_3$), and the ambient temperature ($T_3$).

Note: No onsite pressure or temperature measurements are necessary if the sampler flow indicator does not require pressure or temperature corrections (e.g., a mass flowmeter) or if average barometric pressure and seasonal average temperature for the site are incorporated into the sampler calibration (see section 3.2.2, step 9). For individual pressure and temperature corrections, the ambient pressure and temperature can be obtained by onsite measurements or from a nearby weather station. Barometric pressure readings obtained from airports must be station pressure, not corrected to sea level, and may need to be corrected for differences in elevation between the sampler site and the airport. For samplers having flow recorders but not constant flow controllers, the average temperature and pressure at the site during the sampling period should be estimated from weather bureau or other available data.

13. Stop the sampler and carefully remove the filter, following the sampler manufacturer's instructions. Touch only the outer edges of the filter. See the precautions in step 6.

14. Fold the filter in half lengthwise so that only surfaces with collected particulate matter are in contact and place it in the filter holder (glassine envelope or manila folder).

15. Record the ending time or elapsed time on the filter information record, either from the stop set-point time, from an elapsed time indicator, or from a continuous flow record. The sample period must be 1,440 +/- 60 min. for a valid sample.

16. Record on the filter information record any other factors, such as meteorological conditions, construction activity, fires or dust storms, etc., that might be pertinent to the measurement. If the sample is known to be defective, void it at this time.

17. Equilibrate the exposed filter in the conditioning environment for at least 24-hrs.

18. Immediately after equilibration, re-weigh the filter to the nearest milligram and record the gross weight with the filter identification number. See Section 3.3 for TSP concentration calculations.

### 3.3 Calculations of TSP Concentrations

These calculation instructions are based on 40 CFR 50 Chapter I, Appendix B, 10.0.

1. Determine the average sampler flow rate during the sampling period according to either a or b below.

   a. For a sampler without a continuous flow recorder, determine the appropriate expression to be used from Table 2 corresponding to the one from Table 1 used in section 3.1.2 step 9. Using this appropriate expression, determine $Q_{std}$ for the initial flow rate from the sampler calibration curve, either graphically or from the transposed regression equation:

      $Q_{std} = 1/m$ ( [Appropriate expression from Table 2] - b)

      Similarly, determine $Q_{std}$ from the final flow reading, and calculate the average flow $Q_{std}$ as one-half the sum of the initial and final flow rates.

   b. For a sampler with a continuous flow recorder, determine the average flow rate device reading, I, for the period. Determine the appropriate expression from Table 2 corresponding to the one

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from Table 1 used in 3.1.2 step 9. Then using this expression and the average flow rate reading, determine $Q_{std}$ from the sampler calibration curve, either graphically or from the transposed regression equation:

$Q_{std}$ =1/m ( [Appropriate expression from Table 2] - b)

If the trace shows substantial flow change during the sampling period, greater accuracy may be achieved by dividing the sampling period into intervals and calculating an average reading before determining $Q_{std}$

2. Calculate the total air volume sampled as:

$V\text{-}Q_{std} \times t$

where:

V=total air volume sampled, in standard volume units, std $m^3$;

$Q_{std}$=average standard flow rate, std $m^3$ min;

t=sampling time, min.

3. Calculate and report the particulate matter concentration as:

$TSP=((W_f - W_i) \times 10^6)/V$

Where:

TSP=mass concentration of total suspended particulate matter, µg/std $m^3$ ;

$W_i$=initial weight of clean filter, g;

$W_f$=final weight of exposed filter, g;

V=air volume sampled, converted to standard conditions, std $m^3$,

$10^6$=conversion of g to µg.

4. If desired, the actual particulate matter concentration can be calculated as follows:

$(TSP)_a=TSP\ (P_3/P_{std})(298/T_3)$

where:

$(TSP)_a$=actual concentration at field conditions, µg/$m^3$ ;

TSP=concentration at standard conditions, µg/std $m^3$;

$P_3$=average barometric pressure during sampling period, mm Hg;

$P_{std}$=760 mn Hg (or 101 kPa);

$T_3$=average ambient temperature during sampling period, K.

## 4.0 CAUTIONS AND INTERFERENCES

### 4.1 Meteorological Cautions and Interferences

A meteorological monitoring program is an integral part of site monitoring activities. Meteorological data, which define local terrain impacts on air flow paths, are needed to interpret air concentration data.

Meteorological data may be available from an existing station located near the site (i.e., at a local airport), otherwise a station should be set up at the site. This data will document the degree that samples actually were downwind and verify whether other worst-case assumptions were met. Meteorological parameters to be monitored are, at a minimum, wind speed, wind direction, and sigma theta (which is the horizontal wind direction standard deviation and an indicator of atmospheric stability). The remaining parameters primarily affect the amount of a contaminant available in the air.

#### 4.1.1 Wind Speed

When the contaminant of concern is a particulate, wind speed is critical in determining whether the particulate will become airborne, the quantity of the particulate that becomes airborne, and the distance the particulate will travel from the source. Wind speed also contributes to the volatilization of contaminants from liquid sources. Also, under stagnant wind conditions, exhaust air can be re-sampled.

#### 4.1.2 Wind Direction

Wind direction highly influences the path of airborne contaminants. In addition, variations in wind direction increase the dispersion of pollutants from a given source. Upwind sources can contribute to sample concentration. During periods when the sampler is inoperative, particulate matter may be deposited on the filter by wind.

#### 4.1.3 Atmospheric Stability

Atmospheric stability refers to the degree to which the atmosphere tends to dampen vertical and horizontal motion. Stable atmospheric conditions (i.e., evenings) result in low dispersion, and unstable atmospheric conditions (i.e., hot sunny days) result in higher dispersion.

#### 4.1.4 Temperature

Higher temperatures increase the rate of volatilization of organic and some inorganic compounds and affect the initial rise of gaseous or vapor contaminants. Therefore, worst-case emission of volatiles and semivolatiles occurs at the hottest time of day, or on the hottest day.

#### 4.1.5 Humidity

High humidity affects water-soluble chemicals and particulates. Humid conditions may dictate the sampling media used to collect the air sample, or limit the volume of air sampled and thereby increase the detection limit.

### 4.1.6 Atmospheric Pressure

Migration of landfill gases through the landfill surface and through surrounding soils are governed by changes in atmospheric pressure. Atmospheric pressure will influence upward migration of gaseous contaminants from shallow aquifers into the basements of overlying structures. In many cases, the transport and dispersion of air pollutants is complicated by local meteorology.

### 4.1.7 Physical/Chemical Considerations

Normal diurnal variations (i.e., temperature inversions) affect dispersion of airborne contaminants. Terrain features can enhance or create air inversions and can also influence the path and speed of air flow, complicating transport and dispersion patterns. The chemical characteristics of a contaminant (i.e., molecular weight, physical state, vapor pressure, aerodynamic size, temperature, reactive compounds, and photodegradation) affect its behavior and can influence the method used to sample and analyze it.

## 4.2 Other Influences

### 4.2.1 Loss of Volatiles

During subsequent sampling, shipping, or storage of the filter prior to the post-sampling weighing, volatile particles collected on the filter can be lost. Thus, the filter should be re-weighed as soon as practical after sampling.

### 4.2.2 Artifact Particulate Matter

A higher than true TSP determination can result from artifact particulate matter forming on the surface of alkaline glass fiber filters by oxidation of acid gases in the sample air.

### 4.2.3 Filter Handling

The filter should be handled carefully between the pre-sampling and post-sampling weighing in order to avoid loss of fibers or particles from the filter. To minimize error from handling, a filter paper cartridge or cassette can be used to protect the filter.

## 4.3 Detection Limits

Detection limits depend on the contaminants being investigated and the particular site situation. It is important to know why the data are needed and how the data will be used. Care should be taken to ensure the detection limits are adequate for the intended use of the final results. Some equipment may be sensitive to humidity and temperature extremes.

**Table 1. Expressions for Plotting Sampler Calibration Curves**

| Type of sampler flow rate measuring device | Expression | |
|---|---|---|
| | For actual pressure and temperature corrections | For incorporation of geographic average pressure and seasonal average temperature |
| Mass flow meter | 1 | 1 |
| Orifice and pressure indicator | • $(I(P_2/P_{std})(298/T_2))$ | • $(I(P_2/P_a)(T_a/T_2))$ |
| Rotameter or orifice and pressure recorder having square root scale. | I• $((P_2/P_{std})(298/T_2))$ | I• $((P_2/P_a)(T_a/T_2))$ |

**Table 2. Expressions for Determining Flow Rate During Sampler Operation**

| Type of sampler flow rate measuring device | Expression | |
|---|---|---|
| | For actual pressure and temperature corrections | For use when geographic average pressure and seasonal average temperature have been incorporated into the sampler calibration |
| Mass flowmeter | 1 | 1 |
| Orifice and pressure indicator | • $(I(P_2/P_{std})(298/T_3))$ | • I |
| Rotameter or orifice and pressure recorder having square root scale. | I• $((P_2/P_{std})(298/T_3))$ | I |

# STANDARD OPERATING PROCEDURE NO. 14.6
# REAL-TIME AIR MONITORING

## 1.0 METHOD SUMMARY

This standard operating procedure (SOP) provides guidance for real-time air monitoring

## 2.0 EQUIPMENT/APPARATUS/REAGENTS

### 2.1 Direct Reading Instruments (Air Monitoring Instruments)

There are two general types of direct reading instruments: portable screening devices and specialized analytical instruments. Generally all these techniques involve acquiring, for a specific location or area, continuous or sequential direct air concentrations in real-time. None of these instruments acquires true time-weighted average concentrations. In addition, these instruments are not capable of acquiring simultaneous concentration readings at multiple locations, although several are able to sequentially analyze samples taken remotely from different locations. The document, "Guide to Portable Instruments for Assessing Airborne Pollutants Arising from Hazardous Waste Sites," provides additional information about air sampling and monitoring. See the ACGIH TLVs and the OSHA PELs for safe working levels as hazard levels for airborne contaminants vary.

### 2.2 Equipment List

- Camera
- Site logbook
- Clipboard
- Chain of custody records
- Custody seals
- Air sampling worksheets
- Appropriate real-time air monitoring instrumentation

## 3.0 PROCEDURES

### 3.1 Calibration

Follow manufacturer's instructions for calibration of a particular real-time air monitor.

### 3.2 Procedure

Follow the manufacturer's instructions for the proper use of a particular real-time air monitor. The monitor should be appropriate for the analytes of concern and analytical detection limit to be achieved. See the sampling plan for proper monitor.

## 4.0 CAUTIONS AND INTERFERENCES

### 4.1 Meteorological Cautions and Interferences

A meteorological monitoring program is an integral part of site monitoring activities. Meteorological data, which define local terrain impacts on air flow paths, are needed to interpret air concentration data.

Meteorological data may be available from an existing station located near the site (i.e., at a local airport), otherwise a station should be set up at the site. This data will document the degree that samples actually were downwind and verify whether other worst-case assumptions were met. Meteorological parameters to be

monitored are, at a minimum, wind speed, wind direction, and sigma theta (which is the horizontal wind direction standard deviation and an indicator of atmospheric stability). The remaining parameters primarily affect the amount of a contaminant available in the air.

### 4.1.1 Wind Speed

When the contaminant of concern is a particulate, wind speed is critical in determining whether the particulate will become airborne, the quantity of the particulate that becomes airborne, and the distance the particulate will travel from the source. Wind speed also contributes to the volatilization of contaminants from liquid sources.

### 4.1.2 Wind Direction

Wind direction highly influences the path of airborne contaminants. In addition, variations in wind direction increase the dispersion of pollutants from a given source. Upwind sources can contribute to sample concentration.

### 4.1.3 Atmospheric Stability

Atmospheric stability refers to the degree to which the atmosphere tends to dampen vertical and horizontal motion. Stable atmospheric conditions (e.g, evenings) result in low dispersion, and unstable atmospheric conditions (e.g., hot sunny days) result in higher dispersion.

### 4.1.4 Temperature

Higher temperatures increase the rate of volatilization of organic and some inorganic compounds and affect the initial rise of gaseous or vapor contaminants. Therefore, worst-case emission of volatiles and semivolatiles occurs at the hottest time of day, or on the hottest day.

### 4.1.5 Humidity

High humidity affects water-soluble chemicals and particulates. Humid conditions may dictate the sampling media used to collect the air sample, or limit the volume of air sampled and thereby increase the detection limit.

### 4.1.6 Atmospheric Pressure

Migration of landfill gases through the landfill surface and through surrounding soils is governed by changes in atmospheric pressure. Atmospheric pressure will influence upward migration of gaseous contaminants from shallow aquifers into the basements of overlying structures. In many cases, the transport and dispersion of air pollutants is complicated by local meteorology.

### 4.1.7 Physical/Chemical Considerations

Normal diurnal variations (i.e., temperature inversions) affect dispersion of airborne contaminants. Terrain features can enhance or create air inversions and can also influence the path and speed of air flow, complicating transport and dispersion patterns. The chemical characteristics of a contaminant (e.g., molecular weight, physical state, vapor pressure, aerodynamic size, temperature, reactive compounds, and photodegradation)

affect its behavior and can influence the method used to sample and analyze it.

## 4.2 Other Influences

Natural sources, such as biological waste, can produce hydrogen sulfide and methane which may contribute to the overall contaminant level. Extraneous anthropogenic contaminants (i.e., burning of fossil fuels; emissions from vehicular traffic, especially diesel; volatile compounds from petrochemical facilities; and effluvium from smoke stacks) may also contribute. Air sampling stations should be strategically placed to identify contributing sources. Positive errors in concentrations may occur due to retention of gaseous species, such as sulfur dioxide and nitric acid, on filters.