

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

Chapter IO-3

**CHEMICAL SPECIES ANALYSIS OF
FILTER-COLLECTED SUSPENDED
PARTICULATE MATTER (SPM)**

OVERVIEW

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Chapter IO-3 CHEMICAL SPECIES ANALYSIS OF FILTER-COLLECTED SUSPENDED PARTICULATE MATTER (SPM)

OVERVIEW

As discussed in Chapter IO-2, the EPA's approach toward regulating and monitoring SPM in ambient air has evolved over time. Initially, the EPA was concerned about total concentrations of SPM and lead (Pb); recently, however, interest has focused on smaller particles as well as other types and quantities of various inorganic components of SPM. A comprehensive discussion of the various approved methods and technology used for time-integrated sampling of SPM are presented in Chapter IO-2. These methods principally include:

- High volume samplers for collecting TSP (total suspended particulate with aerodynamic diameters less than 100 μm) and PM_{10} (particulate matter with aerodynamic diameters less than 10 μm); and
- Low volume samplers for collecting PM_{10} utilizing dichotomous and Partisol® samplers.

Chapter IO-3 contains the options available for identifying and quantifying the inorganic compounds in SPM. This overview is intended to introduce these analytical options and provide information to help guide the selection of options appropriate to the particular task at hand.

Two methods of sample preparation for quantitative analysis of chemical species in SPM are described in Compendium Method IO-3.1. These methods include hot acid extraction and microwave digestion. Both methods are described in detail in Section IO-3.1.

Chapter IO-3 includes six options for the quantitative analysis of inorganic compounds in PM. These options are:

Method	Analytical Technique
Method IO-3.2	Flame and graphite furnace atomic absorption spectroscopy (FAA/GFAA)
Method IO-3.3	X-Ray fluorescence spectroscopy (XRF)
Method IO-3.4	Inductively coupled plasma atomic emission spectroscopy (ICP)
Method IO-3.5	Inductively coupled plasma/mass spectrometry (ICP/MS)
Method IO-3.6	Proton induced X-Ray emission spectroscopy (PIXE)
Method IO-3.7	Neutron activation Analysis (NAA)

These options are described in detail in Methods IO-3.2 through IO-3.7. A brief summary of each of the techniques is provided below.

Method IO-3.2 **Atomic Absorption Spectroscopy (FAA and GFAA)**

The two atomic absorption analysis options included in Compendium Method IO-3.2, FAA and GFAA, are similar in that the measurement principle for these two options is the same. However, they differ in how the sample is introduced into the instrument. Both types of atomic absorption spectroscopy involve irradiating the sample with light of a single wavelength and measuring how much of the input light is

absorbed. Each element absorbs light at a characteristic wavelength; therefore, analysis for each element requires a different light source, and only one element can be determined at a time. In FAA, the sample is atomized and introduced into the optical beam using a flame, typically air/acetylene or nitrous oxide/acetylene. In GFAA, a graphite furnace electrothermal atomizer is used. These analytical techniques are destructive and require that the sample be extracted or digested for introduction into the system in solution. The detection limit of GFAA is typically about two orders of magnitude better than FAA. High-volume samplers are typically used for sampling when FAA or GFAA analysis is planned, as documented in Figure 1.

Method IO-3.3
X-ray Fluorescence Spectroscopy (XRF)

In XRF analysis, the sample is irradiated with a beam of x-rays, and the elements in the sample emit X-rays at characteristic wavelengths. The wavelengths that are detected indicate which elements are present, and the quantity of each element is determined from the intensity of the X-rays at each characteristic wavelength. X-ray fluorescence spectrometry can be used for all elements with atomic weights from 11 (sodium) to 92 (uranium), and multiple elements can be determined simultaneously. This analysis technique is nondestructive and requires minimal sample preparation--the filter is inserted directly into the instrument for analysis. This technology is relatively inexpensive; however, the detection limit is higher than other analysis techniques. Because high-volume samplers utilizes quartz-filters which causes high background when employing XRF, analysis by XRF usually includes those Teflon® or Nylon filters used in the dichotomous or the Partisol® samplers.

Method IO-3.4
Inductively Coupled Plasma Spectroscopy (ICP)

In ICP analysis, the sample is excited using an argon plasma "torch." When the excited atoms return to their normal state, each element emits a characteristic wavelength of light. The wavelengths detected and their intensities indicate the presence and amounts of particular elements. Up to 48 elements can be determined simultaneously. As with FAA and GFAA, the SPM sample must be extracted and digested for ICP analysis, and the material introduced into the instrument is destroyed during analysis. An ICP instrument is more costly than FAA or GFAA instruments. The ICP detection limit for many elements is equal to or somewhat better than that for FAA. (With particular elements, however, one or the other analysis technique is very superior to the other.) The GFAA detection limit is better than that for ICP for most elements. As indicated in Figure 1, high-volume samplers are typically used for sampling when ICP analysis is planned.

Method IO-3.5
Inductively Coupled Plasma/Mass Spectrometry (ICP/MS)

Analysis by ICP/MS also uses argon plasma torch to generate elemental ions for separation and identification by mass spectrometry (MS). This analysis technique allows many more than 60 elements to be determined simultaneously, and even the isotopes of an element can be determined. For ICP/MS analysis, the SPM sample must be extracted or digested, and the analysis is destructive. An ICP/MS instrument is the most costly of those included in this Chapter, and its detection limit is the lowest. Sampling is typically conducted using high-volumes when ICP/MS analysis is planned, as shown in Figure 1.

Method IO-3.6

Proton Induced X-ray Emission Spectroscopy (PIXE)

PIXE analysis is very similar to XRF analysis in that the sample is irradiated by a high energy source, in this case high energy protons, to remove inner shell electrons. Fluorescent x-ray photons are detected using the same detection methods as XRF. Analysis by PIXE also typically involves collecting SPM by dichotomous or by Partisol® samplers.

Method IO-3.7

Neutron Activation Analysis (NAA)

In NAA analysis, the sample and an appropriate standard are exposed to a high neutron thermal flux in a nuclear reactor or accelerator. The sample elements are transformed into radioactive isotopes that emit gamma rays. The distribution or spectrum of energy of the gamma rays can be measured to determine the specific isotopes present. The intensity of the gamma rays can also be measured and is proportional to the amounts of elements present. NAA is a simultaneous, multi-element method and does not generally require significant sample preparation. It is highly sensitive, though it does not quantify elements such as silicon, nickel, cobalt, and lead. NAA is a non-destructive technique and does not require the addition of any foreign materials for irradiation; thus, the problem of reagent introduced contaminants is avoided. Analysis by NAA is compatible with sampling by high-volume, dichotomous and Partisol® samplers.

Comparative Selection Criteria

Some of the analytical techniques listed above typically are used only with particular sampling methods. The relationships between sampling technologies and compatible analytical techniques is illustrated in Figure 1. Furthermore, the type of filter medium used to capture the sample is a factor in the choice of analytical technique and vice-versa.

Most importantly, the choice of analytical method will depend on the inorganic compounds of interest and the detection limits desired. A relative comparison of the ranges of detection limits that are typical for the various techniques is provided in Figure 2. Table 1 contains a more detailed summary of the species measured and the respective minimum detection limits associated with analytical options discussed in this Chapter.

Some of the advantages and disadvantages associated with the analytical options presented in Compendium Method IO-3 are summarized in Figure 3. While factors such as element specificity and sensitivity are critically important, considerations such as cost and throughput (the number of samples and number of elements to be determined per sample) are also important. A comparison of the typical throughput for the analytical options in Compendium Method IO-3 is provided in Figure 4.

Unfortunately, no one analytical method can address all data quality objectives for a particular ambient air monitoring program. Each method has its own attributes, specificities, advantages, and disadvantages, as previously discussed. However, Compendium Method IO-3 attempts to encompass into one chapter the various analytical options, in a step-by-step methodology, to facilitate accurate and reliable data for SPM and metal concentration in the ambient air.

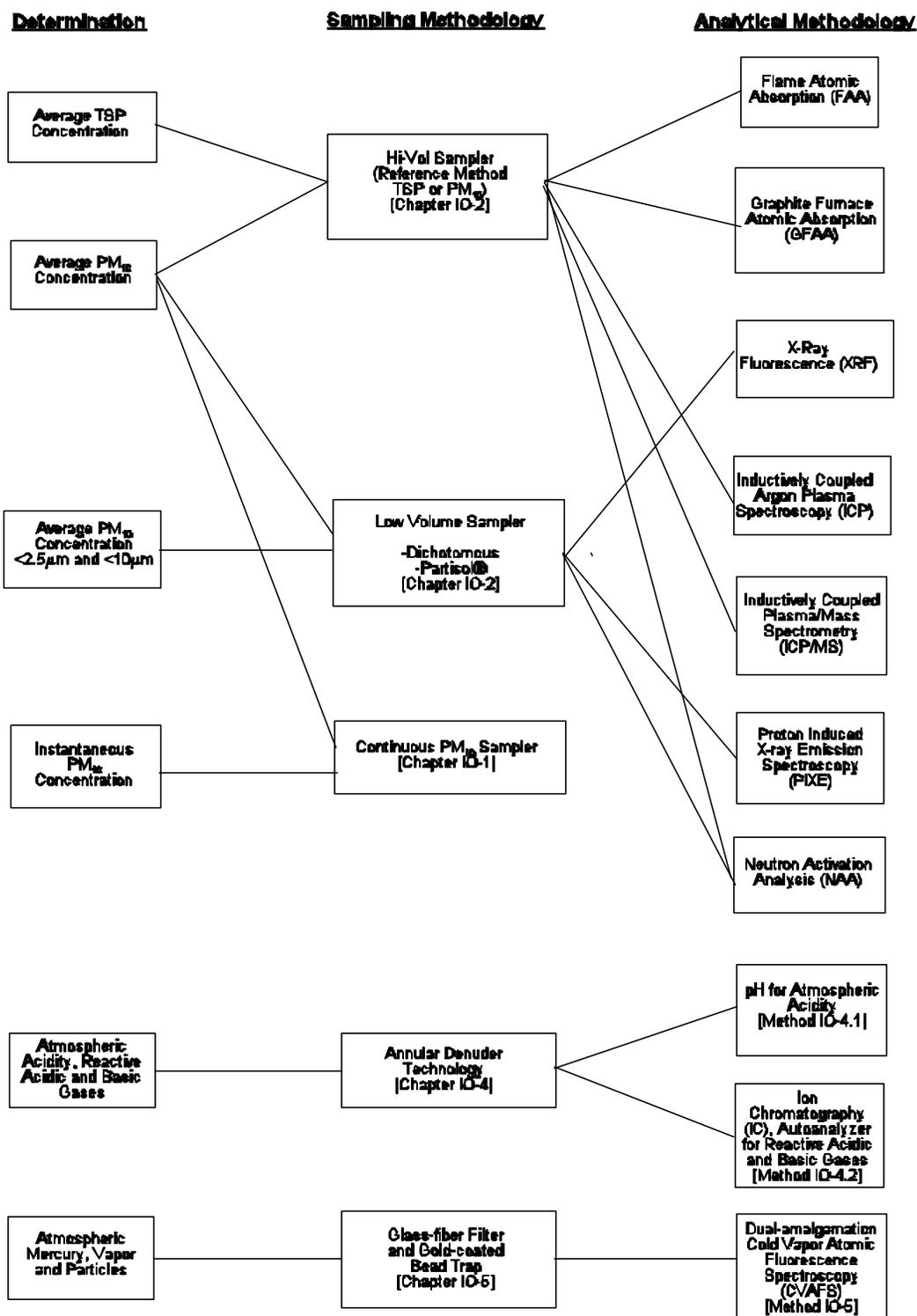


Figure 1. Relationship between Chapter IO-1 and IO-2 sampling technologies and Chapter IO-3 analytical techniques.

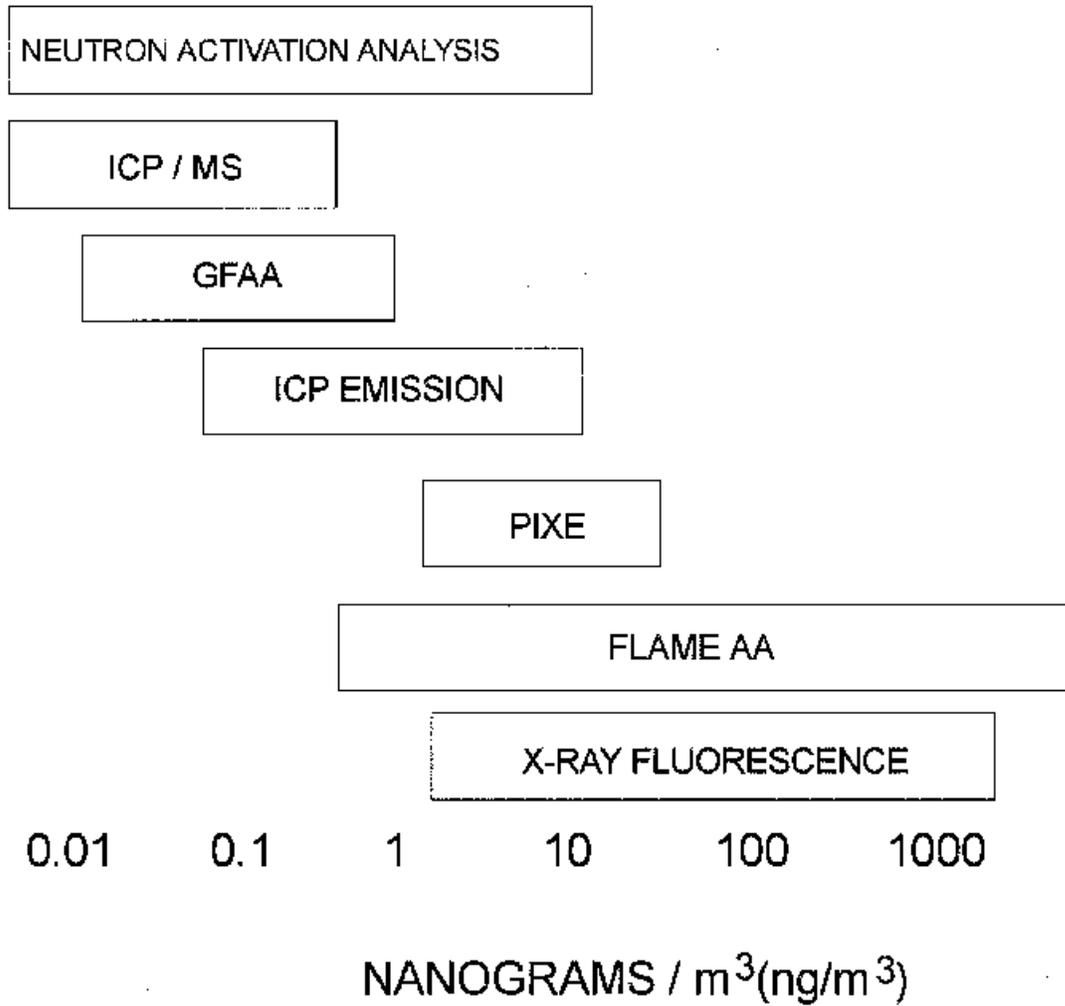


Figure 2. Example of typical detection limits for Chapter IO-3 analytical options.

	ADVANTAGE	DISADVANTAGE
FLAME AA	<ul style="list-style-type: none"> • easy to use • extensive applications • low detection limits 	<ul style="list-style-type: none"> • higher concentration • sample dissolution is required • one (1) element at a time
GFAA	<ul style="list-style-type: none"> • well documented applications • lower detection limits than Flame AA 	<ul style="list-style-type: none"> • limited working range sample • low sample throughput • one element at a time • more operator skill • sample dissolution is required
ICP	<ul style="list-style-type: none"> • multi-element • high sample throughput • well documented applications • intermediate operator skill • linear range over 5 orders of magnitude 	<ul style="list-style-type: none"> • more expensive (~ 120K) • sample dissolution is required • other elements can interfere
ICP / MS	<ul style="list-style-type: none"> • multi-elements • low concentrations • isotopic analysis • intermediate operator skills 	<ul style="list-style-type: none"> • most expensive (~ 250K) • limited documented applications • sample dissolution is required
PIXE	<ul style="list-style-type: none"> • multielement • non-destructive • minimal sample preparation 	<ul style="list-style-type: none"> • standard/sample must match closely (matrix) • matrix offsets and background impurities may be a problem
XRF	<ul style="list-style-type: none"> • multielement • non-destructive • minimal sample preparation 	<ul style="list-style-type: none"> • standard/sample must match closely (matrix) • matrix offsets and background impurities may be a problem
NAA	<ul style="list-style-type: none"> • multielement • non-destructive • minimal sample preparation • % to ppb range • high sample throughput • well documented applications 	<ul style="list-style-type: none"> • some elemental interferences • standard sample matrix corrections • required access to research nuclear reactor

Figure 3. Example of advantages/disadvantages associated with analytical options presented in Chapter IO-3.

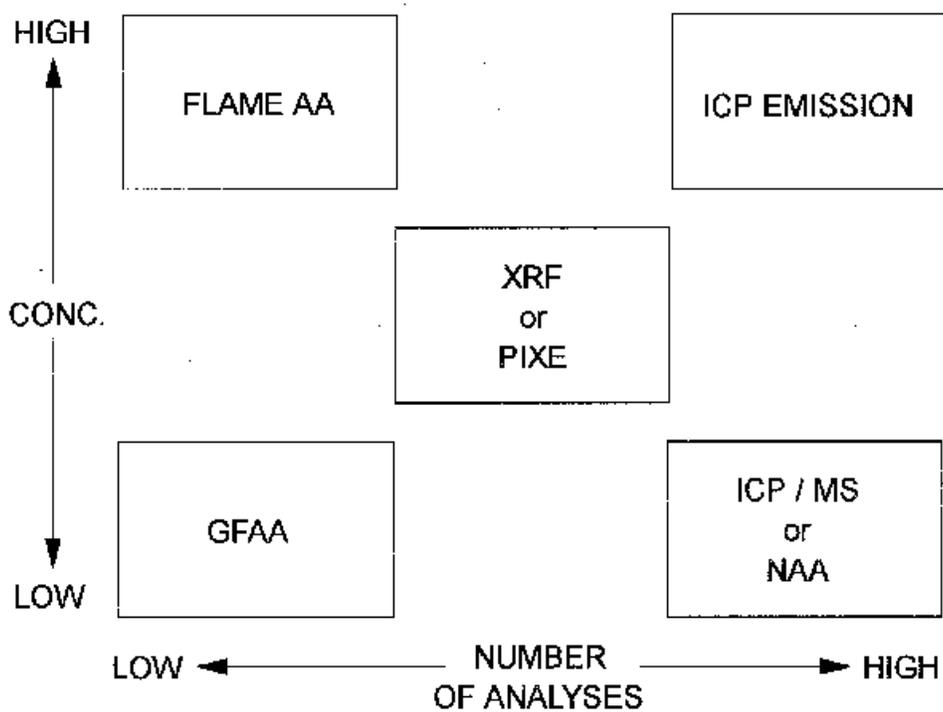


Figure 4. Example of throughput of analytical options presented in Chapter IO-3.

Table 1. Example of Minimum Detection Limits (ng/m³) of Air Filter Samples
For Different Chapter IO-3 Analytical Methods^{1,2}

Species	Analytical Technique						
	FAA	GFAA	XRF	ICP	ICP/MS	PIXE	NAA ⁴
Ag	0.4	0.005 ³	6.02	1 ³	0.01	165.81	0.04
Al	4.4	0.01 ³	5.29	13.5	0.01	16.25	5
Ar	NA	NA	NA	NA	NA	NA	0.04
As	100 ³	0.20 ³	0.24	5.5	0.3	5.42	0.09
Au	21 ³	0.10 ³	0.51	1.9	NA	14.44	0.09
B	NA	NA	NA	6.6	NA	NA	NA
Ba	1.8	0.04 ³	15.59	0.7	0.1	22.57	2.3
Be	2.00 ³	0.05 ³	NA	0.4	0.02	NA	NA
Bi	5.5 ³	NA	NA	226.6	NA	16.85	NA
Br	NA	NA	0.18	NA	NA	12.34	0.04
Ca	0.1	0.05 ³	2.71	22.7	NA	8.12	23.1
Cd	0.2	0.0003 ³	6.62	1.1	0.02	201.62	4.2
Ce	NA	NA	NA	10.6	NA	18.06	9.2
Cl	NA	NA	1.44	NA	NA	12.34	9.2
Co	2.2	0.02 ³	0.12	3.3	0.01	2.37	0.4
Cr	0.7	0.01 ³	0.90	2.6	0.01	3.91	0.9
Cs	NA	NA	14.62	NA	NA	25.28	0.02
Cu	0.4	0.02 ³	0.21	2.2	0.01	2.71	0.9
Dy	NA	NA	NA	NA	NA	9.63	0.01
Er	NA	NA	NA	NA	NA	8.73	0.2
Eu	21.0 ³	NA	NA	0.08 ²	NA	10.53	0.01
Fe	1.1	0.02 ³	0.21	7.5	0.01 ³	2.71	4.6
F	NA	NA	NA	NA	NA	NA	92.5
Ga	NA	NA	0.48	42.0 ²	NA	3.61	9.2
Gd	NA	NA	NA	NA	NA	10.23	NA
Ge	NA	NA	0.33	17.5	NA	4.21	NA
Hf	2,000 ³	NA	NA	16.0 ³	NA	10.53	3.2
Hg	NA	21.0 ³	0.45	12.1	NA	14.44	0.9
Ho	NA	NA	NA	NA	NA	9.34	0.01
I	NA	NA	10.68	NA	NA	29.19	0.05
In	4.4	NA	6.0 ³	18.5	NA	239	0.01
Ir	NA	NA	NA	NA	NA	12.34	0.01
K	0.4	0.02 ³	1.89	45.1	NA	9.93	0.9
Kr	NA	NA	NA	NA	NA	NA	0.5
La	2,000 ³	NA	2.12	1.5	NA	20.76	0.2
Li	0.1	NA	NA	NA	NA	NA	NA
Lu	NA	NA	NA	NA	NA	10.83	0.01
Mg	0.1	0.004 ³	0.96	5.3	0.02 ³	18.66	231

Table 1. Minimum Detection Limits (ng/m³) of Air Filter Samples
For Different Chapter IO-3 Methods (cont).

Species	Analytical Technique						
	FAA	GFAA	XRF	ICP	ICP/MS	PIXE	NAA ⁴
Mn	0.4	0.01 ³	0.24	0.9	0.02	3.01	0.02
Mo	31.0 ³	0.02 ³	0.48	1.9	0.02	57.17	0.05
Na	0.1	0.01 ³	1.59	NA	NA	28.28	0.2
Nb	NA	NA	NA	2.4	NA	43.63	NA
Nd	NA	NA	NA	NA	NA	15.05	9.2
Ni	1.1	0.10 ³	0.18	3.1	0.02	2.37	NA
Os	NA	NA	NA	NA	NA	12.94	NA
P	100,000	NA	0.78	22.9	NA	14.44	NA
Pb	2.2	0.05 ³	0.45	7.0	0.01	16.85	NA
Pd	10.0 ³	NA	6.89	42.0 ³	NA	134.21	0.09
Pm	NA	NA	NA	NA	NA	12.64	NA
Pr	NA	NA	NA	NA	NA	15.95	0.04
Pt	NA	NA	NA	23.5	NA	13.54	1.8
Rb	0.4	NA	0.21	NA	NA	17.75	18.5
Re	NA	NA	NA	33.0	NA	13.24	0.2
Rh	NA	NA	7.79	440	NA	104.72	0.1
Ru	NA	NA	NA	41.1	NA	89.37	0.9
S	NA	NA	0.78	10 ³	NA	12.94	6000
Sb	31.0 ³	0.20 ³	9.45	5.5	0.01	376.16	0.4
Sc	50.0 ³	NA	0.45	0.06 ³	NA	7.82	0.09
Se	100.0 ³	0.50 ³	0.21	34.3	1.1	6.32	0.09
Si	85.0 ³	0.10 ³	2.41	37.8	NA	14.14	NA
Sm	2,000 ³	NA	NA	5.4	NA	12.04	0.04
Sn	31.0 ³	0.20 ³	9.18	9.2	0.01 ²	272.64	9.2
Sr	0.4	0.20 ³	0.33	0.2	NA	23.17	0.4
Ta	2,000 ³	NA	NA	52.1	NA	10.83	4.2
Tb	NA	NA	NA	NA	NA	9.34	2.3
Tc	NA	NA	NA	NA	NA	73.12	NA
Te	NA	NA	7.91	4.6	NA	30.99	4.6
Th	NA	NA	NA	63 ³	0.01	33.7	3.2
Ti	95.0 ³	NA	2.0 ³	0.7	0.01 ³	6.62	4.6
Tl	2.2	0.10 ³	5.08	33.4	0.01	16.55	NA
Tm	NA	NA	NA	NA	NA	10.23	NA
U	25,000 ³	NA	1.0 ³	21.0 ³	0.01	43.94	0.2
V	8.8	0.20 ³	1.59	1.5	0.01	5.42	0.04
W	1,000 ³	NA	10.23	12.5	0.01 ³	12.04	0.09
Y	300.0 ³	NA	0.36	0.9	0.01 ³	28.59	0.2
Yb	NA	NA	NA	NA	NA	10.53	0.09

Table 1. Minimum Detection Limits (ng/m³) of Air Filter Samples
For Different Chapter IO-3 Methods (cont).

Species	Analytical Technique						
	FAA	GFAA	XRF	ICP	ICP/MS	PIXE	NAA ⁴
Zn	0.2	0.0001 ³	0.30	26.4	0.04	3.61	9.2
Zr	1,000 ³	NA	0.36	1.8	NA	35.51	9.2

¹Minimum detection limit is three times the standard deviation of the blank for a filter or 1 cm² area.

²NA = Detection limits have not been established or reported for this analyte using the indicated analytical technique.

ICP = Inductively Coupled Plasma Atomic Emission Spectroscopy.

ICP/MS = Inductively Coupled Plasma/Mass Spectrometry

FAA = Flame Atomic Absorption Spectroscopy

GFAA = Graphite Furnace Atomic Absorption Spectroscopy

PIXE = Proton Induced X-ray Emission Spectroscopy

XRF = X-ray Fluorescence

NAA = Neutron Activation Analysis

³Reported minimum detection limits are these found in the various analytical methods in Chapter 3 except where indicated with this reference. These detection limits were extracted from Dr. Judy C. Chow's paper entitled: "Measurement Methods to Determine Compliance with Ambient Air Quality Standards for Suspended Particles," *J. Air and Waste Manage. Assoc.*, Vol. 45:320-382, 1995.

⁴Based upon dichotomous sampling for 24-hours using a 37-mm Teflon[®] filter at a sampling rate of 0.9 m³/hr.