TRACE METAL PARTICULATES IN COAL-FIRED POWER PLANT EMISSIONS

by

LANETTE SIMONE MARETT

(Under the Direction of GEOFFREY D. SMITH)

ABSTRACT

Since coal-fired power plants produce approximately 50% of U.S. energy, the toxic and environmental damaging effects of this energy source are important. Trace metals are emitted in both the gas phase as well as particulates, referred to as coal fly ash, during the incineration of coal. The sources, health and environmental effects, and fate and transport are discussed to lay the foundation of importance of trace metals in the atmosphere. Quantitative measurements from various worldwide studies are discussed, which use the following instrumentations: AAS (atomic absorption spectrometry), ICP-MS (inductively couple plasma mass spectrometry), INAA (instrumental neutron activation analysis), and aerosol TOF-MS (time-of-flight mass spectrometry). The partitioning of the trace metals during combustion as well as post-combustion and gas phase and particulate interactions are explored as well as possible future laboratory experiments to further develop the field of trace metal emission coal combustion.

INDEX WORDS: COAL COMBUSTION, TRACE METAL PARTICULATES, PARTITIONING

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DEDICATION

I want to dedicate this body of work to my late Father David Marett whom I know has smiled down on me from heaven during this process.

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There are several people who have been instrumental in helping me to reach my goal of a masters degree: Geoffrey Smith, John Hearn, Lindsay Renbaum, Charles Gates, Selenah Seabrooks, Vicky Will, and Stephen Boone. All of your help and advice is greatly appreciated.

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CHAPTER 1

HEALTH EFFECTS, ENVIRONMENTAL EFFECTS, SOURCES, FATE, AND TRANSPORT OF PARTICULATES

There are many factors that affect the fate, transport, and environmental impact of metal particulate emissions and particulates in general: topographical influences, emission sources, and "meteorological properties of the atmosphere"; however, the inherent properties of these particulates such as density, shape, and hygroscopicity must also be considered.[1] The inherent properties of the particulates are also important when human health is concerned: the smaller the airborne particle, the more damaging effects to humans due to inhalation via the nose and mouth. Typically, particles smaller than 1 μm to 2.5 μm in diameter (this size range referred to as fine and ultrafine particles), PM_1 and $PM_{2.5}$ respectively, are of concern relating to adverse health effects.[1] In urban and industrial settings, there are many more anthropogenic sources and therefore more human exposure and subsequent health effects related to metals in suspended particulates.[1] Anthropogenic particulates emitted by high temperature combustion from minerals transformed via coal-fired power plants are referred to as coal fly ash (CFA), which is a primary particle emitted.[2] Depending on the type of incineration process used (boiler type), the type of coal used for incineration, and the type of precipitation technique used (scrubber type), various metal particulates and sizes can be produced.[3,4] According to the EPA's standards set by the Clean Air Act of 1990, out of the 188 Hazardous air pollutant substances (HAPS), 10 metal compounds are found on this list: As, Be, Cr^{6+}, Co, Pb, Mn, Hg, Ni, Se, and the emissions of diesel engines.[5] Since the EPA produced this study, several other metals have been proposed and found to have negative health effects ranging from respiratory disturbances to severe damage on the cellular and DNA level, which can eventually lead to cancer if the subject is exposed to the toxin for a prolonged period of time.

Importance of studying particulates: health effects

The particles that are most concerning for potential health side effects are 2.5 μm in diameter and smaller. Submicron and supermicron particles are released upon coal incineration, and particles larger than 1 μm can mostly be eliminated with scrubbers, which will be further discussed later in chapter 2. Unfortunately, the ever-advancing science of eliminating by-products from coal production still has its limitations because the scrubbers' lowest collection efficiencies are in the size range 0.1-1 μm-the most detrimental size range for human health risks.[2] Since smaller particles can be transported longer distances, inhalation hazards are a concern for citizens who surround the plant, citizens who live hundreds of miles from the plant, and especially steam plant workers that are surrounded by higher concentrations of CFA for prolonged periods.[2]

Pulmonary and respiratory agitations and conditions are the most common side effects linked to CFA exposure. For example, deposits of particulates into the lung can cause leaching of genotoxic compounds and the altering of immunological mechanisms. The biochemical reaction mechanisms are still widely unknown, but many hypothesis lean to the formation of "metal generation of reactive oxygen species" as the culprit of the damaging human health effects.[6] Metals in particulate matter cause a response by "acellular generation of hydroxyl radicals, the release of inflammatory cytokines, and oxidative DNA damage."[7] In vivo studies were performed on rats predominately to see the effects of multiple types of coal fly ash via inhalation or intratracheal administration.[3] The studies were performed to see the effects of the CFA on the development of fibrosis, which is the formation of fibrous tissues in excess between tiny air sacs of the lung.[8] The serious issue with the development of this condition is that it can lead to infection, emphysema, or heart problems.[8] The following paragraphs will discuss some of the specific metals that are emitted from coal combustion (refer to anthropogenic sources from this chapter for a complete guide of metals emitted) and their proposed health implications to humans.

There are a variety of metals emitted from coal combustion that can lead to adverse human effects, even some that are readily used in the body on a daily basis. Some of the elements that can be carcinogenic to humans in the size range ≤ 2.5 μm are As (typically As(III) is more carcinogenic than As(V)), Be, Cd, Co, Cr (Cr(VI) is more toxic than Cr(III)), Hg, Ni, Pb, Rn, V, Fe, and Se.[6,9] For example, Fe, an essential metal for human survival, can cause injury to the human body in the form of nucleic acid damage and even cancer if acquired in excess.[6] In previous epidemiological studies, vanadium exposure-V(IV) and V(V) are the important forms when related to physiologic alterations-has been linked to inducing forward mutations and cross-linking in DNA protein: ultimately this can cause lung cancer.[6] Higher emission factors of vanadium are typically linked to oil combustion, but vanadium is also emitted from coal combustion.[4,6]

Inhalation via the mouth or nose is not the only human health concern of metals emitted into the atmosphere: metals that are soluble-a very important attribute to ecotoxicity-can be deposited into the earth, rivers, lakes, etc, which can lead to geochemical accumulation as well as bioaccumulation.[5] These deposits of metals effect not only the environment but aquatic life and eventually humans through oral consumption of bioaccumulated toxicity. Another inherent chemical property of ultrafine particles is their increased solubility compared to chemically similar particles that are larger in size due to the increased surface to volume ratio.[5] The metal particulates' multiple effects not only to the environment but humans make them a very important topic to research further across multiple disciplines in the sciences.

Sources of trace metal particulates into the atmosphere

Biogenic

Trying to accurately define the amounts of a particular metal particulate in the atmosphere is very challenging and large discrepancies exist between multiple scientists that have taken on the challenge of trying to quantify these emissions, both anthropogenic and biogenic. The main sources of metal particulates, as seen in Table 1.1, into the atmosphere come from seasalt, vegetation, forest wild-fires, volcanic eruptions, and windblown dust.[4,10] Biogenic sources, as calculated by scientists sampling the atmosphere from around the world, contribute 30-50% of As, Cd, Cu, Mn, Pb, Sb, and Zn and over 50% of Se and Mo.[10] The two largest contributors of biogenic emissions are windblown dust and volcanoes.[4] For example, in the Sahara area in northern Africa alone, it contributes 60-200*10^6 tons of soil dust to the troposphere per year, and satellite images in Figure 1 show the vast flux into the atmosphere off

Table 1.1: Natural sources of global emission (*10^6 kg/year).[4]

Source Category	As	Cd	Co	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	V	Zn
Windblown Dust	2.6	0.2	4.1	27	8	0.05	221	1.3	11	3.9	0.78	0.18	33	19
Seasalt Spray	1.7	0.06	0.07	0.7	3.6	0.02	0.86	0.22	1.3	1.4	0.56	0.55	3.1	0.44
Volcanoes	3.8	0.82	0.96	15	9.4	1.0	42	0.4	14	3.3	0.71	0.95	5.6	9.6
Wild Forest Fires	0.19	0.11	0.31	0.09	3.8	0.02	23	0.57	2.3	1.9	0.22	0.26	1.8	7.6
Biogenic:														
Continental Particulates	0.26	0.15	0.52	1.00	256	0.02	27	0.4	0.51	1.3	0.2	0.12	0.92	2.6
Continental Volatiles	1.3	0.04	0.06	0.05	0.32	0.61	1.3	0.06	0.1	0.2	0.04	2.6	0.13	2.5
Marine	2.3	0.05	0.08	0.06	0.39	0.77	1.5	0.08	0.12	0.24	0.05	4.7	0.16	3
Total Emission (Median Values)	12	1.3	6.1	44	28	2.5	317	3	30	12	2.4	9.3	28	45

the west coast of Africa.[4] Not all of the soil dust consists of trace metal particulates, but this number is still very impressive.

Figure 1.1: Satellite images of Sahara windblown dust off of the western coast of Africa.[11]

Anthropogenic

Many anthropogenic sources of trace metal particulates exist; however, the main sources include: coal combustion, oil combustion, non-ferrous metals, iron and steel manufacturing, refuse incineration, phosphate fertilizers, cement production, and fuel wood combustion. As seen in Table 1.2, coal combustion emits a large portion of each of the metals when compared to the other anthropogenic sources.[10] Coal combustion accounts for 84% of Mo, 58% of Hg, 47% of Se, 37% of Sb, 37% of Cr, 29% of Mn, 25% of Ni, and 15% of Sn of the total anthropogenic emissions of each of these metals worldwide.[10]

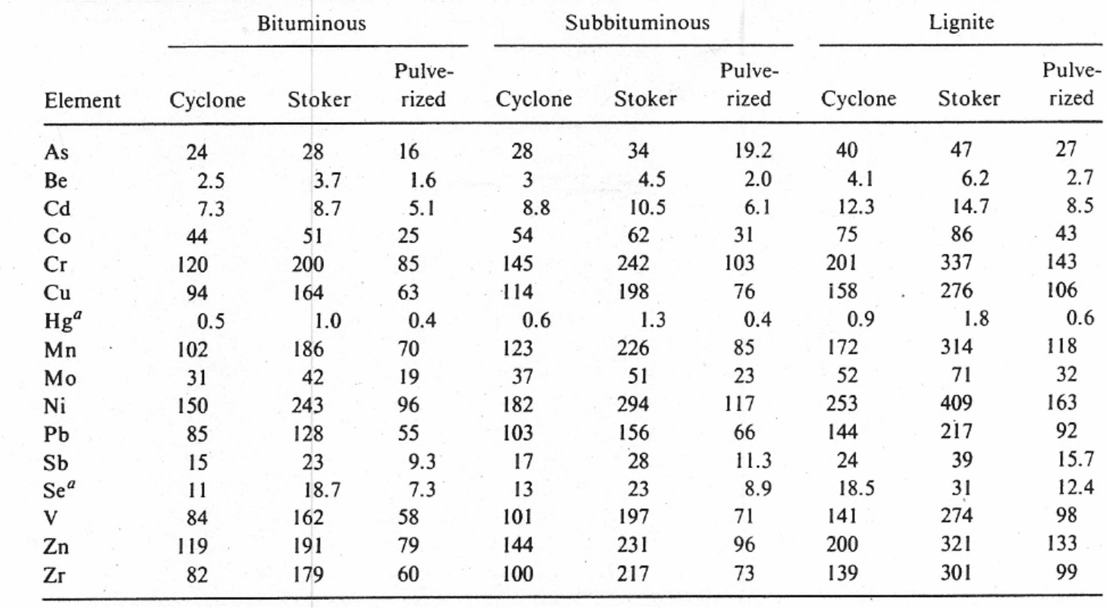
There are two ways that metals can be emitted by a coal combustion power plant: in the gaseous or solid form.[12] In the solid form, metals can be trapped in the bottom ash or the fly ash. The bottom ash is typically collected at the bottom of the boilers and then deposited in areas surrounding the power plants until enough is accumulated to be transported to area landfills. There are obviously several issues that can arise with this type of disposal: 1. leaching of the metal contaminants from the ash into the soil; 2. possible ground water contamination from the soil; 3. run-off water from the ash contaminating surrounding soil and water supplies; and 4. contamination at the landfill site to soil and water.

Table 1.2: Anthropogenic emissions of trace metals worldwide (*10^6 kg/year).[4]

Source Category	As	Cd	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sn	V	Zn
Coal combustion	2.0	0.53	11	5.2	2.1	11	2.7	14	8.2	1.3	1.8	1.0	7.9	11
Oil combustion	0.06	0.14	1.4	1.9		1.4	0.55	27	2.4		0.48	3.3	76	1.4
Non-ferrous metals:														
Mine operation	0.06	–	–	0.48	–	0.62		0.80	2.6	0.10	0.10	–	–	0.46
Pb production	1.2	0.12		0.27	0.01			0.33	21	0.29	0.29		0.06	0.33
Cu/Ni production	11	2.6		22	0.12	2.6		7.6	16	1.1	0.85	1.1		6.4
Zn production	0.46	2.8		0.48					8.5	0.07	0.16			64
Secondary non-ferrous metals				0.11		15			0.76	0.02	0.02			0.86
Iron and steel manufacture	1.4	0.16	16	1.5				3.7	7.6				0.74	20
Refuse incineration	0.31	0.75	0.84	1.6	1.2	8.2		0.36	2.4	0.67	0.06	0.81	1.2	5.9
Phosphate fertilizers		0.17		0.41				0.41	0.16					4.1
Cement production	0.53	0.27	1.3					0.49	7.1					9.8
Fuel wood combustion	0.18	0.12		0.90	0.18			1.2	2.1					3.6
Miscellaneous sources	2.0								253**					3.2
TOTAL EMISSON:	19	7.6	30	35	3.6	38	3.2	56	332	3.5	3.8***	6.2	86	132

The main focus of this paper will be on the fly ash (in the form of aerosol particles and flue gas) that is emitted from the incineration of coal. The type of metal particulates emitted into the fly ash depends on the type of coal used and the type of incineration process used (these two variations will be discussed further in chapter 2), as seen in Table 1.3.[4,10,13-15] Typically, stoker type boilers emit the most metals out of all of the coal firing units; however, these boilers are only used in industrial type settings so they contribute a small amount of the power provided compared to electrical power plants, which produce a much larger scale of electricity daily. Cyclone boilers typically emit more metals compared to pulverized boilers, and the coal class used also varies the type of metal emitted. From Table 1.3, the amount of metals emitted increases in the order: bituminous, subbituminous, and lignite.[4] The amount of these metals emitted also depends on the type of cleaning procedure used which is typically a scrubber-types include venturi wet scrubber and electrostatic precipitator (precipitators will be discussed in greater detail in chapter 2).

Table 1.3: Coal-fired power plants emissions factor of trace elements (μg/MJ).[4]



	Bituminous			Subbituminous			Lignite		
Element	Cyclone	Stoker	Pulve-rized	Cyclone	Stoker	Pulve-rized	Cyclone	Stoker	Pulve-rized
As	24	28	16	28	34	19.2	40	47	27
Be	2.5	3.7	1.6	3	4.5	2.0	4.1	6.2	2.7
Cd	7.3	8.7	5.1	8.8	10.5	6.1	12.3	14.7	8.5
Co	44	51	25	54	62	31	75	86	43
Cr	120	200	85	145	242	103	201	337	143
Cu	94	164	63	114	198	76	158	276	106
Hg[a]	0.5	1.0	0.4	0.6	1.3	0.4	0.9	1.8	0.6
Mn	102	186	70	123	226	85	172	314	118
Mo	31	42	19	37	51	23	52	71	32
Ni	150	243	96	182	294	117	253	409	163
Pb	85	128	55	103	156	66	144	217	92
Sb	15	23	9.3	17	28	11.3	24	39	15.7
Se[a]	11	18.7	7.3	13	23	8.9	18.5	31	12.4
V	84	162	58	101	197	71	141	274	98
Zn	119	191	79	144	231	96	200	321	133
Zr	82	179	60	100	217	73	139	301	99

Fate and transport of trace metal particulates

There are a variety of ways that metals can be emitted during the combustion process of coal. Any transition elements that are partially or fully vaporized are typically condensed and enriched onto submicron particles.[16] There are three basic classes to describe the enrichment behavior of the elements onto submicron particles, which are basically classified upon volatility: "Class I: elements approximately equally distributed between the bottom ash and fly ash, or show no significant enrichment or depletion in the bottom ash; Class II: elements enriched in the fly ash and depleted in the bottom ash, or show increasing enrichment with decreasing fly ash particle size; Class III: Elements totally emitted in the vapor phase."[16] Even though there are clear definitions between the classes, certain trace elements exhibit intermediate behavior. Below, in Figure 1.2, volatility can be seen to increase from Class I to Class III. The divisions of the classes show that most of the transition metals are distributed between the bottom ash and the fly ash (Class I and Class II) so they will contribute to earth, soil, and atmospheric environmental contamination, whereas the elements in Class III are emitted in the vapor phase. Just because metals are emitted in the vapor phase after incineration does not mean that they cannot be condensed, coagulated, or nucleated to form an aerosol. After the gases or particles are carried away from the combustion area, there are three very complex and integrated processes that can occur to alter or transform the emissions: adsorption, condensation, and chemical transformation.[16] Figure 1.3 shows pathways of how trace elements are separated into vapor, submicron aerosols, and supermicron aerosols, and how aerosols can coagulate, condense, and nucleate from the vapor phase.[16]

Once particulates are emitted into the atmosphere, focus must be shifted to transportation of the particulates to understand how humans will be affected whether they live close to the source or hundreds of miles from the source. To understand particulate dispersion, studies must analyze data at both the emission site and sites surrounding this.[17] Banic et. al and other studies have analyzed size distribution of particulates and the effectiveness of cloud scavenging of the particulates from the atmosphere.[17] The mixing of the plume being emitted from the plant is

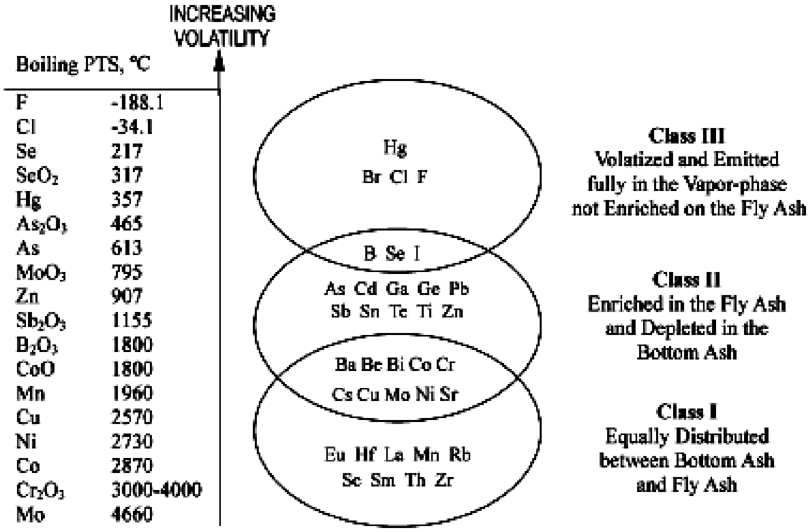


Figure 1.2: Trace elements categorized by enrichment and volatility.[16]

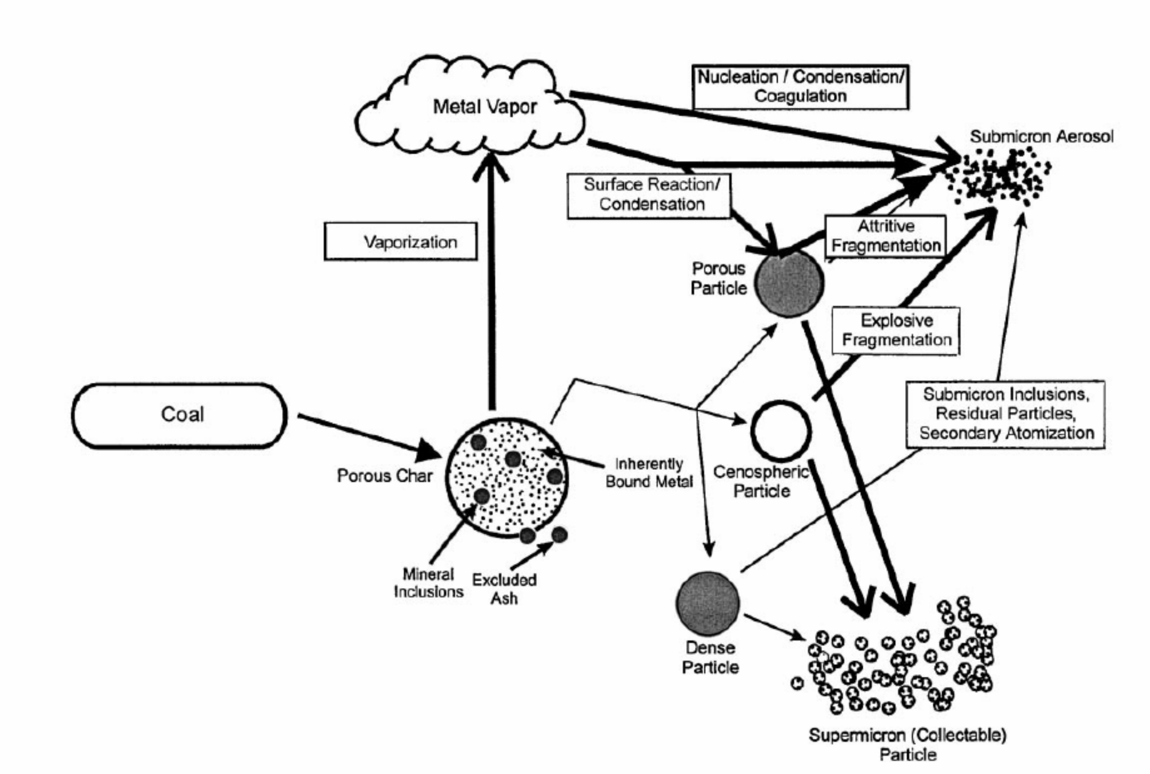


Figure 1.3: Particle formation in a combustion system.[18]

observed at ground level and in both the summer and the fall and day and night.[17] Mixing can occur in both seasons if either of the two following meteorological conditions exist: the surrounding uneven terrain or trees can create wind disturbances that create turbulence, or mixing can be initiated via "forced surface heating".[17] One other parameter that can alter the mixing of the plume is the height of the smoke stack from ground level-the higher the smoke stack, the less ground level mixing that occurs. For ultrafine particulates, they have a higher concentration closest to the source, but their residence time in the atmosphere is longer than supermicron particles.[16,19] As the distance from the source is increased, the concentration of ultrafine particles tend to decrease because of humidity effects-water can condense onto the particles causing growth-and particle growth from reactions in the atmosphere.[19] However, the overall general trend upon emission is that particulate concentration in almost every single size range increased from emission from the plume as compared to ambient air.

To gain a better understanding of how particulates can lead to environmental contamination by means other than the atmosphere and contribute to negative human health, the removal processes from the atmosphere will be discussed. There are two removal processes for trace elements from the atmosphere: wet deposition and dry deposition-a general schematic of transformation and deposition of the particles from the stack is shown in Figure 1.4.[20] Dry deposition is generally thought of as gravitational settling from the atmosphere, but it cannot be thought of only in these terms because transportation via turbulent eddies and inertial effects must also be considered.[20] In other words, there is some dry deposition close to the site of emission; however, there may also be dry deposition located farther from the emission site due to transportation. Wet deposition is deposited to the earth via cloud coverage-definitely an issue in the mountains because they are saturated in lower levels of cloud coverage due to their height above sea level, which can cause deposition of particulates onto trees, soil, and water-or rain processes. Both dry and wet deposition are an issue because they can deposit emissions into the

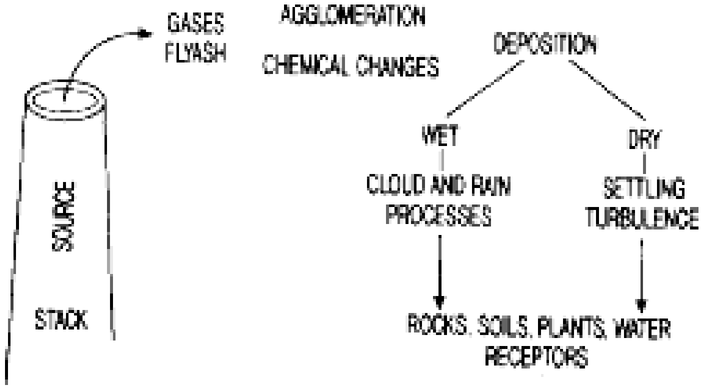


Figure 1.4: Schematic of the fate of trace elements in the stack emissions.[20]

rocks, soil, plants, and water close to the emission site and distances away from the site, causing environmental impacts to the surrounding communities.

Since over half of the country is powered by coal and our natural reserves are large compared to other natural resources such as oil and natural gas, it is of grave concern that multiple metals found in the atmosphere are largely produced by anthropogenic sources, namely coal. Also, the metals emitted into the atmosphere, both in the particulate form and the vapor form, from the combustion of coal can be transported to the surrounding community as well as distances far from the emission source. Once in the atmosphere, transportation, coagulation, condensation, nucleation, and deposition are of concern to both the environment and human health. Although great strides in emission controls and knowledge of the metals emitted have progressed over the past decades, exploration of the particulates in the post-combustion zone and in the atmosphere is needed to fully understand the effects of coal combustion. There is such a large uncertainty when trying to track emissions from a specific source over great distances because of the multitude of sources of metal emissions close to the specific source, the multitude of environmental effects on the metal emissions, such as meteorological and mixing of atmospheric layers, and the inability to tag a specific particulate emission from the source. However, modeling and data collected from specific site sources is slowly beginning to progress the science of emissions transportation.

CHAPTER 2

COAL AS AN ENERGY SOURCE: TYPES OF COAL USED, INCINERATION PROCESSES, AND SCRUBBERS

Types of coal used: lignite, subbituminous, bituminous, and anthracite

There are four types of coal available to incinerate to produce energy: lignite, subbituminous, bituminous, and anthracite. Almost every element in the periodic table is in coal and can be divided into three groups: 1. major elements, which are found at levels above 1000 ppm (C, H, O, N, S); 2. minor elements, which are found at levels between 100 and 1000 ppm (Si, Al, Ca, Mg, K, Na, Fe, Mn, Ti) and halogens (F, Cl, Br, I); and 3. trace elements, which are found at levels below 100 ppm (transition metals or heavy metals).[16] The four types of coal are a combination of inorganic mineral matter and organic matter that have been formed over millions of years of heat and pressure to layers of vegetation that has fallen.[21] Essentially, the process starts from an area that was a swamp millions to hundreds of millions of years ago during the "Carboniferous Period"-a time period when the atmosphere was depleted of CO_2, and swamps, tropical forests, large primitive trees, and ferns dominated the planet.[22] As layers of vegetation, moss, trees, plants, and sedges, fell into the swamp, they started to decompose and disintegrate at the bottom into a dark brown or black residuum known as peat. The vegetation was not eaten by microbes or bacteria because the swamps were devoid of oxygen, an aspect required for microbes and bacteria survival.[22] As the peat laid at the bottom of the swamp, it was covered by layers of dirt and water as seen in Figure 2.1. Over time, the heat and pressure applied to the peat from the layers of dirt and water above cause coal to be formed. The energy from the coal is derived from the energy stored in the plants. As an estimate, it takes about 10,000 years to transform peat into 12 inches thick of coal.[22]

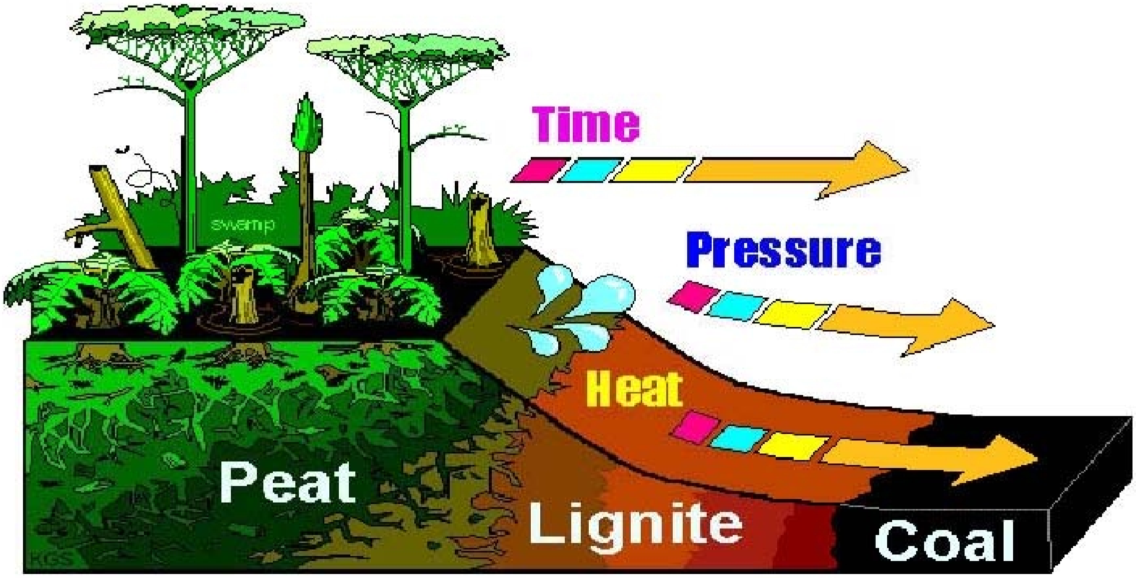


Figure 2.1: Formation of coal.[23]

To classify coal, commonly referred to as ranking coal, two things must be considered: first, there is a natural progression from lignite to anthracite over the lifetime of the coal, and second, classification depends on oxygen, inherent moisture, fixed carbon, and volatile matter.[21] To increase in coal rank from lignite to anthracite, "fixed carbon increases and the amount of volatile matter and moisture decreases."[21] Lignite has the highest moisture content and the smallest amount of fixed carbon, causing less power to be produced from the same mass amount burned as a higher ranked coal, bituminous or anthracite. Progressing from lignite to subbitimunous to bituminous to anthracite the moisture content in the coal decreases and the carbon content increases. Essentially, the coal that has the longest period of metamorphosis has the highest rank, anthracite.[24] Since bituminous, subbituminous, and lignite coal make up the vast majority of mined coal, they will be the focus of incineration, emission, and filtration via wet scrubbers, electrostatic precipitation, etc.

Lignite

Lignite is the youngest of all four types of coal, which contributes to it being the softest and the smallest distance from the earth's surface. The two main areas in the United States where this type of coal is found and mined is the Texas and North Dakota regions. Due to the abundance of lignite and small transportation distance, lignite is the main energy source used in coal-fired power plants in these regions of the U.S. In the North Dakota region, the deposits are contained in North Dakota, South Dakota, Montana, and small portions adjacent to this region in Canada.[13] The overall region estimates about 465 billion tons of lignite resources with 350 billion tons which are in North Dakota alone.[13] In the Texas region, the deposits are contained in Alabama, Mississippi, Arkansas, northern Louisiana, and southeastern Texas. The entire region contains approximately 68 billion tons of resources with Texas having 52 billion tons. Typically, due to the transportation costs of coal, the power plants will access coal from the closest sites available.

Being the initial coal rank as stated above, the moisture content is very high between 20-40 weight % because heat and pressure have been applied for a relatively small period of time compared to other forms of coal, so less water is removed, and the carbon content is 25-35%.[13] This type of coal also has a low heating value (less energy) of around 5,000 to 7,500 Btu/lb (British thermal units/pound).[13] There are several advantages to using lignite in a steam/electric power plant: it is relatively abundant in the U.S., it is much cheaper to mine because it is surface mined, and it is low in sulfur content compared to other ranks of coal, which alleviates issues of post-combustion emission devices.[13] However, with lignite, the many disadvantages outweigh the inherent advantages. For example, some of the disadvantages are: (1) the lower heating value requires additional lignite to produce the same amount of energy as higher ranking coal;

(2) additional energy is needed to cut lignite into the smaller sizes required to incinerate; (3) boiler efficiency is lost because of the additional moisture trapped in the lignite; (4) the fly ash produced in the incineration process requires more sootblowing; and (5) due to its low heat value and high moisture content, it cannot be easily transported and therefore must be used close to the mining site.[13] Most of these disadvantages are all related to increased expenditure for lignite compared to other forms of coal.

Due to the differences in the geography and plant habitation of areas around the country, inorganic material in coal varies.[4] There are two types of inorganic matter present in coal: elemental and “physically identifiable inclusions in the coal matrix,” which refers to metals that are contained in mineral components of the coal.[4] Upon combustion of the coal, lignite releases the largest amount of metals.[4]

Subbituminous

Subbituminous coal has a lower moisture content than lignite but a higher moisture content than bituminous coal, and it is slightly older than lignite coal being at least 100 million years old.[21] Since this type of coal has formed longer, it has not only a higher percentage carbon than lignite, 35-45%, but it also has a higher heating value of approximately 9,420 to 10,130 Btu/lb “on an as-mined basis” and 8,300-11,500 Btu/lb “on a wet, mineral-matter-free basis”.[21] Subbituminous coal also has a lower sulfur content than bituminous coal making it a good choice for an alternative fuel to be used in boilers that were once designed for bituminous coal since less sulfur oxides will be emitted into the environment, reducing the expense necessary for scrubbers.[21]

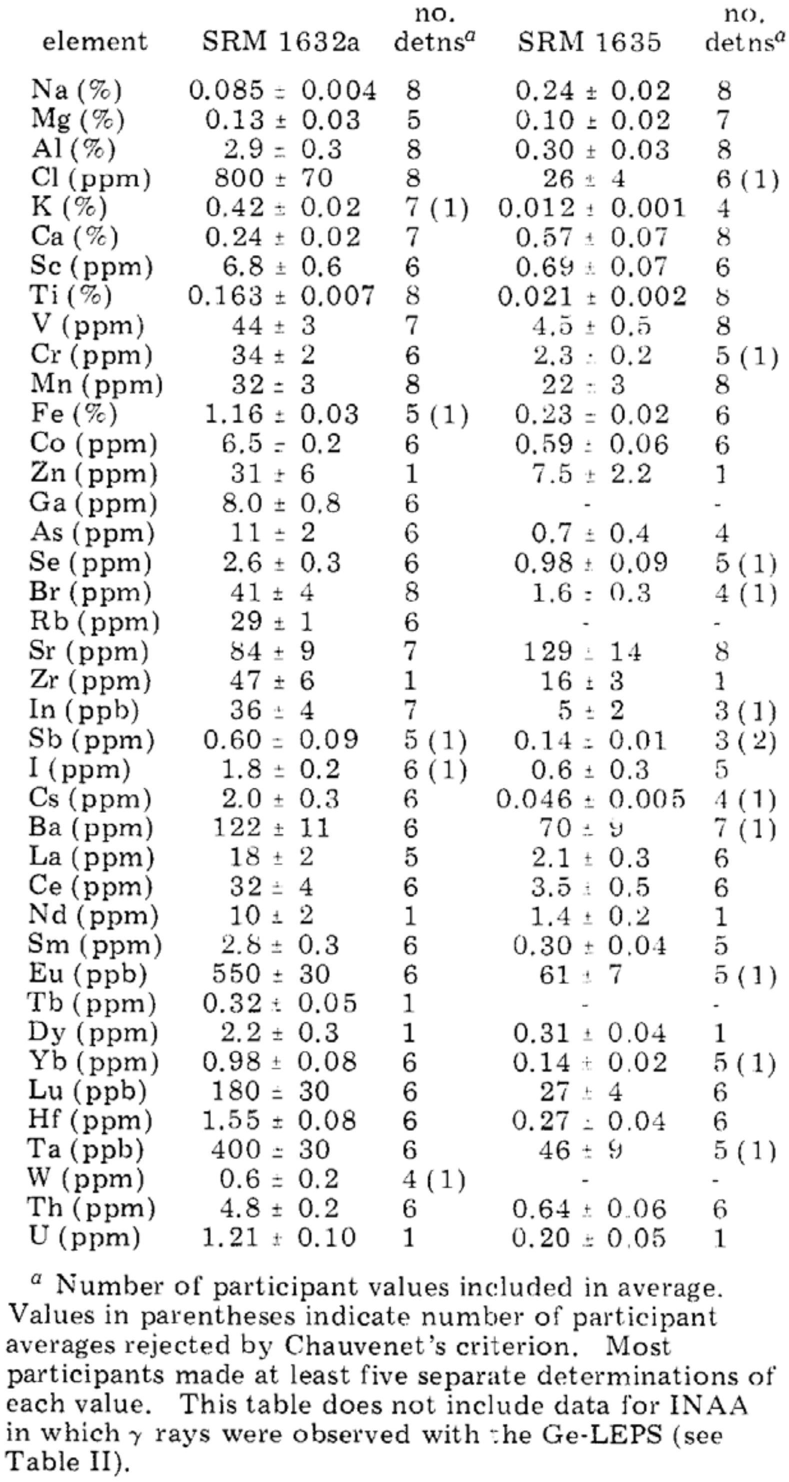
Below in Table 2.1, the elemental metals in both bituminous and subbituminous coal, pre-incineration, are listed. SRM 1632a refers to bituminous coal mined from Pennsylvania, and

SRM 1635 refers to subbituminous coal mined from a Colorado site.[25] The samples were analyzed by multiple groups around the country and via multiple instrument types: neutron-capture prompt γ-ray activation analysis (PGAA), instrumental photon activation analysis (IPAA), and 14-MeV neutron activation.[25] There are a multitude of metals found in the samples of coal, and a wide range of concentrations from tens of ppb to hundreds of ppm are observed. There were even multiple radioactive elements present, U, for example, with a concentration of 0.2 ± 0.05 ppm.[25] The largest values of metals observed were Sr, 129 ± 14 ppm, Mn 22 ± 3 ppm, and Ba 70 ± 9 ppm.[25] The metals with the smallest concentrations were In 5 ± 2 ppb, Eu 61 ± 7 ppb, Lu 27 ± 4 ppb, and Ta 46 ± 9 ppb.[25] For all of the transition metals observed, the values were less for subbituminous coal as compared to bituminous coal-most likely due to the smaller time period subbituminous coal is subjected to the elements of heat and pressure; however, subbituminous coal releases more metals into the atmosphere upon combustion.

Bituminous

As the rank of coal is increased, next in line is bituminous, which is older than subbituminous. Bituminous is the largest group out of all four types of coal and has a lower moisture content, lower volatile matter, and higher fixed carbon than subbituminous.[21] It also has very good slagging and agglomerating characteristics.[21] Slag refers to any residues left behind after incineration due to impurities, and agglomerate refers to any deposits from the fly ash.[26] Because residues left behind can stick to the outer walls of the tubes in the boiler causing a decrease in the heat transfer and damage to the boiler, slagging is a very important consideration.[26] Besides anthracite, bituminous has the largest heating values of the coals aforementioned, 10,720-14,730 Btu/lb as mined and 10,500-14,000 Btu/lb "on a wet, mineral-matter-free basis."[21] A large part of the bituminous mined comes from the Appalachian

Table 2.1: Concentrations of elements in SRM 1632a (bituminous) and SRM 1635 (subbituminous) as determined by PGAA, IPAA, and 14-MeV neutron activation



element	SRM 1632a	no. detns[a]	SRM 1635	no. detns[a]
Na (%)	0.085 ± 0.004	8	0.24 ± 0.02	8
Mg (%)	0.13 ± 0.03	5	0.10 ± 0.02	7
Al (%)	2.9 ± 0.3	8	0.30 ± 0.03	8
Cl (ppm)	800 ± 70	8	26 ± 4	6 (1)
K (%)	0.42 ± 0.02	7 (1)	0.012 ± 0.001	4
Ca (%)	0.24 ± 0.02	7	0.57 ± 0.07	8
Sc (ppm)	6.8 ± 0.6	6	0.69 ± 0.07	6
Ti (%)	0.163 ± 0.007	8	0.021 ± 0.002	8
V (ppm)	44 ± 3	7	4.5 ± 0.5	8
Cr (ppm)	34 ± 2	6	2.3 ± 0.2	5 (1)
Mn (ppm)	32 ± 3	8	22 ± 3	8
Fe (%)	1.16 ± 0.03	5 (1)	0.23 ± 0.02	6
Co (ppm)	6.5 ± 0.2	6	0.59 ± 0.06	6
Zn (ppm)	31 ± 6	1	7.5 ± 2.2	1
Ga (ppm)	8.0 ± 0.8	6	-	-
As (ppm)	11 ± 2	6	0.7 ± 0.4	4
Se (ppm)	2.6 ± 0.3	6	0.98 ± 0.09	5 (1)
Br (ppm)	41 ± 4	8	1.6 ± 0.3	4 (1)
Rb (ppm)	29 ± 1	6	-	-
Sr (ppm)	84 ± 9	7	129 ± 14	8
Zr (ppm)	47 ± 6	1	16 ± 3	1
In (ppb)	36 ± 4	7	5 ± 2	3 (1)
Sb (ppm)	0.60 ± 0.09	5 (1)	0.14 ± 0.01	3 (2)
I (ppm)	1.8 ± 0.2	6 (1)	0.6 ± 0.3	5
Cs (ppm)	2.0 ± 0.3	6	0.046 ± 0.005	4 (1)
Ba (ppm)	122 ± 11	6	70 ± 9	7 (1)
La (ppm)	18 ± 2	5	2.1 ± 0.3	6
Ce (ppm)	32 ± 4	6	3.5 ± 0.5	6
Nd (ppm)	10 ± 2	1	1.4 ± 0.2	1
Sm (ppm)	2.8 ± 0.3	6	0.30 ± 0.04	5
Eu (ppb)	550 ± 30	6	61 ± 7	5 (1)
Tb (ppm)	0.32 ± 0.05	1	-	-
Dy (ppm)	2.2 ± 0.3	1	0.31 ± 0.04	1
Yb (ppm)	0.98 ± 0.08	6	0.14 ± 0.02	5 (1)
Lu (ppb)	180 ± 30	6	27 ± 4	6
Hf (ppm)	1.55 ± 0.08	6	0.27 ± 0.04	6
Ta (ppb)	400 ± 30	6	46 ± 9	5 (1)
W (ppm)	0.6 ± 0.2	4 (1)	-	-
Th (ppm)	4.8 ± 0.2	6	0.64 ± 0.06	6
U (ppm)	1.21 ± 0.10	1	0.20 ± 0.05	1

[a] Number of participant values included in average. Values in parentheses indicate number of participant averages rejected by Chauvenet's criterion. Most participants made at least five separate determinations of each value. This table does not include data for INAA in which γ rays were observed with the Ge-LEPS (see Table II).

mountain and Ohio Valley regions, and since this coal is older and located farther under the earth's surface, it cannot be surfaced mined but rather must be mined underground. This factor not only creates much more damage environmentally; it also creates more hazards physically to the miners.

Unlike subbituminous, all of the metals analyzed in Table 2.1 were found in bituminous. Once again, as with subbituminous, a wide range of concentrations from tens of ppm to hundreds of ppm were observed. The largest concentration, 122 ± 11 ppm contained in the coal was Ba.[25] Only four elements contained ppb levels, Eu-550 ± 30, Ta-400 ± 30, In-36 ± 4, and Lu-180 ± 30.[25] Coals of the lignite nature that are mined in the western United States have a larger amount of Cr(VI); whereas the bituminous coal used in the eastern portion of the United States has very low Cr(VI).[27] Referring to post-combustion emission of metals, bituminous coal releases the smallest amount into the atmosphere.[4]

Anthracite

The highest ranking coal, anthracite, typically has 4% volatile matter, 5% moisture, 10% ash, and 80% fixed carbon (sulfur and nitrogen content approximately 1%) and is mined in northeastern Pennsylvania.[14] Compared to the aforementioned coals, anthracite has much less moisture due to the prolonged (on the time scale of millions to hundreds of millions of years) geological conditions-heat, pressure, and increased deposits of dirt on the top most layer of exposed earth. Due to the small amounts of volatile matter and elevated carbon content, anthracite burns at much higher ignition temperatures than lignite and bituminous coal causing increased heating values, 12,000-14,000 Btu/lb (6,700-7,800 kcal/kg).[14] There is also another form of anthracite called culm, or anthracite refuse, that is used in incineration processes; the scarcity of this material limits the amount used for fossil fuel power generation, therefore little data has been collected and will not be discussed in the scope of this paper.[14]

Classification of boilers via incineration processes : pulverized, cyclone, and stoker

Lignite, bituminous, anthracite, and subbituminous can be incinerated by three main types of boilers: pulverized, cyclone, and stoker.[4,14,21] The boilers can also be further classified by construction, fuel, and type. "Boiler types are identified by the heat transfer method (watertube, firetube, or cast iron), the arrangement of the heat transfer surfaces (horizontal or vertical, straight or bent tube), and the firing configuration (suspension, stoker, or fluidized bed)."[21] The vast majority of coal-fired power plants use the watertube method to transfer

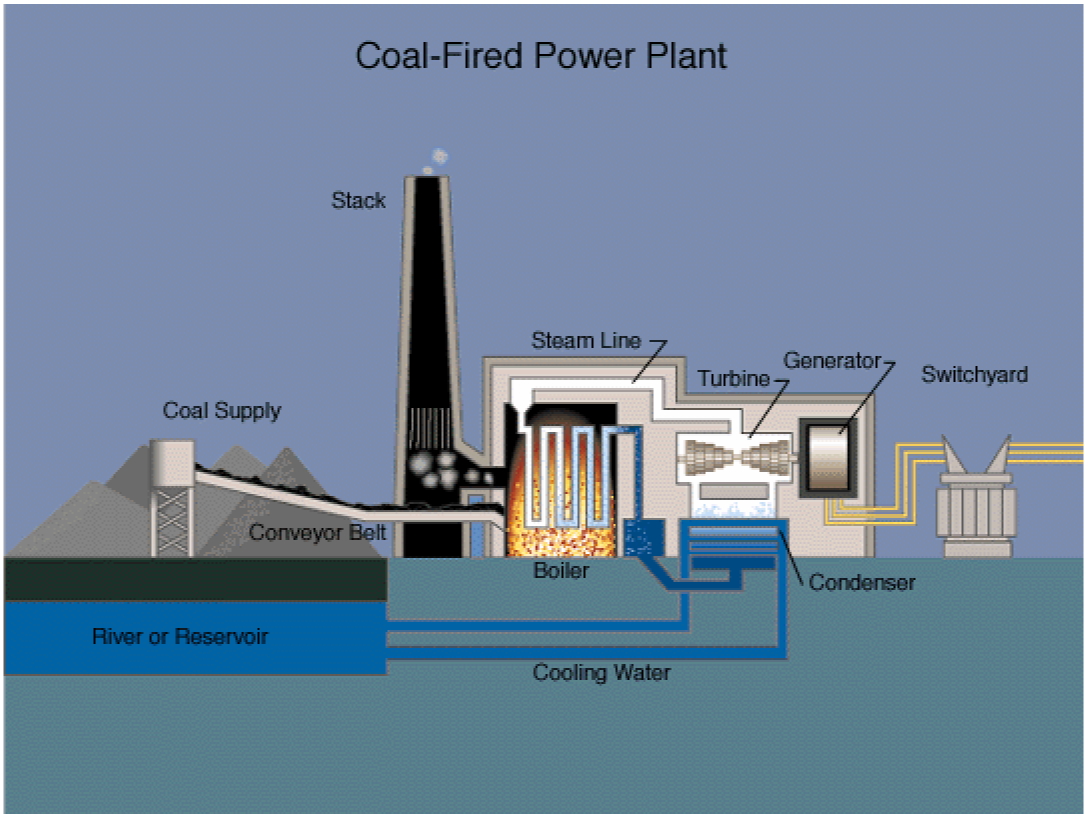


Figure 2.2: Schematic of a coal-fired power plant (Tennessee Valley Authority).[28]

heat in the boiler, as seen in Figure 2.2.[13] Because of the multiple types of boilers and variations of firing methods for these boilers, trace metal emissions vary from power plant to power plant across the country. Pulverized and cyclone boilers, the most prevalent in coal-fired power plants, will be introduced first followed by stoker-fired systems, which are most abundantly used across the country in commercial, industrial, and institutional settings that power their own facilities either entirely or partially.[4]

Pulverized

In a watertube type boiler, the tubes contain the water and steam, and the combusted gas collides with the outside of the tube.[15] In pulverized coal boilers, commonly referred to as PC-boilers, the combustion process takes place in the furnace where the fuel is suspended as seen in Figure 2.3.[15] Due to combustion in suspension, 80% of the ash contained in coal is released in the flue gas, which directly correlates to higher particulate emissions.[4] To further break down the classification of PC-boilers, the ash can be removed from the coal by two methods depending on the phase, solid or molten.[15] The classifications are referred to as "dry bottom or wet bottom"

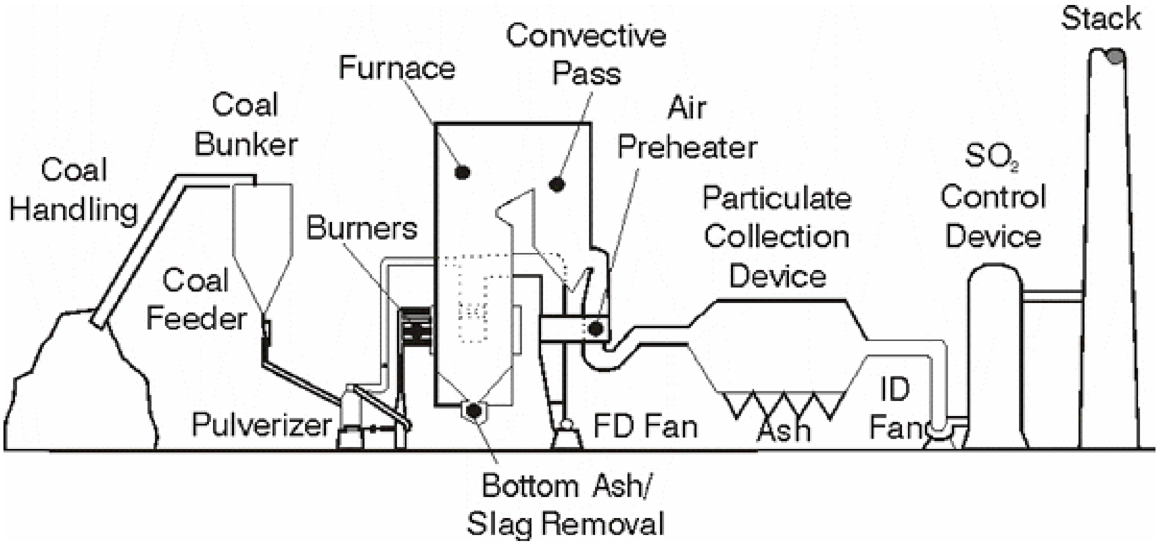


Figure 2.3: Schematic of a typical pulverized boiler.[29]

respectively.[15] "Wet bottom", the most common type and referred to as slag top furnaces from the slag produced in the process, uses bituminous coal, which has low fusion temperatures.[15] "Dry bottom" uses coal with higher fusion temperatures.

To add further complexities to the multiple types of PC-boilers, there are two different firing possibilities: corner firing and face firing (cyclone firing is another type but most consider it a completely separate incineration process).[13,15,21] Derived from the placement and firing direction of the burners, corner firing, more commonly referred to as tangential boilers, uses opposite corner alignment burners, which are in vertical rows, while firing tangential to an imaginary circle inside the boiler.[13,21] Using this method, flame spreads through the entire furnace effectively using the entire volume.[13] For face firing PC-boilers, the burners are typically located on opposite walls, although a small portion of these can only have burners on a single wall, where they are aligned horizontally.[13] Pulverized boilers emit the smallest amount of metals upon combustion when compared to cyclone and stoker boilers.[4]

Cyclone

Although cyclone boilers pulverize the coal like PC-boilers, the major difference is that the coal is not crushed into a powder; instead, it is pulverized into 4-mesh size (4.75 mm) pieces.[15,21] Much like corner firing PC-boilers, cyclone boilers introduce the coal tangentially through burners, which creates a swirling vortex.[15] Because of the centrifugal force of the vortex, the slag is forced to the outside wall.[13] The larger coal particles fed into the boiler then adhere to the slag on the walls until they are completely combusted, whereas the smaller coal particles are suspended in the furnace like PC-boilers.[15] To remove slag, a "slag tap", much like a toilet, is used to continuously remove slag from the outer walls.[13] Another similarity to the aforementioned boiler is the "wet bottom system" that is maintained at high temperatures because a small layer of the slag must line the wall to continue the process of incinerating the coal.[13,21] In the incineration process of a cyclone boiler, it emits more metals as compared to a pulverized boiler.[4]

Stoker

The final boiler type, stoker, is the most common watertube boiler used for coal-fired industrial, commercial, and institutional applications across the country.[15] A Stoker boiler introduces the coal into the system, which is completely different than pulverized and cyclone boilers. There are one of two ways that the approximate 2-inch pieces of coal is added into the system: it can either be fed on a slow moving grate or a stationary grate.[15] With the moving grate, much more common with this type of boiler, ash is formed at one end of the boiler, coal is introduced on the other end of the boiler, and ash is dumped into the collection hopper and transported to a dumping site-much like the way bottom hopper transfer trucks work.[13] Another major difference between stoker units compared to PC and cyclone units is that stoker units are "dry bottom" systems. As mentioned previously, "dry bottom" systems use coal with higher fusion temperatures-lower temperatures are required to incinerate than PC and Cyclone types.[13] One common feature of all stokers is that "overfire air" is applied from the top down to the grate and that air is underfed from the bottom up to the grate.[15] These two methods help to evenly incinerate the coal so all of the materials are combusted.[15] Stoker fired boilers emit the most metals out of all three boiler types upon incineration.[4]

Emission control devices: electrostatic precipitators and wet scrubbers

Electrostatic precipitators (ESPs)

Electrostatic Precipitators are the most common device used to remove emissions of the solid form from coal-fired combustion units, and a schematic of the side view is shown in Figure 2.4.[30] The usage of ESPs will not have an effect on the combustion process.[31] Particle size distribution, fly ash mass loading, fly ash electrical resistivity, and precipitator voltage and current all contribute to the operational performance of ESPs.[31] Some of the advantages of using ESPs are the long lifetime of the apparatus, collection efficiencies of up to 99% for newer versions, collection for multiple size fractions, collection even with varying gas volumes, and low cost for operation.[30] One of the draw-backs is that the collection efficiency varies with size of the particle.[30] Particles in the size range of 0.2-1.0 μm are the most difficult to size fraction for collection.[30]

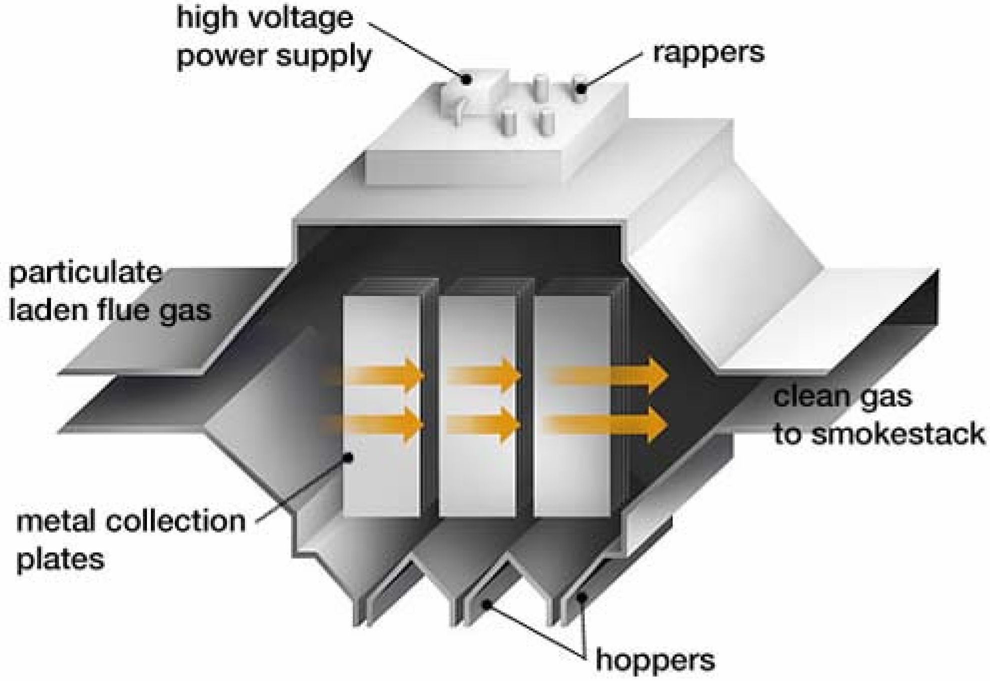


Figure 2.4: Side view schematic of an electrostatic precipitator.[32]

Wet scrubbers

Wet scrubbers can be used as an emission control device for both particulates emitted in the fly ash and for gas phase components. Scrubbers employ inertial effects to remove the particulates from the plant stack emissions as shown in Figure 2.5.[33] The collection efficiency for the scrubber system is dependent upon gas pressure drop through the scrubber, particle size distribution, and scrubbing liquor pressure.[30] The collection efficiency for 2 μm particles is in the range of 95-99%.

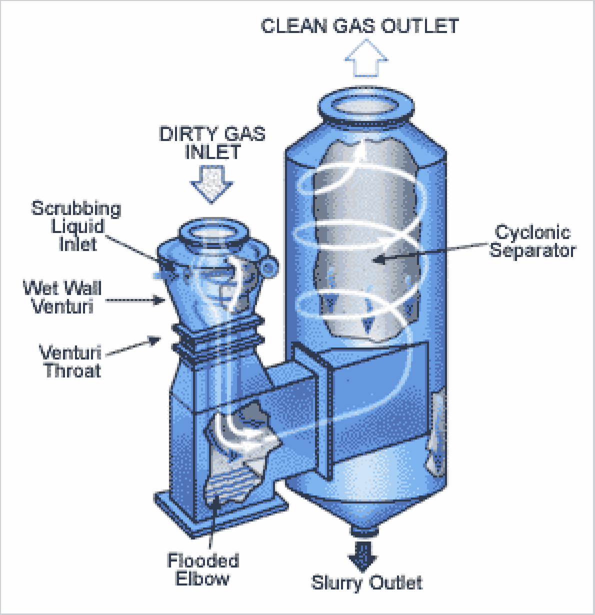


Figure 2.5: Schematic of a Venturi wet scrubber.[34]

CHAPTER 3

SAMPLE COLLECTION, PREPARATION, AND ANALYTICAL TECHNIQUES USED TO QUANTITATIVELY MEASURE METAL PARTICULATES: INAA, AAS, ICP-MS, AND AEROSOL TOF-MS

Measuring metal particulates in coal fly ash, although many strides have been made, has inherent problems such as precision and accuracy much like analyzing samples in other fields. There are many techniques used to analyze coal fly ash: ion chromatography (IC), atomic absorption spectrometry (AAS), electrothermal atomic absorption spectrometry (ETAAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma optical emission spectrometry (ICP-OES), instrumental nuclear activation analysis (INAA), and inductively coupled plasma mass spectrometry (ICP-MS); however, the focus of this paper will be INAA, AAS, and ICP-MS with the introduction of single particle TOF-MS for future implications.[35]

As previously mentioned in chapter 1, the metal particulates of interest in coal fly ash are typically smaller in size, on the scale <2.5 μm, which creates sample size limitations when trying to collect, prepare, and quantify emissions from a power plant smoke stack. Typically, four parameters should be considered before developing an analytical method: 1. To avoid sample contamination, minimal sample preparation should be required; 2. The technique needs to be sensitive to smaller sample size since dealing with trace elements; 3. The technique allows multielement characterization that is time and cost effective; and 4. No interferences should be observed that will compromise the data.[36] When analyzing particles from ambient emissions, multiple techniques are often employed to combat analytical limitations.[36]

Sample collection

A difficult aspect in quantifying trace elements from coal power plant emissions is collecting the samples without compromising the data. To collect particles, a filter, inertial impactor, diffusion, interception, or electrostatic or thermal precipitation is generally used in combination with a pumping device, although other techniques exist.[35,37,38]

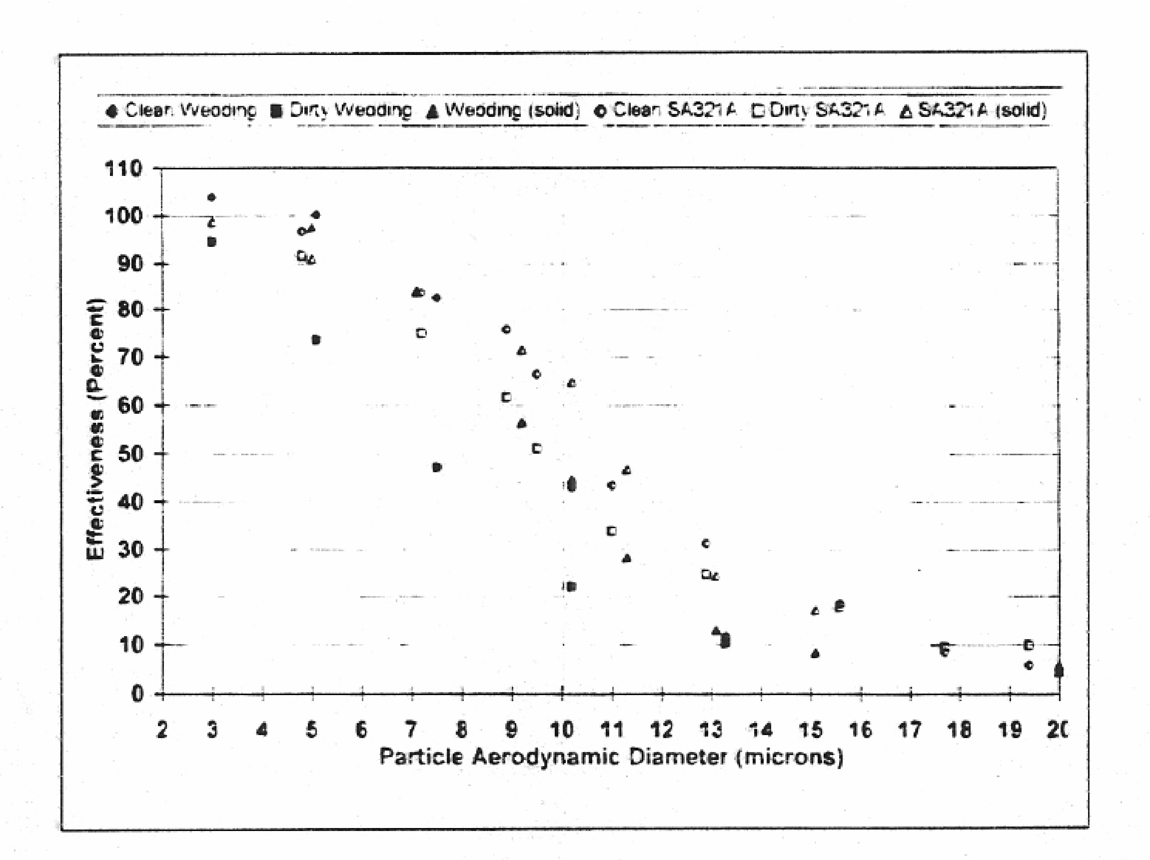


Figure 3.1: Cutpoint curves from EPA wind tunnel studies for two PM_{10} inlets both dirty from field sampling and clean. The data was obtained using liquid oleic acid particles. Solid data was obtained using ammonium fluorescein.[38]

When analyzing ambient particles, a size-selective device is used before filtration, or in some cases, only the size-selective device is used. The ambient air is directed through an inlet that specifies the size of a particle that is allowed to pass through. The inlet is quantified by a cutpoint curve, which is defined by the 50% cutpoint diameter-the size at which 50% of the particles pass through the inlet and 50% are lost on the surface.[38] In Figure 3.1, the cutpoint curve for two standard hi-vol inlet devices-Wedding IP_{10} inlet and Sierra-Anderson 321A-are shown with known concentrations of liquid oleic acid particles and solid ammonium fluorescein particles on both clean and dirty inlets.[38] From the study, as the inlet becomes dirty after extended sampling, the curve shifts to smaller particle sizes; therefore these inlets must be cleaned and greased regularly to insure correct sample size selectivity.[38] There are a multitude of inlets ranging from high volume to low volume used to sample ambient particles, which are shown in Table 3.1. The most common way to separate the particles by size is to use some type of inertial separation device more commonly known as an impactor, which was introduced by May in 1945.[39] The impactors are made of materials such as aluminum, plastic, galvanized steel, and stainless steel.[38] There are several types of impactors commonly employed: impactor plate, cyclonic, and virtual impactor-the most recent innovation in this field.

An impactor plate is used to collect particles, and the plate is placed in the flow of the incoming air.[37] Based on the size of the particle, it either bends around the plate with the air flow, or it either sticks to the plate because the size of the particle is too large to diverge around the plate. The larger the particle, the larger inertia it obtains; therefore, it will strike the plate with a larger force.[37] Usually, multiple plates are arranged in series, called a cascade impactor, as seen in Figure 3.2.[40] The schematic has multiple collection deposits located on each plate, which is not always the case. Cascade impactors are advantageous because the later plates, referred to as stages, can be maintained at reduced pressures to collect smaller particle sizes

~0.05 µm-typically impactor plates only collect particles in the size range of 0.5-30 µm.[37] This can be achieved by making the orifice sizes between the impaction plates increasingly smaller to

Table 3.1: Aerosol sampling size-selective inlets.[38]

Inlet Identifier (Manufacturer)	*Operating Principle*	*d_{50} (µm): Slope (no unit)*	*Flow Rate (L/min)*	*PM_{10} Reference or Equivalence Reference Number*[a]	*Comments*
High-Volume					
SA[b] or GMC[c] Model 320[61] (Graseby Andersen, Atlanta, GA)	Impactor	15; 1.5	1,133	NA	Single-stage, no greased shim.
SA or GMW Model 321A[305,306]	Impactor	10.2; 1.45	1,133	RFPS-1287-065	Two-stage with greased shim.
SA or GMW Model 321B[306,307]	Impactor	9.7; 1.40	1,133	RFPS-1287-064	Two-stage with greased shim.
SA or GMW Model 1200[84,92-94,306]	Impactor	9.7; 1.40	1,133	RFPS-1287-063	Single-stage with greased shim (body hinged).
GMW Wedding PM_{10}[304] (General Metal Works, Village of Cleves, OH)	Cyclonic Flow	8.8;	1,133	None	No inlet cleaning port.
Wedding IP_{10} PM_{10}[86,304] (Wedding & Associates, Fort Collins, CO)	Cyclonic Flow	9.6; 1.37	1,133	RFPS-1087-062	Inlet cleaning port on top of inlet.
Medium-Volume					
SA 254 Medium-Volume PM_{10} Inlet[308]	Impactor	10; 1.6[d]	113	RFPS-0389-071	Several small screws must be removed to clean.
Wedding Medium Flow PM_{10} Inlet[309]	Cyclonic Flow	9.5; 1.12	113	None	No cleaning port.
Bendix 240 Cyclone[310,311] (Sensidyne, Inc., Clearwater, FL)	Cyclonic Flow	2.5; 1.7	113	None	Plastic cap acts as a hopper to collect large particles.
Low-Volume					
SA 246B[312,313]	Virtual Impactor	10.2; 1.41	16.7	RFPS-0789-073, EQPM-0990-076	Top unscrews to allow access to impaction surface.
Sierra-Anderson 244 and 245[314,315]	Virtual Impactor	2.5;	16.7	None	Virtual impactor can be re-assembled backwards when taken apart for cleaning.
Wedding IP_{10}[316]	Cyclonic Flow	9.9; 1.32[d]	16.7	EQPM-0391-081	Plastic cap acts as a hopper to collect large particles.
Bendix Unico 18[310]	Cyclonic Flow	2.5; 1.83[d]	18	None	
AIHL Cyclone[317] (Air & Industrial Hygiene Laboratory, Berkeley, CA)	Cyclonic Flow	2.2; 1.87[e] 2.5; 1.38[e] 3.5; 1.40[e]	26.6 21.7 15.4	None	Screw-on cap acts as a hopper to collect large particles.
Stacked Filter Unit[318-320] (Corning CoStar [formerly Nuclepore Corp.], Cambridge, MA)	Selective Filtration	2 to 3;	10	None	Uses large pore (8 µm) etched polycarbonate filters.
BGI-4[321,322] (BGI Inc., Waltham, MA)	Cyclonic Flow	4;	2.3	None	Generally used in personal sampling applications.
MSA[321,322] (Mine Safety Appliances Co., Pittsburgh, PA)	Cyclonic Flow	3.5;	2	None	Generally used in personal sampling applications.
Sensidyne Model BDX 99R[321,322] (Sensidyne Inc., Clearwater, FL)	Cyclonic Flow	3.5;	1.7	None	Also known as Dorr-Oliver design. Generally used in personal sampling applications.
SKC Cat. No. 225-01-02[321,322] (SKC Inc., Eighty Four, PA)	Cyclonic Flow	5;	1.9	None	Generally used in personal sampling applications.
MST Low Flow Rate Sharp Cut Impactor[323]	Impactor and Virtual Impactor	2.5; 1.02[d] 10 ; 1.11[d]	4	None	Designed for use in indoor air pollution health studies.

[a] See Table II for Federal Register citation and notice date.
[b] Sierra-Andersen
[c] General Metal Works
[d] Slope = $\sqrt{d_{16}/d_{84}}$, as defined in text
[e] Slope is estimated based on $\sqrt{d_{16}/d_{84}}$

decrease the flow of air going through the system as seen in Figure 3.2.[37] Although the cascade impactor can collect particles over a wide range from the multiple stages, there are inherent difficulties: particle bounce, overload, re-entrainment, and interstage loss.[41] When the adhesion force is not as strong as the force from the momentum of the oncoming particle, the particle will not stick to the plate and will continue with the air flow, which can cause other disturbances at later stages.[41] Overload, as its name implies, occurs when too many particles stick to the impaction plate and alter the collection efficiency of the plate.[41] Re-entrainment occurs because

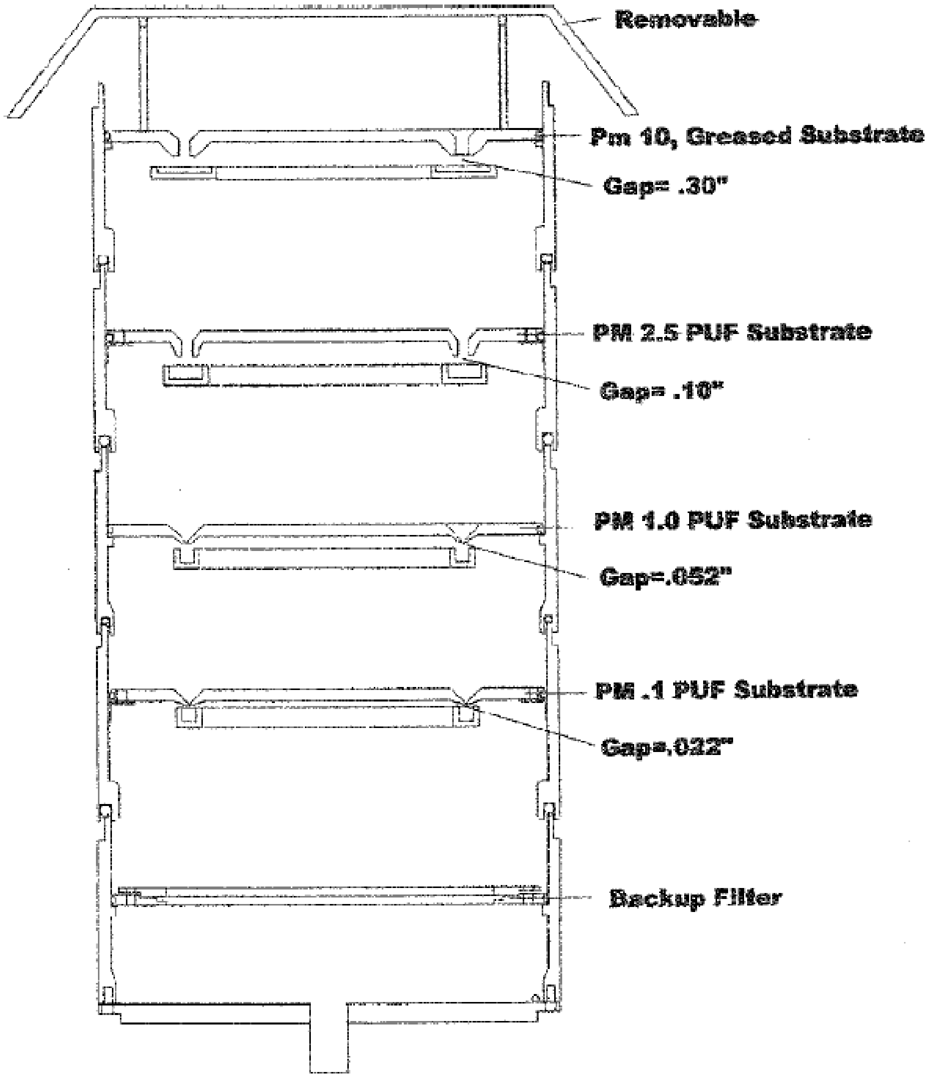


Figure 3.2: Schematic of a high volume cascade impactor.[40]

of particles impacting and removing other particles that have already impacted the plate or by the air flow removing a particle already impacted on the plate.[41] One modification in recent years has been to coat the impact surface with an oil-like material to prevent particle bounce.[38,41]

Another type of impactor referred to in Table 3.1 is the cyclonic flow version. The air encounters an impeller that initiates a circular motion and then enters a cylindrical tube, which is perpendicular to the impeller, where it begins to spiral downwards.[38,42] The particles separate from the air flow based on inertial and centripetal forces and are thrown to the wall or to the hopper at the bottom of the impactor.[42] Similar to the impactor plates, oil-like material is often added to the cyclone impactors to adhere the particles to the wall. Cyclones have typically been used for larger particle sizes, but advances in the last decade have helped to decrease the cutpoint.[43]

Virtual impactors use two orifices or slits located in line with one another, the smaller orifice typically being the first inlet as shown in Figure 3.3. The orifices are separated by a specific gap distance (denoted S in Figure 3.3) dependent on the particle sizes needed-that separates the particles based on inertial effects. The larger particles tend to be accelerated through the gap distance into the second orifice. A pump can be used to remove the gases-the inlet labeled D8 in Figure 3.3-because these smaller species can make bends in the gap distance to be pumped away, whereas the larger particles cannot. Virtual impactors are advantageous because particle bounce and re-entrainment do not have to been considered.[38] Several methods of particle growth via condensation methods at both high and low volume air flows have also been developed using virtual impactors to concentrate the particles for analysis with instrumentation that would not have been able to detect the small amounts of particles at preconcentrated values; in other words, sensitivity is increased.[44,45] The concentrators are referred to as versatile aerosol concentrator enrichment systems (VACES) because they are small and

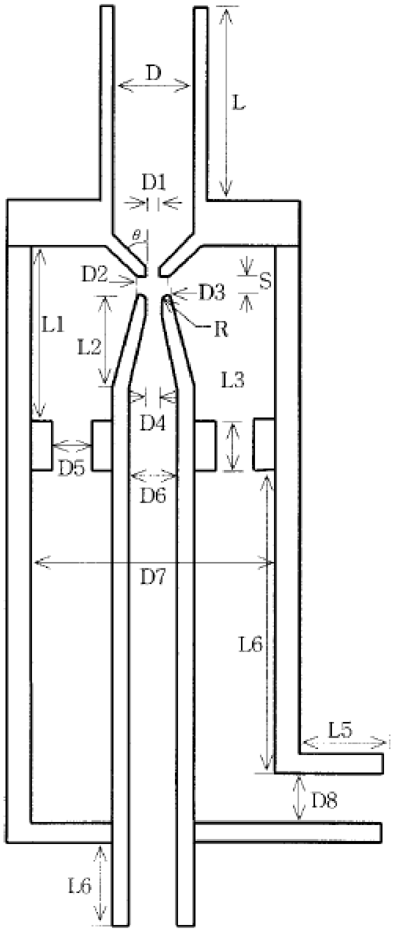


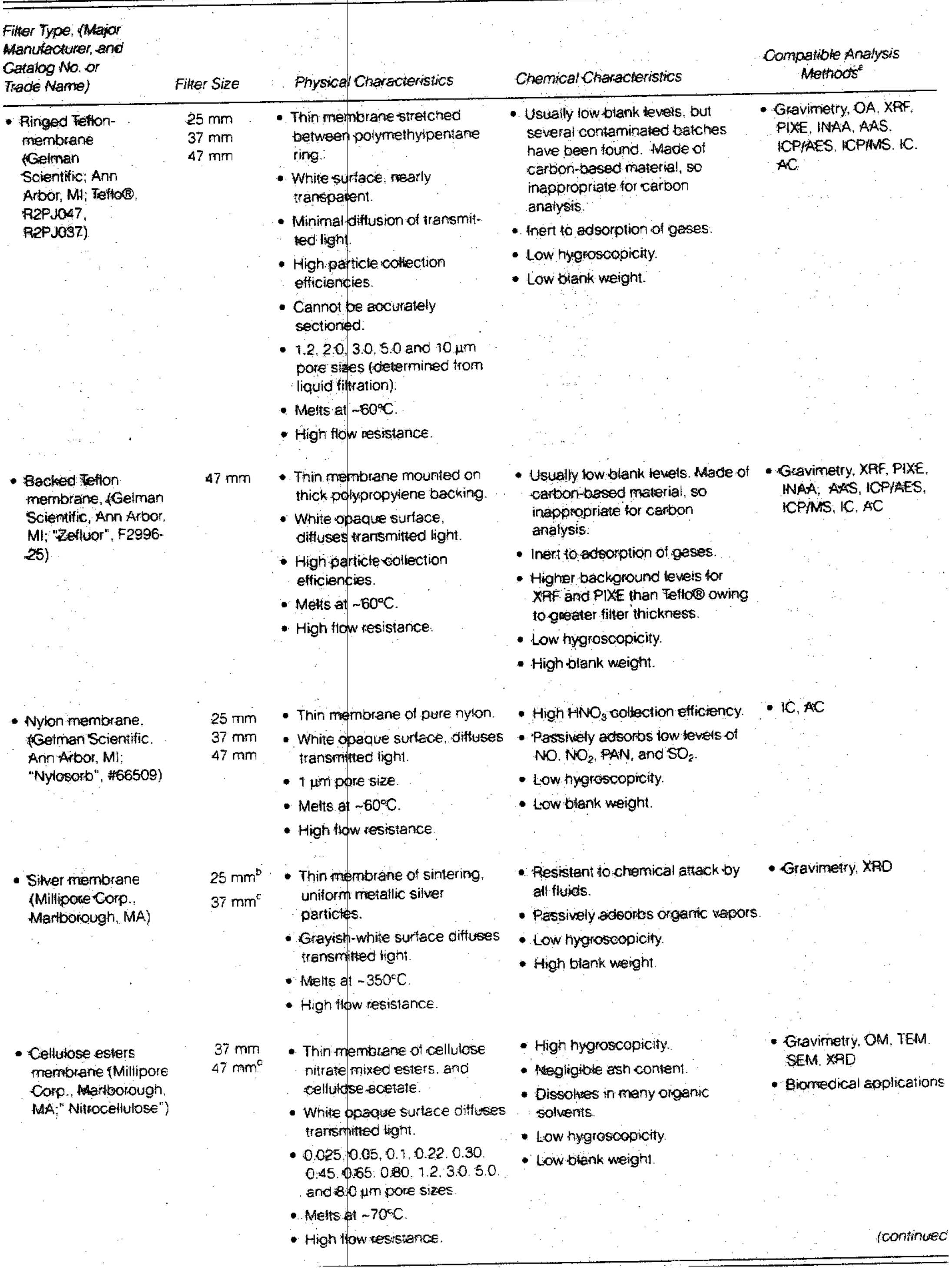
Figure 3.3: Schematic of a Specific virtual impactor.[46]

mobile for easy transportation to sample ambient sources and for in vivo and in vitro epidemiological inhalation studies.[44,46] The systems use a water saturated warm region to place water vapor in the air and particle stream followed by a cold region, which condenses the water onto the particles growing them.[44,46] The particles are then accelerated through the virtual impactor and through a dryer to remove the water. The chemical or physical properties of the particles are not altered through the growth process, and the system allows ultrafine particles below 150 nm not normally able to be separated via the virtual impactor to be analyzed.[44]

Once size selectivity of the particles is employed, they must be collected for analysis, and filters are used to accomplish collection when combined with impaction. A multitude of materials can be used for filters each with their own characteristics, such as impurities and inherent collection inefficiencies.[35,37] The characteristics which define filters are the reactions that occur on the surface of the filter, the particle collection efficiencies as a function of size, the pressure drop as a function of flow velocity, the temperature stability, the consistency of blank concentrations, and the cost and availibility.[37,38,43] Particle collection efficiency of filters is very important, and they should remove about 99% of the particles.[38] The surface of the filter should lie flat in the sample holder creating a strong seal and should not be brittle because this can cause discrepancies when taking mass measurements.[38] Chemically speaking, reactions should not occur at the surface of the filter or with the addition of solvents in the extraction process.[38] Temperature stability is vital during the sampling and sample preparation processes. The filters should not contain high or variable concentrations pre-sampling because the blank concentrations will have an impact on the metals of interest during analysis.[38] Finally, the flow of air through the filter should not be compromised with continuous sampling, and the flow should be consistent with the flow rate of the inlet control device for the particles.[38] One important factor to remember when using filters to analyze ambient samples is that they should be loaded into sample holders and out of the sample holders in a controlled lab environment, typically a laminar flow hood, to avoid contamination.[38]

There are two main classes of filters which are used to collect particles: membrane and fibrous mats.[37] Within the two classes, there are a multitude of various sub classes with their own inherent characteristics. Fibrous mat and membrane filters are the most commonly used so a vast list of these are shown in Tables 3.2-3.4 comparing physical and chemical characteristics as well as which analytical methods can be used in combination with the filters.[38]

Table 3.2: Common filter types used for sampling particulates.[38]



Filter Type, (Major Manufacturer, and Catalog No. or Trade Name)	*Filter Size*	*Physical Characteristics*	*Chemical Characteristics*	*Compatible Analysis Methods*^{e}
• Ringed Teflon-membrane (Gelman Scientific; Ann Arbor, MI; Teflo®, R2PJ047, R2PJ037)	25 mm 37 mm 47 mm	• Thin membrane stretched between polymethylpentane ring. • White surface, nearly transparent. • Minimal diffusion of transmitted light. • High particle collection efficiencies. • Cannot be accurately sectioned. • 1.2, 2.0, 3.0, 5.0 and 10 µm pore sizes (determined from liquid filtration). • Melts at ~60°C. • High flow resistance.	• Usually low blank levels, but several contaminated batches have been found. Made of carbon-based material, so inappropriate for carbon analysis. • Inert to adsorption of gases. • Low hygroscopicity. • Low blank weight.	• Gravimetry, OA, XRF, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC
• Backed Teflon membrane, (Gelman Scientific, Ann Arbor, MI; "Zefluor", F2996-25)	47 mm	• Thin membrane mounted on thick polypropylene backing. • White opaque surface, diffuses transmitted light. • High particle collection efficiencies. • Melts at ~60°C. • High flow resistance.	• Usually low blank levels. Made of carbon-based material, so inappropriate for carbon analysis. • Inert to adsorption of gases. • Higher background levels for XRF and PIXE than Teflo® owing to greater filter thickness. • Low hygroscopicity. • High blank weight.	• Gravimetry, XRF, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC
• Nylon membrane, (Gelman Scientific, Ann Arbor, MI; "Nylosorb", #66509)	25 mm 37 mm 47 mm	• Thin membrane of pure nylon. • White opaque surface, diffuses transmitted light. • 1 µm pore size. • Melts at ~60°C. • High flow resistance.	• High HNO_3 collection efficiency. • Passively adsorbs low levels of NO, NO_2, PAN, and SO_2. • Low hygroscopicity. • Low blank weight.	• IC, AC
• Silver membrane (Millipore Corp., Marlborough, MA)	25 mm^{b} 37 mm^{c}	• Thin membrane of sintering, uniform metallic silver particles. • Grayish-white surface diffuses transmitted light. • Melts at ~350°C. • High flow resistance.	• Resistant to chemical attack by all fluids. • Passively adsorbs organic vapors. • Low hygroscopicity. • High blank weight.	• Gravimetry, XRD
• Cellulose esters membrane (Millipore Corp., Marlborough, MA;" Nitrocellulose")	37 mm 47 mm^{c}	• Thin membrane of cellulose nitrate mixed esters, and cellulose acetate. • White opaque surface diffuses transmitted light. • 0.025, 0.05, 0.1, 0.22, 0.30, 0.45, 0.65, 0.80, 1.2, 3.0, 5.0, and 8.0 µm pore sizes. • Melts at ~70°C. • High flow resistance.	• High hygroscopicity. • Negligible ash content. • Dissolves in many organic solvents. • Low hygroscopicity. • Low blank weight.	• Gravimetry, OM, TEM, SEM, XRD • Biomedical applications

(continued

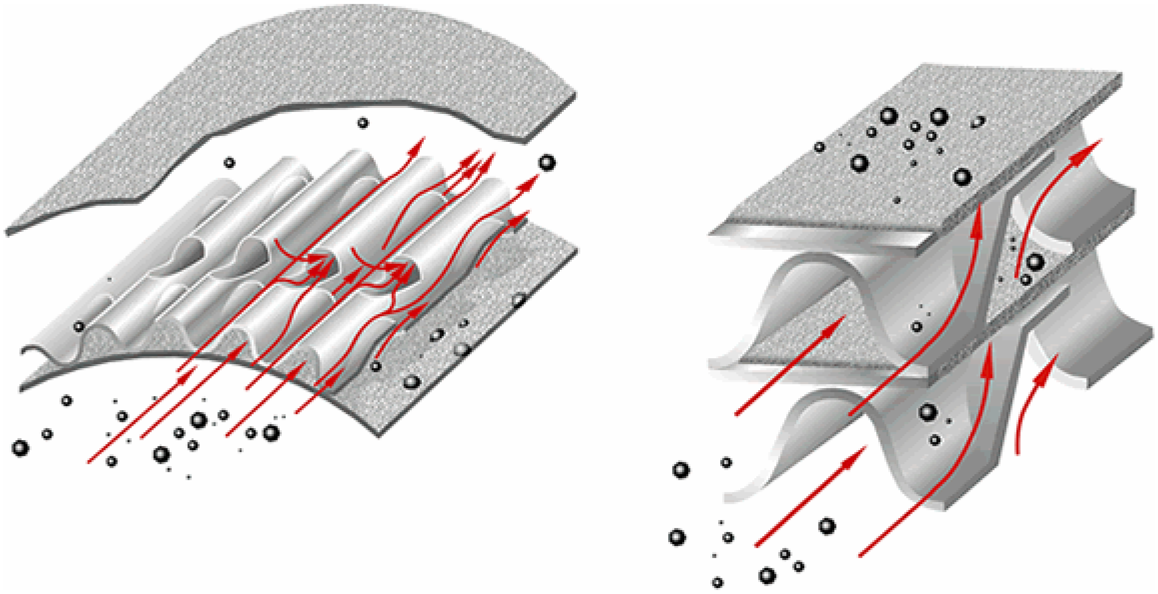
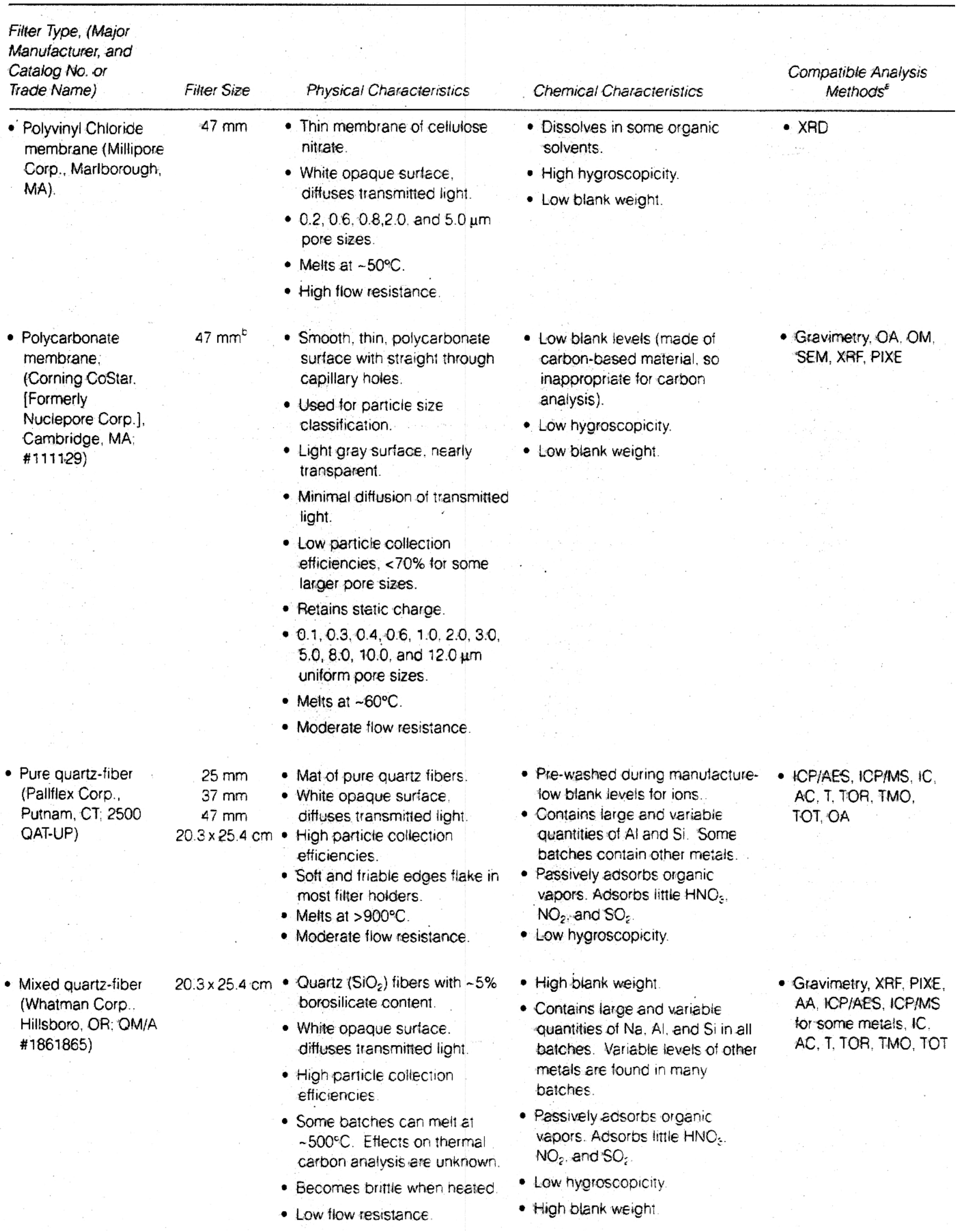


Figure 3.4: Schematic of a typical fiber mat filter.[47]

Fibrous mat filters commonly employed to collect particles include paper (cellulose), quartz, polystyrene, and glass fiber filters.[37,43] A schematic of a common fibrous mat filter is shown in Figure 3.4. These filters are made with either organic or inorganic materials that are aligned in the form of a mat.[10] One common filter used not only for sample collection but air cleaning is the high efficiency particulate air (HEPA) filter. This filter is made from cellulose and mineral fibers combined.[37] Another type of fibrous mat filter commonly used is the high-volume (hi-Vol) filter (~1000 L/min), the medium volume filter (~100 L/min), and the low volume filter (~20 L/min).[35,38] These sampling devices consist of a blower and a filter. A great aspect of the hi-Vol sample collection device is that a high volume of air flow is introduced allowing smaller sampling times, which reduces extraneous sampling impurities, whereas the small and medium volumes typically require longer sampling times.[35,37] In comparison to glass or paper fiber filters, quartz provides the most accurate mass data; however, looking at Table 3.3, quartz or mixed quartz, which is an inorganic fibrous filter, would not be a good choice for analyzing trace metals because these filters contain large quantities of Al, Si, and other metals not specified.[10,35,38] Since glass fiber filters are made of inorganic materials, they are not a good match when trying to analyze with a non-destructive technique such as INAA.[10]

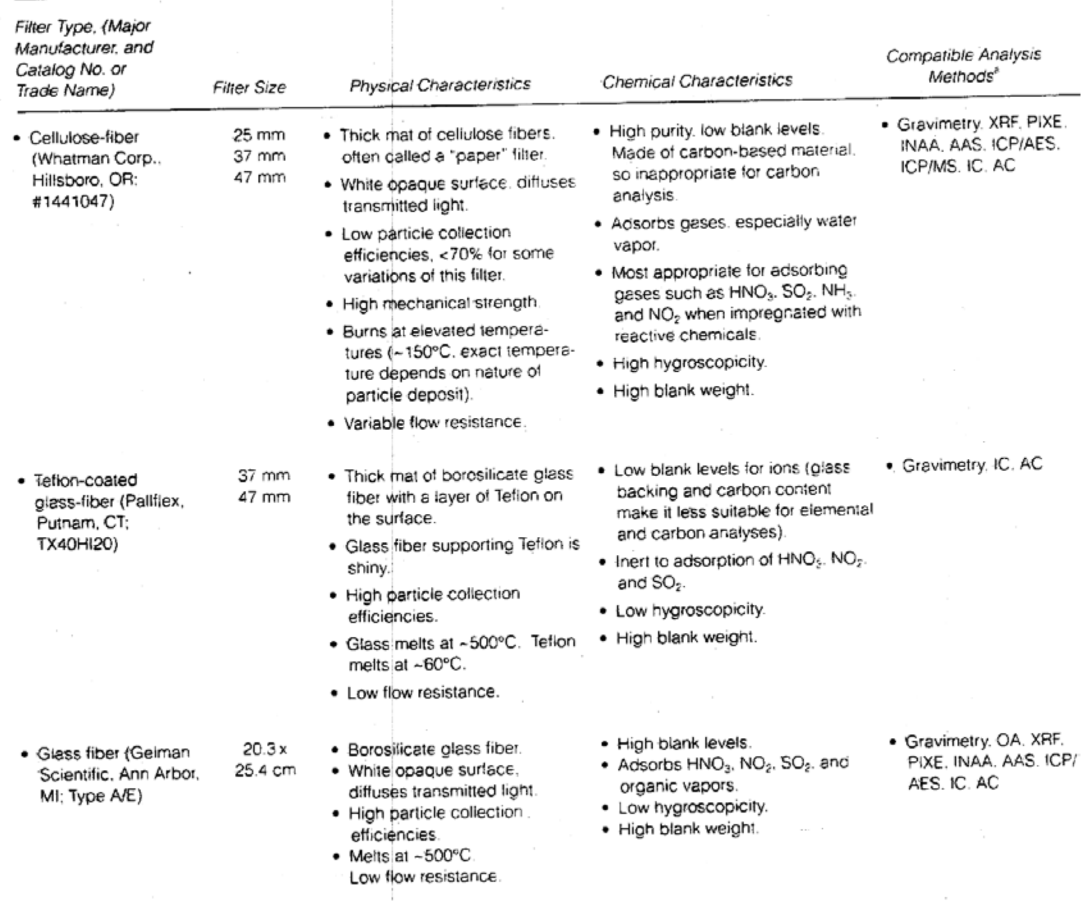
Table 3.3: Continuation of commonly employed filters for sampling particulates.[38]



Filter Type, (Major Manufacturer, and Catalog No. or Trade Name)	*Filter Size*	*Physical Characteristics*	*Chemical Characteristics*	*Compatible Analysis Methods*^{e}
• Polyvinyl Chloride membrane (Millipore Corp., Marlborough, MA).	47 mm	• Thin membrane of cellulose nitrate. • White opaque surface, diffuses transmitted light. • 0.2, 0.6, 0.8, 2.0, and 5.0 µm pore sizes. • Melts at ~50°C. • High flow resistance.	• Dissolves in some organic solvents. • High hygroscopicity. • Low blank weight.	• XRD
• Polycarbonate membrane; (Corning CoStar, [Formerly Nuclepore Corp.], Cambridge, MA; #111129)	47 mm^b	• Smooth, thin, polycarbonate surface with straight through capillary holes. • Used for particle size classification. • Light gray surface, nearly transparent. • Minimal diffusion of transmitted light. • Low particle collection efficiencies, <70% for some larger pore sizes. • Retains static charge. • 0.1, 0.3, 0.4, 0.6, 1.0, 2.0, 3.0, 5.0, 8.0, 10.0, and 12.0 µm uniform pore sizes. • Melts at ~60°C. • Moderate flow resistance.	• Low blank levels (made of carbon-based material, so inappropriate for carbon analysis). • Low hygroscopicity. • Low blank weight.	• Gravimetry, OA, OM, SEM, XRF, PIXE
• Pure quartz-fiber (Pallflex Corp., Putnam, CT; 2500 QAT-UP)	25 mm 37 mm 47 mm 20.3 x 25.4 cm	• Mat of pure quartz fibers. • White opaque surface, diffuses transmitted light. • High particle collection efficiencies. • Soft and friable edges flake in most filter holders. • Melts at >900°C. • Moderate flow resistance.	• Pre-washed during manufacture-low blank levels for ions. • Contains large and variable quantities of Al and Si. Some batches contain other metals. • Passively adsorbs organic vapors. Adsorbs little HNO_3, NO_2, and SO_2. • Low hygroscopicity.	• ICP/AES, ICP/MS, IC, AC, T, TOR, TMO, TOT, OA
• Mixed quartz-fiber (Whatman Corp., Hillsboro, OR; QM/A #1861865)	20.3 x 25.4 cm	• Quartz (SiO_2) fibers with ~5% borosilicate content. • White opaque surface, diffuses transmitted light. • High particle collection efficiencies. • Some batches can melt at ~500°C. Effects on thermal carbon analysis are unknown. • Becomes brittle when heated. • Low flow resistance.	• High blank weight. • Contains large and variable quantities of Na, Al, and Si in all batches. Variable levels of other metals are found in many batches. • Passively adsorbs organic vapors. Adsorbs little HNO_3, NO_2, and SO_2. • Low hygroscopicity. • High blank weight.	• Gravimetry, XRF, PIXE, AA, ICP/AES, ICP/MS for some metals, IC, AC, T, TOR, TMO, TOT

The two membrane filters used most often are Nuclepore and Millipore. The Nuclepore is composed of a "thin polycarbonate plastic sheet" that is applied to contact a uranium sheet that has slow neutrons.[37] The combination of the two sheets creates a smooth thin film with cylindrical pores that are consistent.[37] Nuclepore filters are used when chemical analysis of specific species is needed.[35] In contrast to Nuclepore filters, Millipore filters have pores that are interconnected and spiraled, which can be found in a variety of materials: quartz, silver, cellulose acetate, polycarbonate, and Teflon.[37]

Table 3.4: Continuation of commonly used filters for particulate sampling.[38]



Filter Type, (Major Manufacturer, and Catalog No. or Trade Name)	*Filter Size*	*Physical Characteristics*	*Chemical Characteristics*	*Compatible Analysis Methods*[a]
• Cellulose-fiber (Whatman Corp., Hillsboro, OR: #1441047)	25 mm 37 mm 47 mm	• Thick mat of cellulose fibers, often called a "paper" filter. • White opaque surface, diffuses transmitted light. • Low particle collection efficiencies, <70% for some variations of this filter. • High mechanical strength. • Burns at elevated temperatures (~150°C, exact temperature depends on nature of particle deposit). • Variable flow resistance.	• High purity, low blank levels. Made of carbon-based material, so inappropriate for carbon analysis. • Adsorbs gases, especially water vapor. • Most appropriate for adsorbing gases such as HNO_3, SO_2, NH_3, and NO_2 when impregnated with reactive chemicals. • High hygroscopicity. • High blank weight.	• Gravimetry, XRF, PIXE, INAA, AAS, ICP/AES, ICP/MS, IC, AC
• Teflon-coated glass-fiber (Pallflex, Putnam, CT; TX40HI20)	37 mm 47 mm	• Thick mat of borosilicate glass fiber with a layer of Teflon on the surface. • Glass fiber supporting Teflon is shiny. • High particle collection efficiencies. • Glass melts at ~500°C. Teflon melts at ~60°C. • Low flow resistance.	• Low blank levels for ions (glass backing and carbon content make it less suitable for elemental and carbon analyses). • Inert to adsorption of HNO_3, NO_2, and SO_2. • Low hygroscopicity. • High blank weight.	• Gravimetry, IC, AC
• Glass fiber (Gelman Scientific, Ann Arbor, MI; Type A/E)	20.3 x 25.4 cm	• Borosilicate glass fiber. • White opaque surface, diffuses transmitted light. • High particle collection efficiencies. • Melts at ~500°C Low flow resistance.	• High blank levels. • Adsorbs HNO_3, NO_2, SO_2, and organic vapors. • Low hygroscopicity. • High blank weight.	• Gravimetry, OA, XRF, PIXE, INAA, AAS, ICP/AES, IC, AC

One final aspect of particle sampling that will be briefly touched upon is the filter holder. Much like previously stated with filters, careful consideration of filter holders should be employed because they are made with a variety of materials and configurations. There are two main types of holders, in-line and open-face.[38] In-line filter holders, shown in Figure 3.5, have a small sampling inlet, which then opens into a larger chamber where the filter is stored. The open-face filter holder on the other hand does not have any constrictions prior to the filter compartment as seen in Figure 3.6.[38] An open-face filter holder is preferred for ambient sampling in most cases because the particles tend to impact the filter in the center with the in-line holder configuration, which can bias results if the filters are broken into portions and analyzed.[48]

Figure 3.5: Millipore in-line
Filter holder.[49]

Due to the large range of collection devices, impactors and filters, the technique being used as well as the sample preparation method and volume of ambient air being sampled needs to be considered before choosing. But to give the reader a general idea, for high volume samplers, cellulose or quartz fiber filters are an excellent choice because of their purity, low cost, easy handling, and low pressure drop.[43] For low volume sampling systems, the Nuclepore polycarbonate filters are an excellent choice; however, once again, all parameters from methodology to instrumentation and chemical and physical characteristics desired in the collection process and filter need to be considered to find the best fit.

Figure 3.6: Open face filter holder.[50]

Sample preparation

When dealing with trace atmospheric elements, extreme caution in handling the filters for preparation is required via a laminar flow hood or most preferentially a clean room.[10] The filters are most often cut into fractions for analysis when dealing with ambient aerosols because multiple techniques must be utilized.[43,48] The uncertainty introduced by fractioning the sample is small, typically <6%.[43] To avoid the filter being compromised when fractioning due to brittleness etc., a small amount of acetone can be added to the filter to aid in the process.[43] For INAA, it is conventional to enclose the portion of the filter into pre-cleaned polyethylene vials or bags.[43] Samples collected on organic filters are extremely compatible with INAA because carbon, sulfate, nitrate, and ammonia all have low γ-activities and thus do not interfere with trace metal analysis.[43] Little to no sample preparation is required for INAA. The most important feature of INAA is to properly assess what metals will be analyzed so a proper irradiation-count scheme can be implemented, which will be discussed in the INAA section later in the chapter. As for the other methods of instrumentation to be discussed, each one will require a sample preparation phase that will include either an extraction process from the filter or from the impactor plates or a microwave digestion method for filters.

Traditionally when analysis of ambient aerosols is required, extraction of the particles must be achieved to analyze the samples via AAS and ICP-MS.[36] AAS can use solid samples or slurries, but interferences are much more abundant than with liquid samples.[10] There are a multitude of extraction solvents used; however, the most common are HNO_3, HNO_3 + HCl, HNO_3 + HCl + HF, and HNO_3 + $HClO_4$.[36] Some groups also use H_2O_2 in addition to the acids to aid in complete oxidation of organic matter, which can be contributed by the filters.[51] Certain acids are better to use when dealing with specific analytical instrumentation. For example, HNO_3 is a great choice for ICP-MS because it destroys organic compounds and oxidizes the metals.[35] It also alleviates precipitation of elements in solution because HNO_3 forms water-soluble salts with the majority of the elements, and H, N, and O are all present in the plasma.[35] HCl and H_2SO_4 are not recommended for use with ICP-MS because interfering elements, S and Cl, are introduced into the system.[35] HCl is preferred when Fe and Ti are analyzed; however, Cl^- can cause matrix disturbances when using ICP-MS.[52] HF is very corrosive and most preparation methods try to avoid using it at all costs; however, silicates found in ambient samples are extremely hard to digest, and the addition of HF is required to digest the silica matrix and dissolve any minerals present in the samples.[35,51] Most of the trace elements are not affected by the addition of HF to the digestion process. Cr recovery is actually improved by the addition of HF; however, Se results are compromised, probably owing to the formation of SeF_6, which is lost due to volatilization upon heating.[51] When using HF, an evaporation step is generally added after digestion to reduce the risk of damages to the instrument.[35] This is extremely important when using ICP-MS because signal drift can occur due to corrosion of the instrument.[35]

Conventional digestion methods have been used for decades when collecting aerosol particles. Filter samples are placed in Teflon vials, often used in environmental sampling when strong acids are introduced, then the acid mixture is added, typically no more than 2.0-8.0 mL of an acid or acid mixture.[53,54] The mixture in the Teflon vial is placed in a conventional oven and heated for 5-6 hours at approximately 150-170°C.[53,54] After digestion and cooling, 5.0-10.0 mL of MilliQ (ultra pure water purchased from Millipore) is added to the vial to dilute the sample.[53]

Microwave-assisted digestion has gained ground in becoming one of the preferred techniques when preparing samples of ambient aerosols during the last decade.[53] Some of the advantages of using the technique are: reduced use of chemicals, reduced loss of volatile elements, smaller sampling times for dissolution, energy transfer without heat transfer, and the interior of the sample is where the heating begins.[52,53] The frequencies used for microwave digestion are 915 MHz and 2.45 GHz, 33.5 cm and 12.2 cm wavelengths respectively, which were chosen as international convention so minimum interferences will occur with communication media.[52] Power settings over 450 MW have exhibited sample loss.[53]

Instrumental neutron activation analysis (INAA)

INAA is an analytical technique that has been used for aerosol determination since the late 1960's to determine the concentration of elements in coal, coal bottom ash, and coal fly ash. A schematic of the source and instrumentation is shown in Figure 3.7. Elements in the sample absorb the thermal neutrons-"neutrons in thermic equilibrium with their surroundings"[55], which causes the stable isotope of the elements to become radioactive isotopes.[43,56] There are varying methods of INAA used; however, the method most commonly used is "slow" neutron generation or "low-energy thermal neutrons".[56] The most common neutron source used for INAA is the nuclear reactor, which allows for a higher intensity flux and a larger neutron spectrum (more isotopes can be activated).[55] γ-rays are emitted by the radioactive isotopes upon decay and are characteristic of a specific element. The γ-rays are used to determine the half-life of the decay.[55]

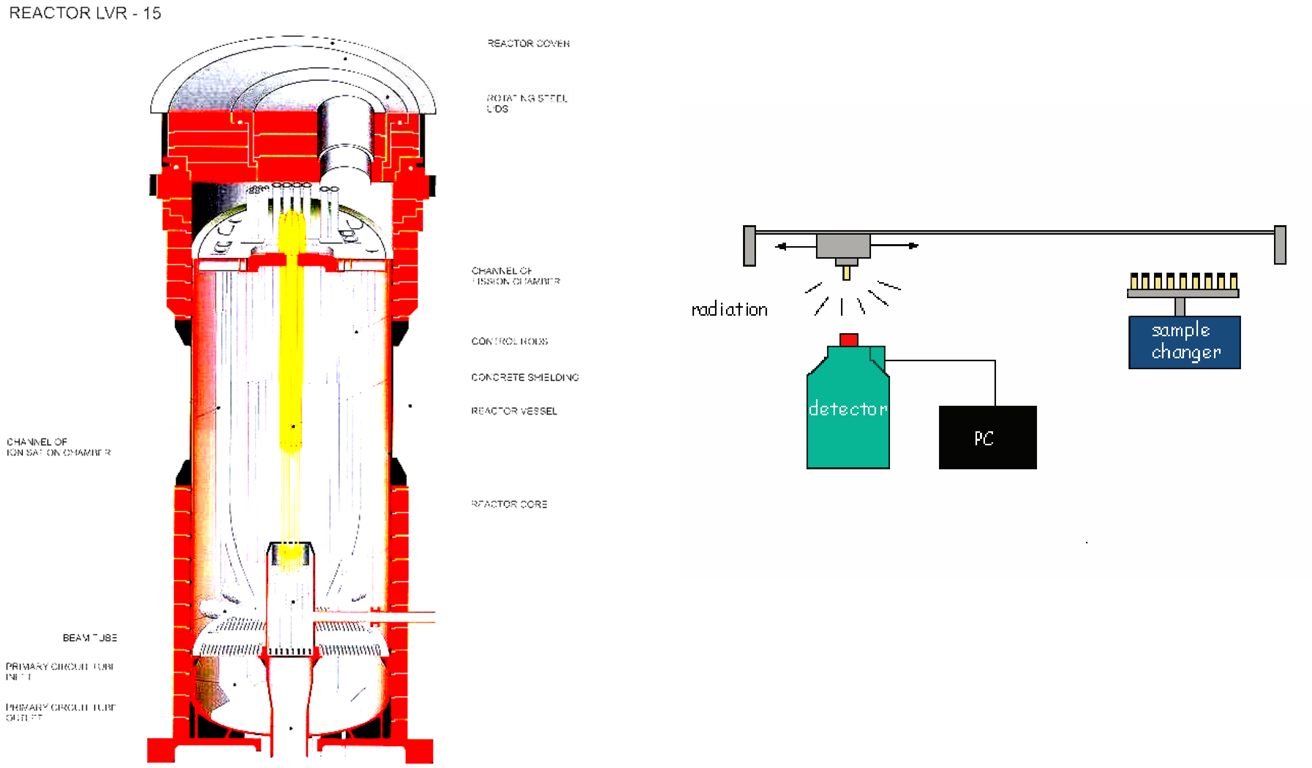
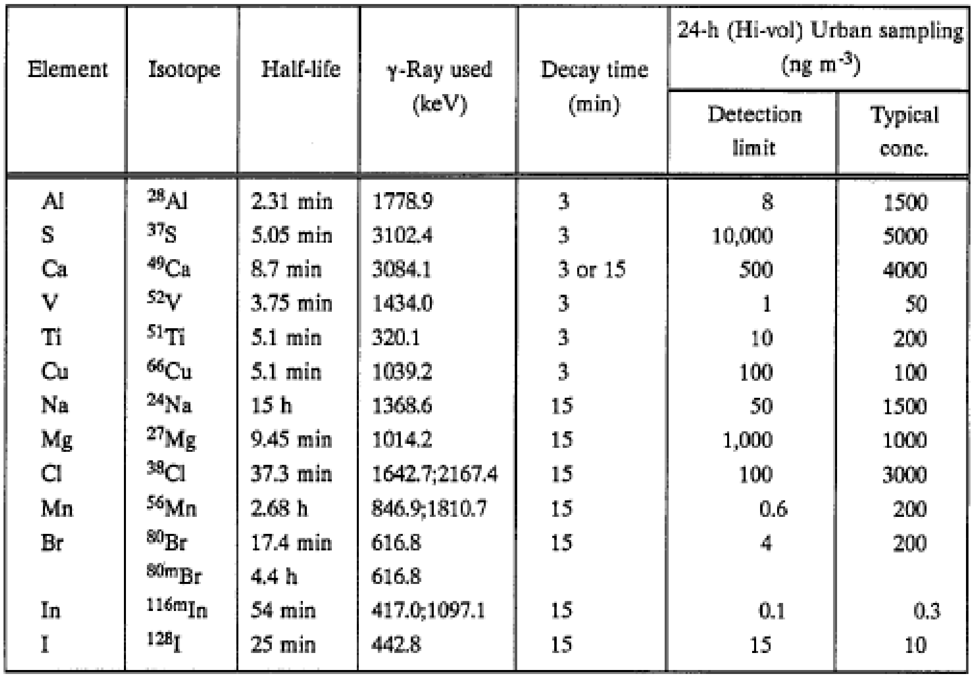


Figure 3.7: Schematic of a nuclear reactor source and instrumental set-up for INAA.[57,58]

Below in Tables 3.5 (after 5 min irradiation) & 3.6 (after several hours irradiation), the isotope, half-life, γ-ray used, expressed in keV, decay time (min), and detection limits of each element are shown to bring a better understanding of what elements can be measured and at what concentrations they can be measured.[56] Typically a Li-doped germanium or silicon detector, or a high purity germanium (HPGe) detector is used.[56,59] The elemental concentration can be determined via the intensity of the γ-spectrum (high resolution spectra obtained via INAA), for which the limit of detection varies widely for each element and is based upon the cross-section of the neutron, the half-life of the isotope, and the amount of γ-rays produced from the element in question.[43,55]

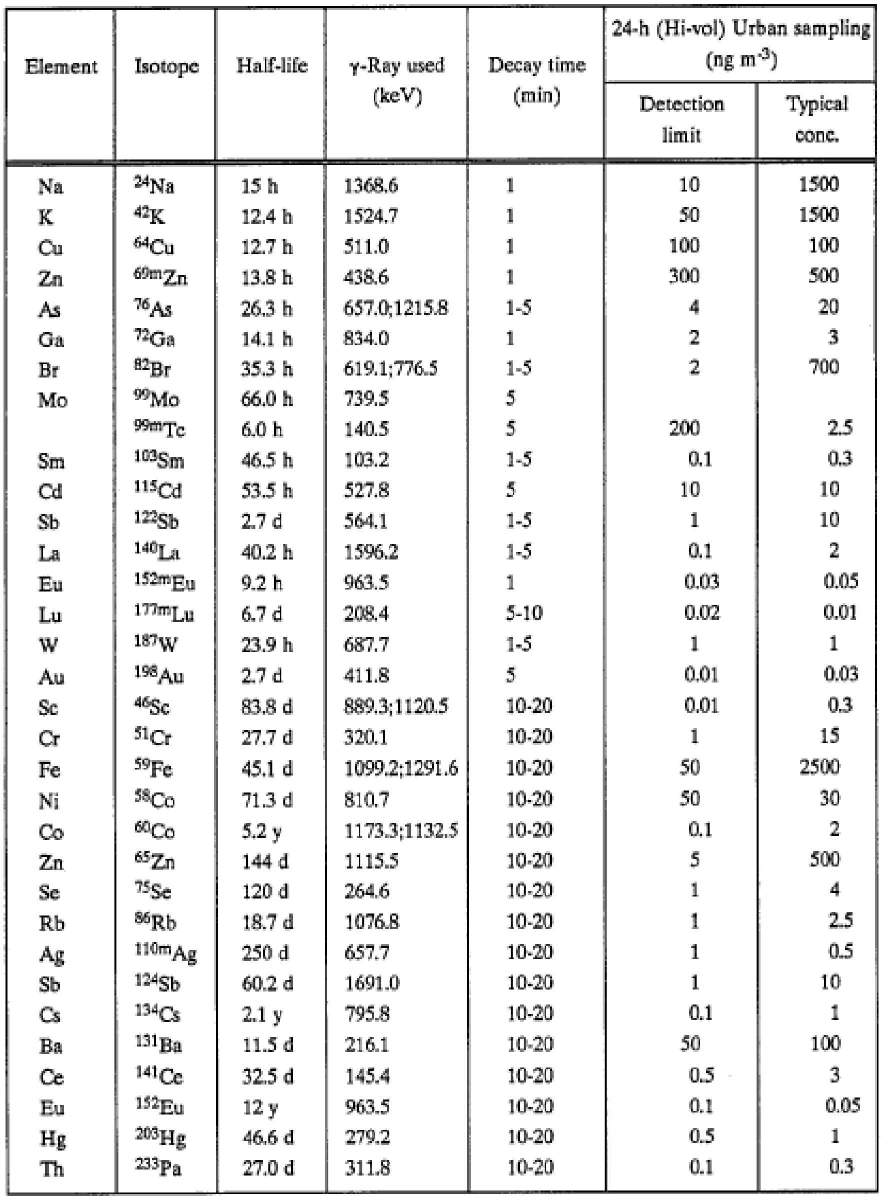
Table 3.5: Detection limits of aerosols after 5 min irradiation time based on nuclear data of isotopes.[43]



Element	Isotope	Half-life	γ-Ray used (keV)	Decay time (min)	24-h (Hi-vol) Urban sampling (ng m^{-3})	
					Detection limit	Typical conc.
Al	^{28}Al	2.31 min	1778.9	3	8	1500
S	^{37}S	5.05 min	3102.4	3	10,000	5000
Ca	^{49}Ca	8.7 min	3084.1	3 or 15	500	4000
V	^{52}V	3.75 min	1434.0	3	1	50
Ti	^{51}Ti	5.1 min	320.1	3	10	200
Cu	^{66}Cu	5.1 min	1039.2	3	100	100
Na	^{24}Na	15 h	1368.6	15	50	1500
Mg	^{27}Mg	9.45 min	1014.2	15	1,000	1000
Cl	^{38}Cl	37.3 min	1642.7;2167.4	15	100	3000
Mn	^{56}Mn	2.68 h	846.9;1810.7	15	0.6	200
Br	^{80}Br	17.4 min	616.8	15	4	200
	^{80m}Br	4.4 h	616.8			
In	^{116m}In	54 min	417.0;1097.1	15	0.1	0.3
I	^{128}I	25 min	442.8	15	15	10

INAA has several advantages when environmental applications are needed: high sensitivity, expressed in terms of counts/μg, determination of 40 elements simultaneously, determination of sub-ppm concentrations for certain elements, and matrix effects are not as critical for this technique compared to others.[43,56,59] It also has inherent disadvantages: a neutron reactor should be used for the best precision, which has availability limitations, B, Be, Cd, Cu, F, Hg, Mo, Ni, Pb, and Tl have large detection limits (expressed in terms of $\mu g_{\text{element of interest}}/g_{\text{sample}}$) because their neutron scattering cross sections are very low, no information is acquired of the chemical state of the element, and the long time the instrument requires to run samples-due to the half-lives and the need to reanalyze samples to remove interferences from short-lived radioactive species.[43,55,56] To alleviate some of the disadvantages, other INAA methods have been developed such as using larger energy epithermal neutrons-“neutrons with kinetic energy between 0.1 to 10^5 eV that are under the thermalization process”[55], which increase sensitivity, and using larger energy (greater than 10^5 eV), fast or rapid neutrons that can be generated by an accelerator.[56,60]

Table 3.6: Detection limits of aerosols after several hours irradiation time based on nuclear data of isotopes.[43]



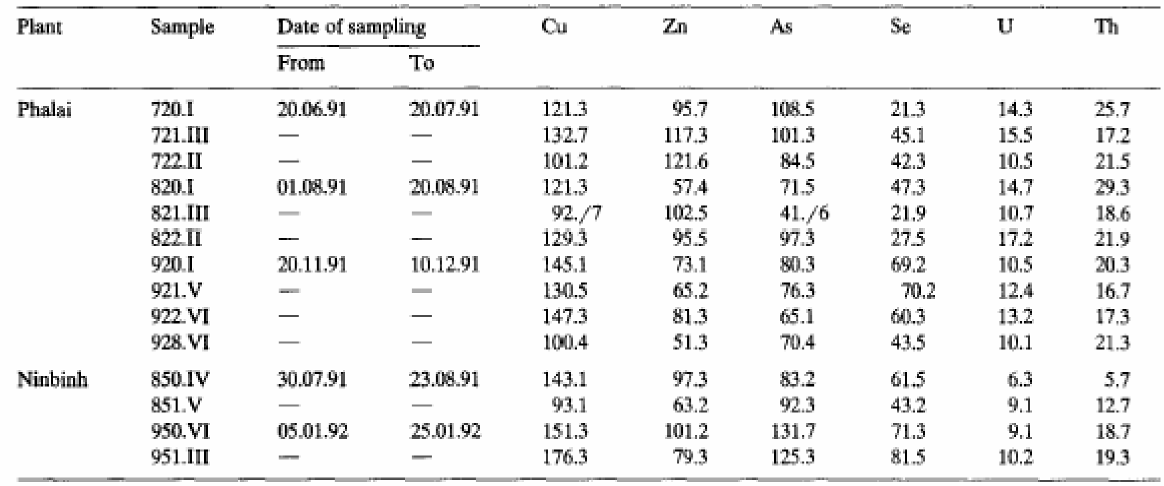
Element	Isotope	Half-life	γ-Ray used (keV)	Decay time (min)	24-h (Hi-vol) Urban sampling (ng m^{-3})	
					Detection limit	Typical conc.
Na	^{24}Na	15 h	1368.6	1	10	1500
K	^{42}K	12.4 h	1524.7	1	50	1500
Cu	^{64}Cu	12.7 h	511.0	1	100	100
Zn	^{69m}Zn	13.8 h	438.6	1	300	500
As	^{76}As	26.3 h	657.0;1215.8	1-5	4	20
Ga	^{72}Ga	14.1 h	834.0	1	2	3
Br	^{82}Br	35.3 h	619.1;776.5	1-5	2	700
Mo	^{99}Mo	66.0 h	739.5	5		
	^{99m}Tc	6.0 h	140.5	5	200	2.5
Sm	^{103}Sm	46.5 h	103.2	1-5	0.1	0.3
Cd	^{115}Cd	53.5 h	527.8	5	10	10
Sb	^{122}Sb	2.7 d	564.1	1-5	1	10
La	^{140}La	40.2 h	1596.2	1-5	0.1	2
Eu	^{152m}Eu	9.2 h	963.5	1	0.03	0.05
Lu	^{177m}Lu	6.7 d	208.4	5-10	0.02	0.01
W	^{187}W	23.9 h	687.7	1-5	1	1
Au	^{198}Au	2.7 d	411.8	5	0.01	0.03
Sc	^{46}Sc	83.8 d	889.3;1120.5	10-20	0.01	0.3
Cr	^{51}Cr	27.7 d	320.1	10-20	1	15
Fe	^{59}Fe	45.1 d	1099.2;1291.6	10-20	50	2500
Ni	^{58}Co	71.3 d	810.7	10-20	50	30
Co	^{60}Co	5.2 y	1173.3;1132.5	10-20	0.1	2
Zn	^{65}Zn	144 d	1115.5	10-20	5	500
Se	^{75}Se	120 d	264.6	10-20	1	4
Rb	^{86}Rb	18.7 d	1076.8	10-20	1	2.5
Ag	^{110m}Ag	250 d	657.7	10-20	1	0.5
Sb	^{124}Sb	60.2 d	1691.0	10-20	1	10
Cs	^{134}Cs	2.1 y	795.8	10-20	0.1	1
Ba	^{131}Ba	11.5 d	216.1	10-20	50	100
Ce	^{141}Ce	32.5 d	145.4	10-20	0.5	3
Eu	^{152}Eu	12 y	963.5	10-20	0.1	0.05
Hg	^{203}Hg	46.6 d	279.2	10-20	0.5	1
Th	^{233}Pa	27.0 d	311.8	10-20	0.1	0.3

One aspect that must be considered when preparing the instrument for samples, since no real sample preparation is required for INAA, is the irradiation-counting scheme. For example, when trying to analyze samples, the Compton effect must be considered-the interaction of electromagnetic radiation with the detector. The Compton effect is negative because low intensity γ-rays can be hidden by the background that is formed from high energy γ-rays.[43] To compensate for this effect, short-lived isotopes can be measured immediately following short irradiation; whereas long-lived isotopes can be measured after increased irradiation and decay times.[43,61] Unfortunately, when measuring multiple elements simultaneously, this procedure cannot be implemented. When measuring multiple elements, two irradiations and three to five γ-spectrometric measurements are taken with small variations from research lab to research lab.[43] Typically, there will be one irradiation for short-lived isotopes-approximate neutron flux for both irradiations is $8 * 10^{12}$ n/cm^{2}s-of approximately 1 min and an immediate count for seven minutes with the detector.[43,62] After the first irradiation and counting, a lag time of 0-15 minutes is typically instituted before recounting for 20 minutes for elements with half-lives in the range of 37 minutes to 15 hours, which include Na, K, Cl, Mn, In, Ba, and Yb.[43,62] For long-lived isotopes (Ca, Sc, Cr, Fe, Co, Zn, As, Se, Br, Mo, Cd, Sb, Cs, La, Ce, Sm, Nd, Hf, Au, Th, U, and Hg), the aforementioned flux value is applied for six hours. The sample is allowed to decay for approximately three weeks before being analyzed by the detector. After six hours of reirradation, the samples were counted for six to ten hours to determine the γ-ray activities via a high resolution γ-ray spectrometer.[62] Using this general radiation counting scheme, anywhere from 37-42 elements can be determined simultaneously.[43,62] Due to the long-lived isotopes, the INAA is a very time intensive technique even though multiple elements can be measured simultaneously with high sensitivity.

To calibrate the instrument, which is relatively simple since no matrix effects have to be considered, a known solution of the metals can be prepared and applied to a clean filter.[43] Care must be taken to use the same procedure on the filter that will be used on the ambient samples, and solutions must be prepared with caution as to not adhere any of the metals to the sides of the glass, since low concentrations will be used. It is also advised to use reference materials from either NIST or SRM in conjunction with the standards prepared in lab.[43]

To explore how important INAA is when trying to find multiple elements emitted in the particle form from ambient samples, multiple data tables and spectra will be presented and discussed from the emission of coal combustion sources and ambient samples taken near industrial areas that contain coal combustion. Duong et. al analyzed not only the coal combustion components but also coal and wet and dry deposition at intervals from 1-20 km from two power plants in Vietnam: the Phalai plant, 1700 million kWh production, and the Ninhbinh plant, 100 million kWh production-both of which use anthracite coal.[59] The trace element content in ppm from the dry fallout from the two plants can be seen in Table 3.7. The wet

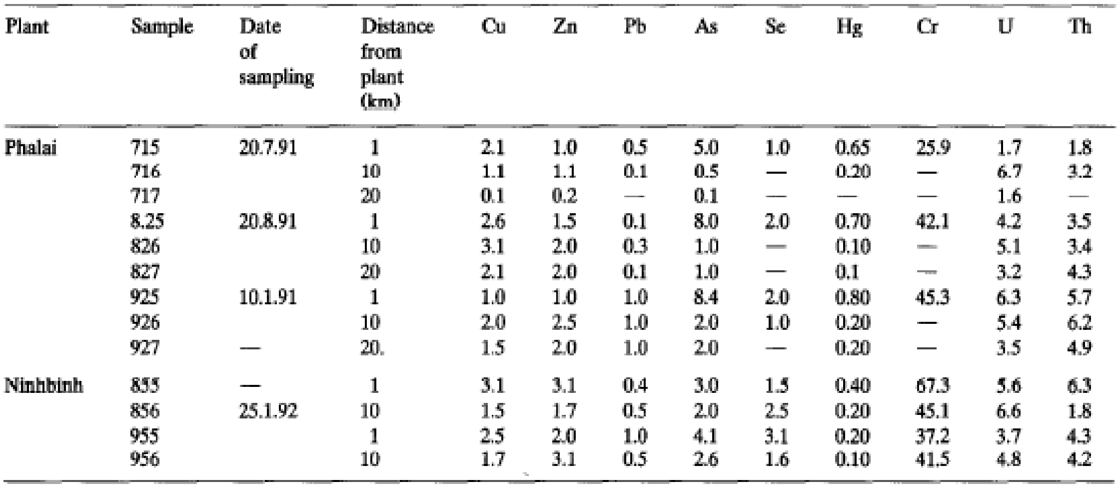
Table 3.7: "Trace element content (ppm) in the dry fallout in the vicinities of the Phalai and Ninhbinh power plants"[59] characterized by INAA.



Plant	Sample	Date of sampling		Cu	Zn	As	Se	U	Th
		From	To						
Phalai	720.I	20.06.91	20.07.91	121.3	95.7	108.5	21.3	14.3	25.7
	721.III	—	—	132.7	117.3	101.3	45.1	15.5	17.2
	722.II	—	—	101.2	121.6	84.5	42.3	10.5	21.5
	820.I	01.08.91	20.08.91	121.3	57.4	71.5	47.3	14.7	29.3
	821.III	—	—	92./7	102.5	41./6	21.9	10.7	18.6
	822.II	—	—	129.3	95.5	97.3	27.5	17.2	21.9
	920.I	20.11.91	10.12.91	145.1	73.1	80.3	69.2	10.5	20.3
	921.V	—	—	130.5	65.2	76.3	70.2	12.4	16.7
	922.VI	—	—	147.3	81.3	65.1	60.3	13.2	17.3
	928.VI	—	—	100.4	51.3	70.4	43.5	10.1	21.3
Ninbinh	850.IV	30.07.91	23.08.91	143.1	97.3	83.2	61.5	6.3	5.7
	851.V	—	—	93.1	63.2	92.3	43.2	9.1	12.7
	950.VI	05.01.92	25.01.92	151.3	101.2	131.7	71.3	9.1	18.7
	951.III	—	—	176.3	79.3	125.3	81.5	10.2	19.3

deposition from the power plant can be seen in Table 3.8 at distances up to 20 km from the source site. From the study, there is less dry deposition from the atmosphere at the site of the plants compared to wet deposition near the site of the plant and distances from the plants. There is also not a clear trend that particulates decrease as distance from the plant increases in the rain samples.

Table 3.8: "Trace element content (mg/L) in rain precipitation in vicinities of the Phalai and Ninhbinh power plants."[59]



Plant	Sample	Date of sampling	Distance from plant (km)	Cu	Zn	Pb	As	Se	Hg	Cr	U	Th
Phalai	715	20.7.91	1	2.1	1.0	0.5	5.0	1.0	0.65	25.9	1.7	1.8
	716		10	1.1	1.1	0.1	0.5	—	0.20	—	6.7	3.2
	717		20	0.1	0.2	—	0.1	—	—	—	1.6	—
	8.25	20.8.91	1	2.6	1.5	0.1	8.0	2.0	0.70	42.1	4.2	3.5
	826		10	3.1	2.0	0.3	1.0	—	0.10	—	5.1	3.4
	827		20	2.1	2.0	0.1	1.0	—	0.1	—	3.2	4.3
	925	10.1.91	1	1.0	1.0	1.0	8.4	2.0	0.80	45.3	6.3	5.7
	926		10	2.0	2.5	1.0	2.0	1.0	0.20	—	5.4	6.2
	927	—	20.	1.5	2.0	1.0	2.0	—	0.20	—	3.5	4.9
Ninhbinh	855	—	1	3.1	3.1	0.4	3.0	1.5	0.40	67.3	5.6	6.3
	856	25.1.92	10	1.5	1.7	0.5	2.0	2.5	0.20	45.1	6.6	1.8
	955		1	2.5	2.0	1.0	4.1	3.1	0.20	37.2	3.7	4.3
	956		10	1.7	3.1	0.5	2.6	1.6	0.10	41.5	4.8	4.2

Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS was commercially used beginning in 1983 and is an excellent method for multielemental analysis, both for fine and ultrafine trace element particulates.[35] Several advantages of ICP-MS are its low detection limits for most elements, approximately 10^{-3} μg/L of solution, and 1 to 2% precision.[35] The ICP-MS can also be interfaced with other techniques, such as HPLC and GC, and can provide isotopic information.[35] A disadvantage of ICP-MS is that the filter is destroyed during analysis.[38]

To introduce samples into the instrument, shown in Figure 3.7, a double jacketed tube is used.[63] The middle and outer tubes carry gas flows, typically argon, that cool the torch and form the plasma, and the inner tube carries samples in a flow of argon gas.[63] Electrons are excited by a tesla coil where they are introduced into the torch region with argon gas.[63] Surrounding the torch is a copper coil, to which a radio frequency (rf) is applied to accelerate the electrons in a magnetic field and allow collisions with the argon gas to produce ions. A continuous radio frequency maintains the plasma.[63] The temperature of an ICP is between 5,000 to 10,000 K, which allows for "desolvation and thermal atomization of analytes introduced into the central region of the plasma."[63] Ionization can occur if the energy incident upon the electron exceeds the 1st ionization energy. Other than Hg, As, Au, and Pt, which are only 30-80% ionized by ICP, the majority of the elements have 1st ionization energies less than 9eV and are more than 80% ionized.[63]

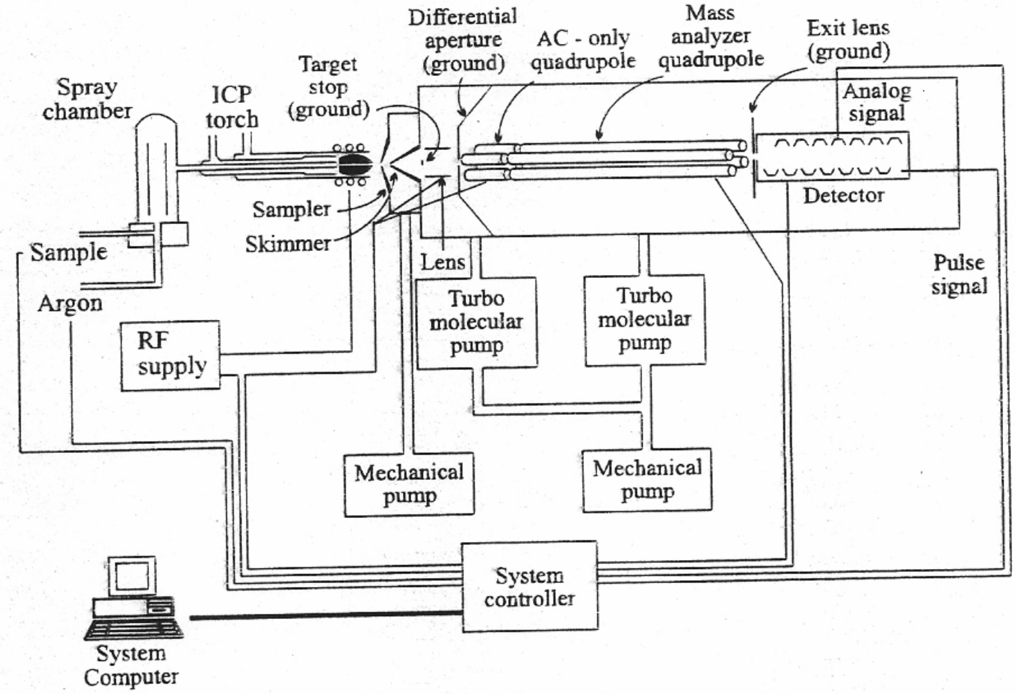


Figure 3.7: Schematic quadrupole ICP-MS.[63]

One of the greatest difficulties to overcome with an ICP-MS system is the large pressure drop required from the atmospheric pressure region of the plasma to the low pressure region (at least 10^{-6} torr or less) of the mass analyzer, as shown from the schematic of an ICP-MS in Figure 3.7.[63] To combat this, the plasma can be horizontal with a H_2O cooled sampler.[63] Another crucial element of the ICP-MS that is essential to high sensitivity is the ion-focusing lenses (the section between the skimmer and mass analyzer in Figure 3.7) used to eliminate scattered ions, which can't be detected.[63] Typically, quadrupole mass analyzers, which are used to separate the ions based on mass-to-charge ratio and measure the relative abundance, are used with ICP-MS, and a spread of kinetic energies of the ions can cause a decrease in sensitivity or resolution.[63] To measure the ion kinetic energies, a retarding potential can be used at the beginning of the quadrupole. Other mass analyzers such as magnetic sector, double-focusing sector, time-of-flight, and ion trap can be used; however, they all have more inherent difficulties when coupled with ICP, so the quadrupole will be the focus of this paper.[63]

To detect the ions, a Faraday cup collector, an electron multiplier, or a channel plate are used, but the electron multiplier is the most common detector used. Once the ions exit the analyzer, they strike a conversion plate, which has a large voltage applied to it to attract the ions.[63] After ions strike the plate, electrons are ejected and accelerated away form the plate by the applied voltage. They are then multiplied by a continuous dynode or a discrete dynode.[63] Multiple papers have been published on the use of ICP-MS in both the laboratory setting and sampling ambient aerosols (urban, industrial, and power generation). A large scale study outside of the Thermoelectric Complex Jorge Lacerda (TCJL), Santa Catarina, Brazil, was conducted by Godoy et. al. The TCJL is comprised of seven coal combusting power plants, the largest in Latin America.[64] The seven power plant units have electrostatic precipitators that are 98% efficient.[64]

Table 3.9: Concentration of elements in the summer and winter of fine particles around TCJL.[64]

Fine Particles			
Element	**# Samples**	**Mean (ng/m^3)**	**SD (ng/m^3)**
(a) summer sampling campaign			
V	105	0.61	0.55
Fe	105	56.5	53.9
Zn	104	5.38	3.92
Ba	105	2.12	1.74
(b) winter sampling campaign			
V	107	0.63	0.46
Fe	111	58.7	30
Zn	110	34.2	31.8
Ba	111	2.24	1.151

The samples were collected from 12 separate sites (1-6 km from the plant) surrounding the complex for 10 days, 24 hours/day, during two different seasons, summer and winter.[64] Stacked filtering units (SFU) were used to collect two fraction sizes: coarse (between 2.0 and 10.0 μm) and fine particles (<2.0 μm). The elemental concentrations of a few selected metals that were assessed from the ambient sampling can be seen in Tables 3.9 and 3.10. In both the summer and

Table 3.10: Elemental concentrations observed at TCJL of coarse particles in the winter and summer.[64]

Coarse particle fraction			
Element	**# Samples**	**Mean (ng/m^3)**	**SD (ng/m^3)**
(a) summer sampling campaign			
V	115	1.72	1.79
Fe	115	325	256
Zn	115	7.24	4.77
Ba	115	7.04	5.43
(b) winter sampling campaign			
V	113	1.63	1.08
Fe	113	431	252
Zn	113	20.9	15.6
Ba	113	10.5	7.18

winter for fine and coarse particles, Fe, Ba, Zn, Ti, Pb, and Mn had larger concentrations when comparing them to the other metals. Overall there was no clear trend of variation of particle size based on the variation of the season.

Atomic absorption spectrometry (AAS)

Atomic Absorption Spectrometry (AAS) is the oldest technique that will be discussed. When measuring particles with AAS, it is very difficult to analyze samples in the solid form directly off the filter paper so a liquid solution is preferred. So like the other techniques, an extraction from the filter paper or microwave digestion must be employed to prepare the sample for analysis.

The basic design of any AAS consists of a “radiation source, a sample holder, a wavelength selector, a detector, and a signal processor and readout,” as shown in Figure 3.8.[65]

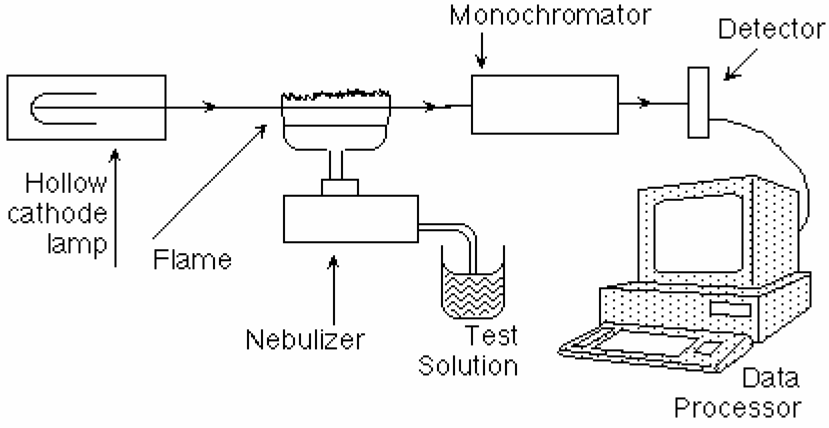


Figure 3.8: Schematic of AAS.[66]

The radiation source is a hollow cathode lamp that contains the metal of interest.[65] The solution is aspirated in the flame where the liquid is evaporated and the solid that remains is atomized.[65,67] The metal in the flame then absorbs the light emitted from the same metal in the hollow cathode lamp.[67] A monochromator is placed after the flame and before the detector to select a specific wavelength of light.[67] One aspect of the instrument that makes it a great choice for measuring trace metals is that it is very specific because of the extremely narrow line of atomic absorption, 0.002 to 0.005 nm, and each element has it's own unique electronic transition.[65] Since the bandwidths are so narrow, this can be an issue because monochromators, the typical wavelength selector employed, have a bandwidth that is much greater, so this needs to be taken into account when the source is chosen.[65] To combat this, the most common source used is a hollow cathode lamp, which consists of the element to be sampled.[65] This alleviates the issue of bandwidth for the source but also makes this method very time consuming and expensive because a separate hollow cathode tube is required for every metal being analyzed. Most ambient sampling of a coal-fired power station requires the analysis of 40 or more metals. Although AAS has been extensively used in the past, because of these issues, today it is typically used in conjunction with other instruments and only used to measure a small percentage of the metals that the other instruments might have difficulty measuring. Another advantage of the instrument is the detection of low concentrations of metals in ambient aerosols (ppm-ppb).[67] To analyze the sample, it must be nebulized by a gaseous oxidant, "mixed with a gaseous fuel, and carried into the flame where atomization occurs."[65] This is an essential step in the process that limits the precision of the instrument.[65] It is also one of the inherent disadvantages of the instrument because most of the sample is lost to the waste container during atomization.[65]

A specific example of AAS in sampling from a coal-combustion source is taken from Martinez-Tarazona et al. The samples were collected from a 2000 MW pulverized coal firing plant with 2 boiler units, which produce 80% fly ash and 20% bottom ash; however, the specific type of coal used in the power plant was not specified in the paper.[68] The fly ash samples were taken before they were processed through the emission control devices, in this case an electrostatic precipitator and a cyclone.[68] Since the fly ash was taken before the emission control devices, the fly ash consisted of much larger particle sizes combined with the smaller particle sizes previously discussed, so a size fraction classifier was used for the sizes below 65 μm to classify them into 7 fractions.[68] In this study, AAS was only used to classify As and Mo and 12 samples were analyzed that were collected over 3 hour periods.[68] As seen in Table 3.11, the concentrations of As and Mo, in sized fractioned samples of fly ash, increased as the particle sized decreased. This is a bad attribute because the smaller particles, as mentioned in chapter 1, have more damaging effects to humans upon inhalation.

Table 3.11: Concentrations of As and Mo characterized by AAS in size fractioned samples of fly ash.[68]

Trace	**> 65 μm**	**40-65 μm**	**25-40 μm**	**15-25 μm**	**10-15 μm**	**5-10 μm**	**2.5-5 μm**	**<2.5 μm**
As (ppm)	18	29	37	57	96	154	186	278
Mo (ppm)	5	5	9	12	20	45	43	69

Aerosol time-of-flight mass spectrometry (ATOF-MS)

An ATOF-MS can give information on a rapid time scale, approximately 1 s, of individual particles pertaining to their chemical composition and their aerodynamic size.[69] The particles enter the instrument through the aerodynamic lens where the particle beam is collimated by passing through a section with successive skimmers, which are orifices, as seen in Figure 3.9.[70] The particles then enter the light scattering region where two continuous wave laser beams (diode at 532 nm) are separated by a predetermined distance.[69,70] The scattered light from each laser is gathered by a separate lens and fiber-optic system and each laser has a photomultiplier for detection.[70] Using an external electronic timing circuit, the scattering from the lasers is used to track the particle in the system.[70] Particle velocity can be measured by the known distance between the lasers and the time it takes for the particles to travel this distance.[70] The velocity is then compared to an external calibration curve of lab generated polystyrene latex (PSL) particles to achieve the aerodynamic diameter as seen in Figure 3.10.[69] Once the particles have gone through this region, they arrive at the ionization region in the reflectron time-of-flight mass spectrometer where a 266 nm Nd:YAG laser is used to ablate and ionize the particles causing desorption of individual molecules.[70] Once the particles are ionized, they follow the flight path

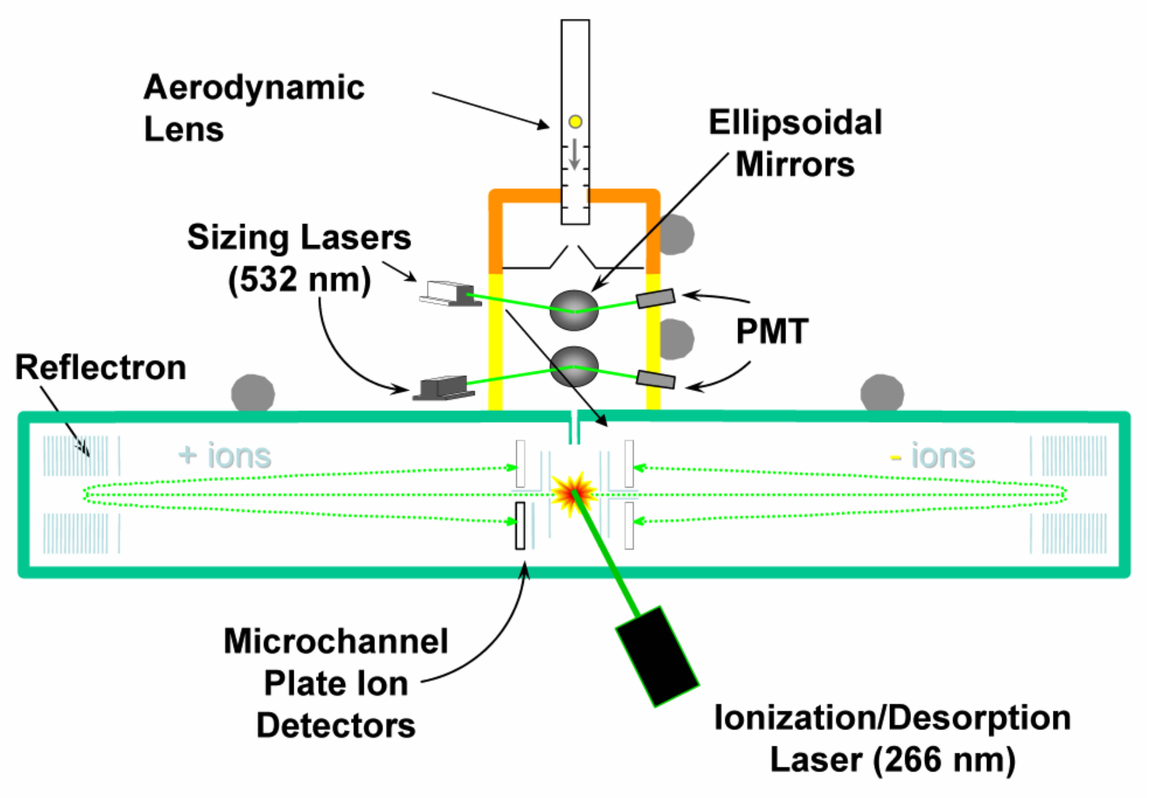


Figure 3.9: Schematic of an ATOF-MS (single particle).[71]

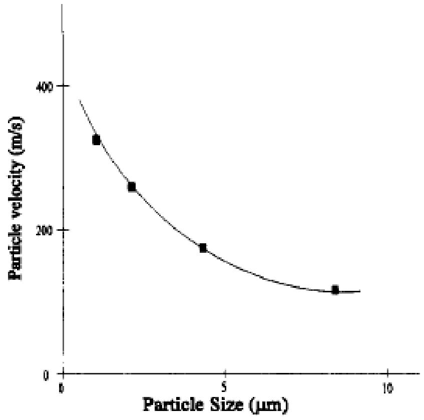


Figure 3.10: Particle velocity vs. particle size calibration curve.[70]

in the reflectron region. Since the particle receives a specific kinetic energy from the electric field in the reflectron, the individual ions produced will separate based on the mass to charge ratio as they travel what is commonly referred to as the drift region of the TOF-MS. With the dual reflectron design, both positive and negative ions can be detected as shown in Figure 3.9.[69] One advantage of using the reflectron is its high resolution.

The mass spectrum of a single particle, KCl/2,5-dihydroxybenzoic acid (0.7 μm) in a 1% concentration of the salt, shows the "softness of the laser desorption technique" from the $K_4Cl_3^+$ clusters found in the appropriate isotopic abundance ratios, as seen in Figure 3.11.[70] The small peaks in the 50-80 m/z range are attributed to gas phase background resulting from laser ionization, which are present in the absence of particle sampling.[70]

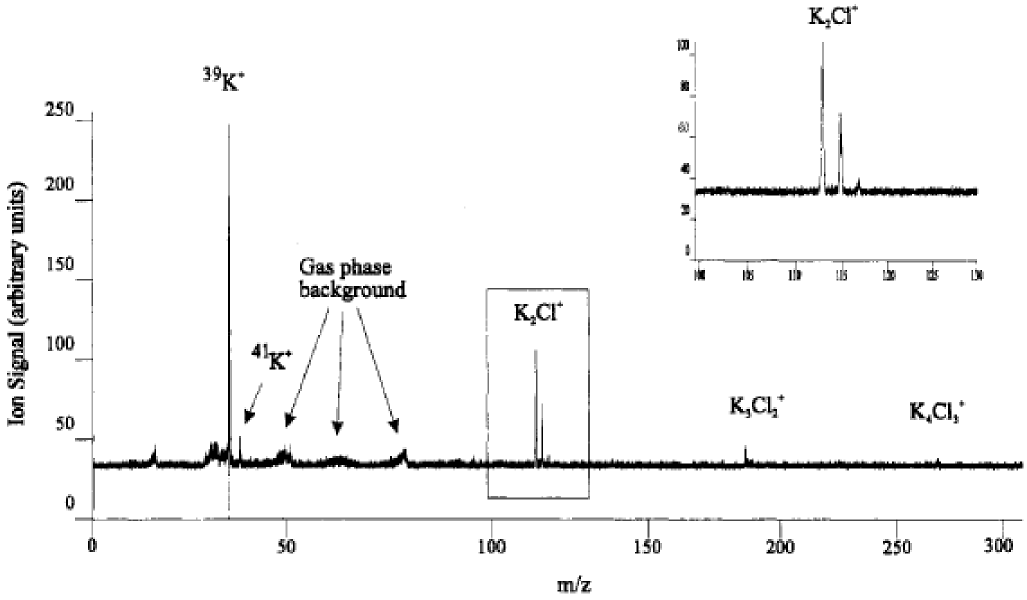


Figure 3.11: Single particle mass spectrum obtained from KCl/2,5-dihydroxybenzoic acid particle (0.7 μm) in a 1:100 mixture. The three possible isotopic configurations of KCl are observed in the inset in the top right hand corner.[70]

Because this technique is relatively new and still in the initial stages of development, extensive specific studies (ex. power industries or steel plants) have yet to be conducted; the technique will give a great advantage to these fields in determining real time data, particle composition, and aerodynamic size of individual particles. Another advantage of ATOF-MS is the omission of the sample preparation step, which can be one of the contributors of contamination. It is also a great method for analyzing particles of unknown composition that contain multi-components.[70] However, an inherent disadvantage of the system is the inability to characterize organic components because of excessive fragmentation. Also, due to the required coordination of the two sizing lasers and the desorption/ionization laser, particles traveling too closely together through the sizing region cannot both be analyzed.[70] Only one of the particles in this situation will be detected.[70]

Comparison of techniques

Now that an understanding of some of the individual techniques has been applied, the techniques combined in several studies will be observed. Two correlation studies were conducted by Bettinelli et al. between ICP-MS and INAA of vanadium and nickel trace metal elements from standards and from power plant emissions-using a quartz fiber filter and microwave digestion.[36] In Figure 3.11, a high degree of correlation is observed when comparing INAA and ICP-MS with an even distribution of overestimates and underestimates for both instruments.[36]

Another study comparing INAA and ICP-MS data was conducted by Maenhaut et. al from samples collected at a Venezuelan power plant at 81 MW capacity using a circulating fluidized bed boiler.[54] A cascade impactor with 11 stages was used to collect the samples.[54] A cyclone sampler was used to prevent overloading on the upper stages of the impactors.[54] Only 13 elements were measured by both the ICP-MS and INAA. In Figure 3.12, the ratio of ICP-MS to INAA were calculated using 5 samples each for stages 8 & 9 from the impactor and averaging these values.[54] INAA data was systematically higher compared to ICP-MS except for As.[54] As and Zn had the highest degree of correlation compared to the other metals. The authors claim that this vast difference is most likely due to incomplete dissolution of the particles.

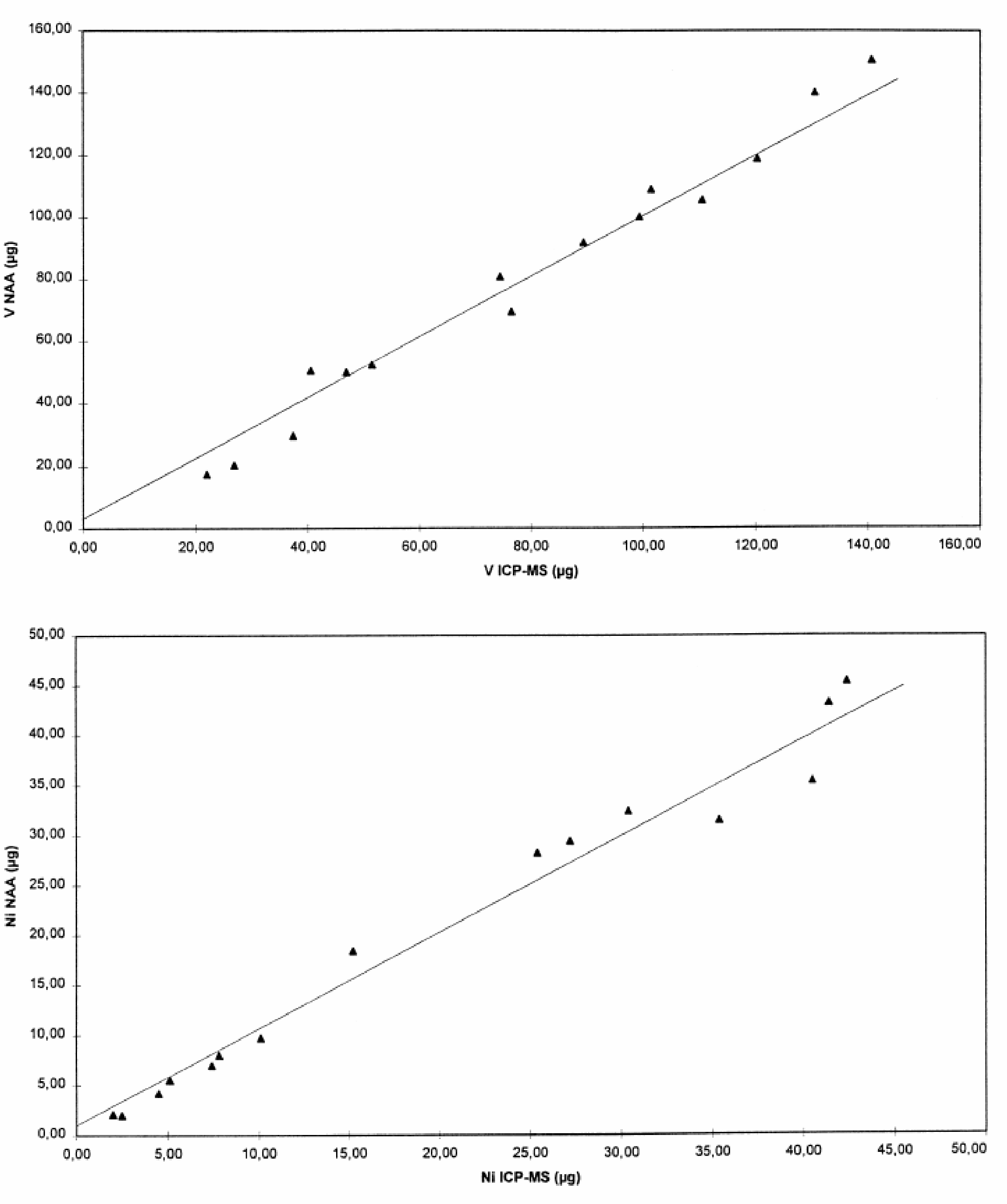


Figure 3.11: V and Ni concentration correlations from coal-fired emissions analyzed by ICP-MS and INAA for 15 samples.[36]

The next study used a combination of multiple techniques, which is more common for trace metal particulates in coal-fired emissions and was conducted on bituminous coal (obtained from New Zealand), bottom ash, fly ash, and flue gas from the combustion process of a stoker fired boiler in a laboratory setting.[72] ICP-MS, ICP-AES (inductively coupled plasma-atomic emissions spectroscopy-not discussed in this paper), WD-XRF (not discussed in this paper), SEM-EDX (not discussed in this paper), and INAA were all used to analyze the samples collected.[72] In Table 3.12, the percentages of metals in each of the phases formed during a laboratory combustion-large bottom ash, small bottom ash, fly ash, and flue gas-were analyzed by the aforementioned techniques. For the most part, the trends observed in Table 3.12 relate directly to the classes of metal partitioning discussed in chapter 1. However, Zn and As are supposed to be distributed mostly in the fly ash phase, which is not observed in this study.

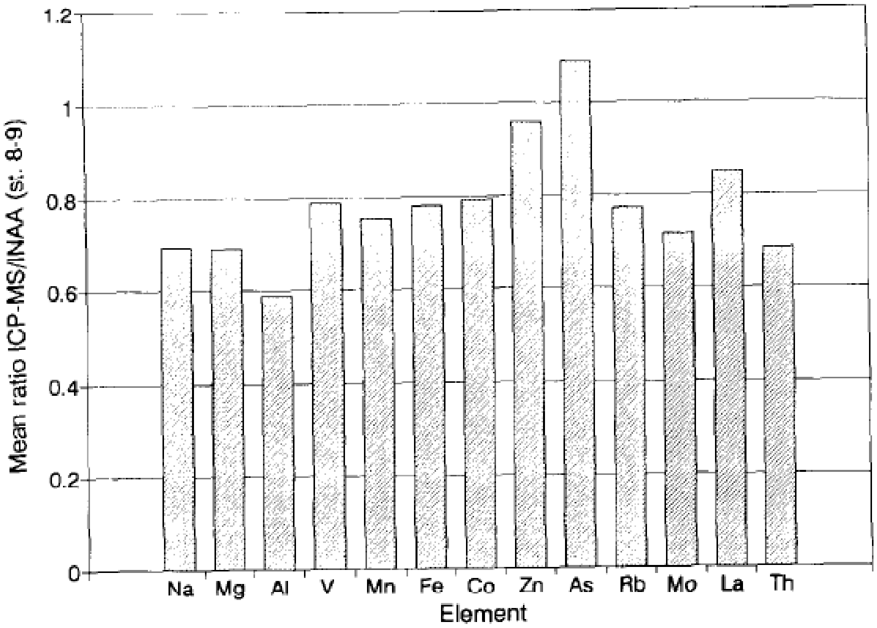
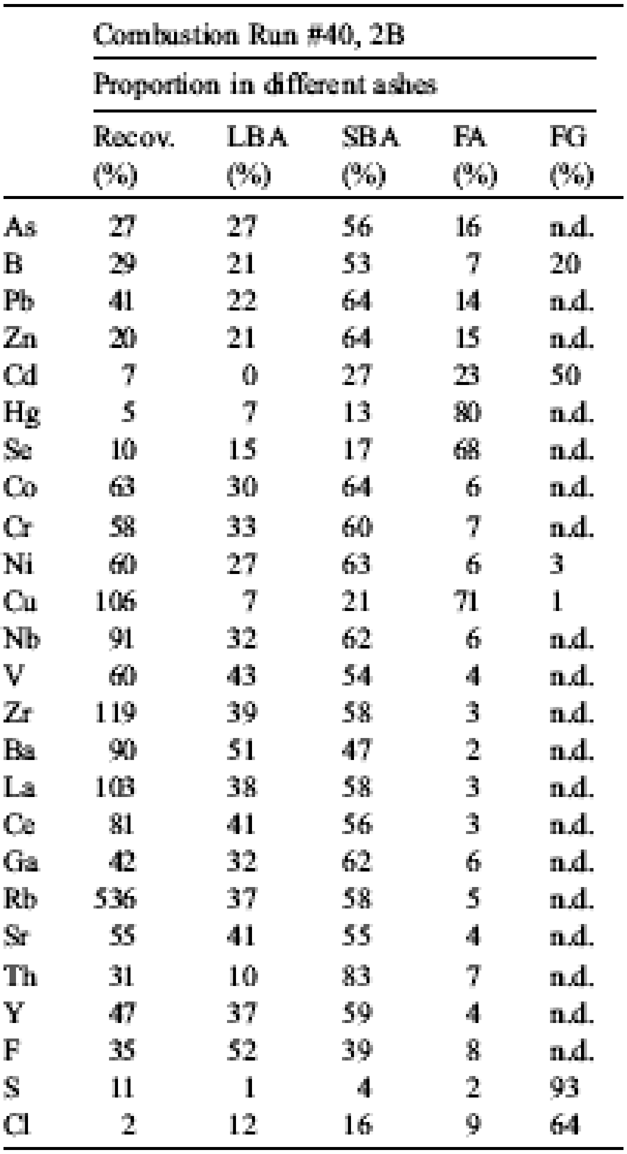


Figure 3.12: "Average ratios ICP-MS/INAA, as obtained by averaging over stages 9 and 8 and over all 5 BLPI samples (N=10). The percentage standard deviations of the plotted ratios are typically 10-20%.[54]

To summarize the instrumentation section of the chapter, in Table 3.13, there is a list of the analysis methods discussed and brief positive and negatives of the instruments. INAA, ICP-MS, and ATOF-MS are great multielement techniques. However, there is no silver bullet when analyzing trace metal particulates from coal-fired emissions. Most studies that try to characterize 35 or more elements will have to use multiple techniques due to the poor sensitivity of some

Table 3.12: "Proportions of trace element partitioning in large bottom ash (LBA), small bottom ash (SBA), fly ash (FA), and flue gas (FG) fractions."[72]



	Combustion Run #40, 2B				
	Proportion in different ashes				
	Recov. (%)	LBA (%)	SBA (%)	FA (%)	FG (%)
As	27	27	56	16	n.d.
B	29	21	53	7	20
Pb	41	22	64	14	n.d.
Zn	20	21	64	15	n.d.
Cd	7	0	27	23	50
Hg	5	7	13	80	n.d.
Se	10	15	17	68	n.d.
Co	63	30	64	6	n.d.
Cr	58	33	60	7	n.d.
Ni	60	27	63	6	3
Cu	106	7	21	71	1
Nb	91	32	62	6	n.d.
V	60	43	54	4	n.d.
Zr	119	39	58	3	n.d.
Ba	90	51	47	2	n.d.
La	103	38	58	3	n.d.
Ce	81	41	56	3	n.d.
Ga	42	32	62	6	n.d.
Rb	536	37	58	5	n.d.
Sr	55	41	55	4	n.d.
Th	31	10	83	7	n.d.
Y	47	37	59	4	n.d.
F	35	52	39	8	n.d.
S	11	1	4	2	93
Cl	2	12	16	9	64

elements of INAA and the non-multielement capability of AAS. Hopefully with advancements in ATOF-MS, one instrument will be capable of autonomous use in the future.

Table 3.13: Instrumental techniques commonly employed for particulate trace element emissions.[36]

Method	Remarks
Atomic absorption spectrometry	Sample solutions are introduced into a graphite tube or aspirated into the flame Trace elements are determined individually Can give accurate data but determinations are done individually
Neutron activation analysis (NAA)	Induced activity is counted for quantification Nondestructive Sample preparation minimal No sample size limitations Multielemental capability Can produce very accurate data Poor sensitivity for some elements Expensive and time consuming
Inductively coupled plasma mass spectrometry (ICP-MS)	Sample solutions are aspirated into a high-temperature argon plasma Multielemental capability from 30 to 40 elements High sensitivity to many elements No sample size limitations Can produce very accurate data Relatively expensive
Aerosol time-of-flight mass spectrometry (ATOF-MS)	Aerodynamic size and masses collected on a single particle basis Multielement technique High resolution Alleviates sample preparation Real time data achieved

CHAPTER 4

GAS PHASE REACTIONS AND PARTITIONING OF METALS UPON COMBUSTION

As mentioned previously, there is partitioning of the trace metals based on vapor pressure and other factors once coal is combusted. Not only are the particles formed as fly ash important to study because of environmental impacts and health effects, but metals emitted into the vapor phase such as Se, Hg, and As are also important because they can undergo gas phase reactions to partition or condense onto particles once cooler temperatures are reached outside of the combustion area. Unfortunately, the chemical transformations of the trace elements is very complex because of the complex interactions between major, minor, and trace elements.[73] Minor element interactions must be considered as they are expected to have a huge impact on the behavior of trace elements.[73] In this chapter, multiple studies will be explored to help aid in the understanding of what metals partition into the bottom ash, fly ash, and flue gas once combusted and what alterations can occur to these metal particulates or vapor after they exit the combustion region.

Partitioning of metals to the bottom ash, fly ash, and flue gas post-combustion

The vast majority of the studies discussing partitioning of trace metals to this point have been based on thermodynamic computer modeling using equilibrium calculations. These models are a great tool used to predict the behavior of elemental chemistry in a multiphase and multicomponent system. The models can help to analyze the system by looking at element interactions, competitive affinity, and dominant species.[73] One limitation of using thermodynamic modeling is that the kinetics and mass transfer knowledge is limited when referring to metal/particle reactions; however, information can be attained on the most stable and favored product distributions using a wide range of temperatures.[73] The reason for this is due to the vast number of trace elements emitted, and the vast number of possible interactions between the trace metals themselves, trace metals and oxygen, trace metals and sulfates, and trace metals with arsenate and chromate to name a few examples. To incorporate the trends in research, two studies will be focused upon: modeling of partitioning using computer programs and partitioning via experimental results.

Yan et al. determined the effects of partitioning during combustion using GEM INI (Gibbs Energy Minimizer) and its database COACH (Computer Aided Chemistry).[74] The computational system contained 54 elements and 3200 of their associated species, which accounts for almost every element and species that exist during coal combustion.[74] Sixteen metals that have been proven to be harmful were focused on during this partitioning study: As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, Te, Tl, V, and Zn. Before this paper, Te and Tl had never been studied thermodynamically.[74] The air-to-fuel ratio was also accounted for by determining a range for reducing and oxidizing atmospheres.[74] These two conditions are important to simulate because a reducing atmosphere exists in the combustion zone at the coal particles surface, whereas an oxygen-rich environment is more prevalent further away from the boiler region and results in mixing of low-valence trace elements with oxygen to form oxides.[74]

From the program, speciation of the trace elements was found to depend on temperature (as discussed in chapter 2) stoichiometry, which refers to oxidizing or reducing conditions, and coal type (as discussed in chapter 2).[74] In Figure 4.1, the dominant species that are formed post-combustion are presented. From this model, two main interactions were confirmed:

(1.) Zn, V, Mn, Cu, Cr, and As all tend to combine with oxygen atoms to form metal aluminosilicates, metal-Fe or metal-Ti oxides, or metal selenates without regard to the combustion process or coal rank (in other word under oxidizing or reducing conditions). Co, Ni, Se, Te, and Tl only form these compounds under oxidizing conditions.

(2.) As, Hg, Ni, Pb, Sn, Se, Te, Tl tend to combine with other metals either in the gaseous or solid form under reducing conditions, and these compounds formed are not dependent upon coal rank.[74]

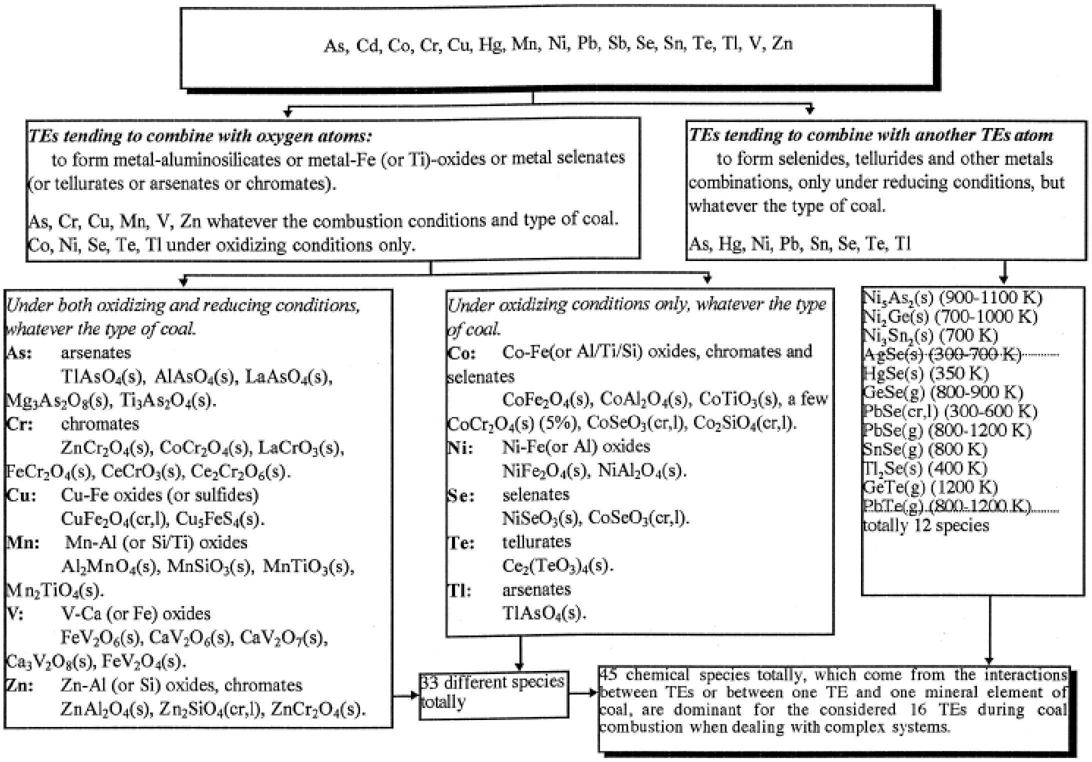


Figure 4.1: "Major interactions between the TEs [trace elements] and the minor elements in coal combustion."[74]

Now that the compounds have been divided into two main groups, the influence of the conditions during combustion, and the types of coal are examined. For oxidizing conditions, the elements can be divided into two groups: I. elements forming solid sulfates, selenates, or tellurates at low temperature (below 1000 K); II. elements forming oxides, halides, or arsenates.[74] To classify elements in Group I at higher temperature, two subgroups must be employed, Group Ia and Ib. Group Ia, at temperatures above 1000 K, had no interaction with other trace elements, and their chemistry can be explained by Equations 1-3:

$$MSO_{4(s)} \leftrightarrow MO_{(s)} + SO_{2(g)} + 1/2O_{2(g)} \qquad (1)$$

$$MO_{(s)} \leftrightarrow MO_{(g)} \qquad (2)$$

$$MO_{(g)} \leftrightarrow M_{(g)} + 1/2O_{2(g)} \qquad (3)$$

where M represents the metal and S can also represent Se and Te.[74] On the contrary, Group Ib exhibited interactions between Si, Al, Fe, Ti, chromate, or arsenate, represented by R in Equation 4, at temperatures above 1000 K:

$$MO_{(g)} + RO_{y(s)} \leftrightarrow MRO_{y+1(s)}.^{74} \qquad (4)$$

Before temperatures are reached to form gaseous oxides and atoms, gaseous trace elements (Cd, Cu, Ni, Pb, and Tl represented by M) can combine with halogens (X represents F, Cl, F, and Br) as can be seen in equilibrium Equation 5:

$$MO_{(s)} + 2HX_{(g)} \leftrightarrow MX_{2(g)} + H_2O_{(g)}.^{74} \qquad (5)$$

Cu and Zn, on the contrary, were mainly found in the forms of M-Fe-oxides and chromates.[74] To reinforce the statements made above, a flow chart was developed for the metals in terms of oxidizing and reducing conditions, seen in Figure 4.2.[74] The main implication of the flow chart is to show how metals partition and what the metals will combine with depending on the gaseous atmosphere, reducing or oxidizing. Also, from the model, it was seen that there are metal-metal interactions upon incineration in both reducing and oxidizing environments. From the flow charts, there is a clear temperature impact on the types of reactions and combinations that will occur in the combustion zone, which has a direct correlation to the boiler type used.

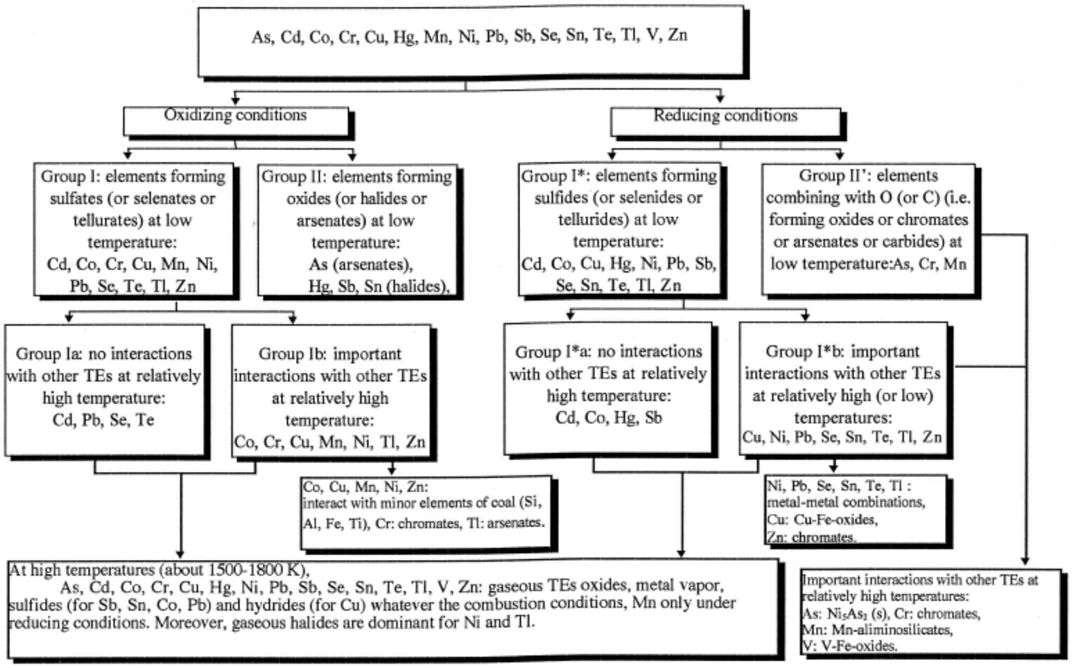


Figure 4.2: Speciation during coal combustion-temperature range 300 K to 1800 K-based on oxidizing and reducing conditions.[74]

The model also analyzed the effect of coal rank on the types of trace element combinations during combustion. For this specific analysis, it was impossible to combine the metals into groups because of the various effects produced by both the coal type and the combustion process. Coals with a high ash content, lignite, were found to not have oxidizing effects because of the insufficient amounts of oxygen in the coal so most of the metals that played a major role during reducing conditions were present under oxidizing conditions.[74] In other words, metals such as Cd, Co, Mn, Ni, Pb, Se, Te, and Zn that form sulfides, tellurides, and selenides under reducing conditions appear during oxidizing conditions.[74] Also, the sulfates that appeared under oxidizing conditions and low temperatures of low ash coal, anthracite, were not present in high ash coal.[74]

Under reducing conditions, the type of coal does not play an instrumental part in altering the types of metal speciation that occurs.[74]

Even though computer models can give researchers a general idea of the processes occurring during combustion, laboratory experiments must be performed to understand the true interactions of the elements upon combustion. Reddy et al. characterized trace metals and their fate during combustion from a coal-fired power plant in Western India that uses a pulverized boiler and bituminous coal to produce 220 MW of power.[75] Not only were the bottom ash, fly ash, and flue gas analyzed, but the particles' interactions with the gas phase were also examined. The ambient samples were collected with a filtration system at 120°C that was coupled with an impinger system in an ice-bath downstream.[75] To collect particles, a filter was placed in the heated region of the sample train seen in Figure 4.3.[75] The impinger system, the bottles on the right side of the schematic, use solutions, typically acids, at a cooler temperature to remove the metals from the gas stream.[76] One advantage of using impingers over solid sorbents is that sample preparation is not required upon collection. To extract the particles from the filter and prepare them for analysis via instrumentation, microwave acid digestion was used.[75]

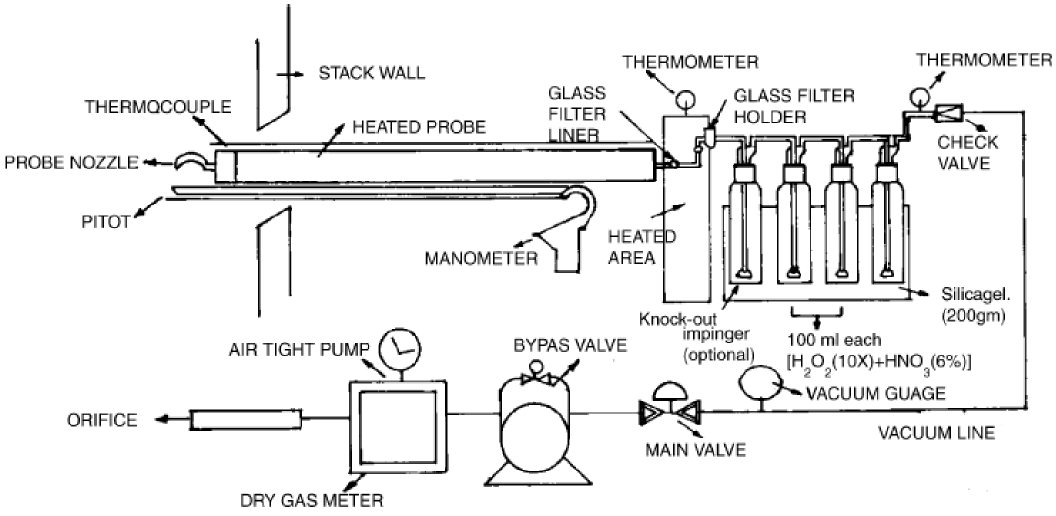
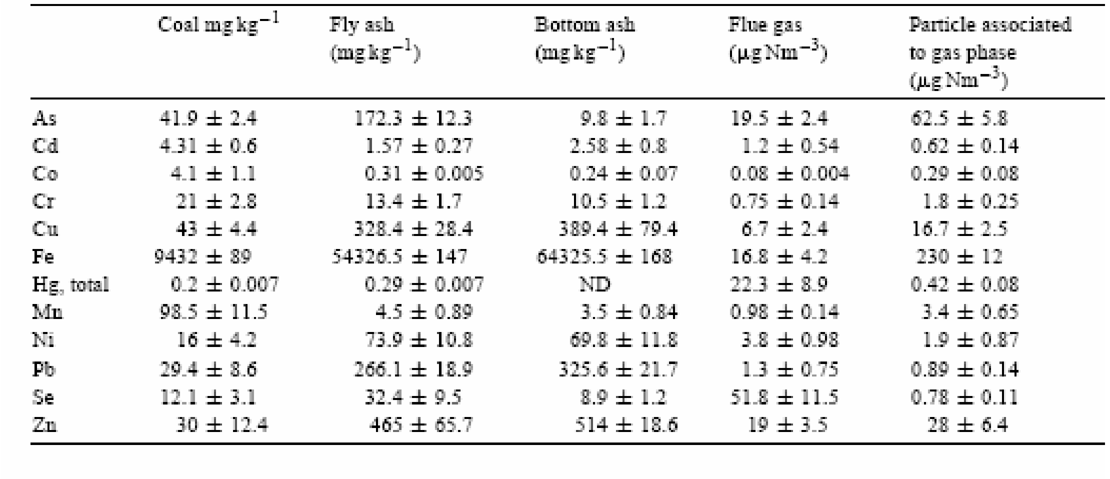


Figure 4.3: The sampling system for particle collection.[75]

The metals associated with the bottom ash, fly ash, and coal were analyzed by x-ray fluorescence, whereas the metals emitted in the flue gas and the particles associated with the gas phase were analyzed with inductively coupled plasma-atomic emission spectrometry, shown in Table 4.1.[75] From the metals analyzed in this study, Cd, Mn, Ni, Pb, and Fe are predominately found in the bottom ash, As, Se, Co, Cr, Cu, and Zn are predominately found in the fly ash, and Hg is almost completely emitted in the vapor phase.[75] As, Cu, Fe, and Zn exist with large concentrations in particles that are associated with the gas phase. Up to this point, no study has been conducted on the scale of the computer model by looking at what exactly is formed from all of the combustion products by sampling ambient emissions and examining these samples in the laboratory. The study conducted by Reddy et. al is a small scale study only analyzing a percentage of the metals emitted upon coal combustion. Under this study and studies similar to it in the literature, reducing and oxidizing conditions as well as coal type are not taken into account and only the metals are analyzed. The metal-metal interactions and organic-inorganic interactions upon combustion are not accounted for either.

Table 4.1: Concentrations of heavy metals found in coal and produced upon combustion. N expressed in the concentration for flue gas and particle associated to gas phase represents the number of samples (N=3) for standard deviation purposes.[75]

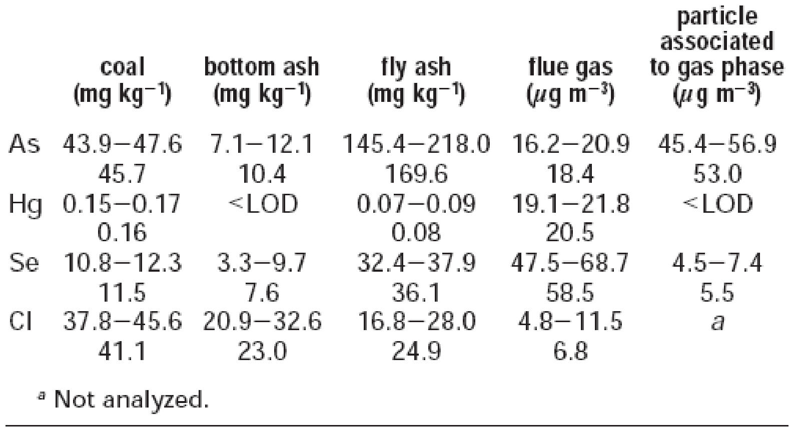


	Coal mg kg^{-1}	Fly ash (mg kg^{-1})	Bottom ash (mg kg^{-1})	Flue gas (µg Nm^{-3})	Particle associated to gas phase (µg Nm^{-3})
As	41.9 ± 2.4	172.3 ± 12.3	9.8 ± 1.7	19.5 ± 2.4	62.5 ± 5.8
Cd	4.31 ± 0.6	1.57 ± 0.27	2.58 ± 0.8	1.2 ± 0.54	0.62 ± 0.14
Co	4.1 ± 1.1	0.31 ± 0.005	0.24 ± 0.07	0.08 ± 0.004	0.29 ± 0.08
Cr	21 ± 2.8	13.4 ± 1.7	10.5 ± 1.2	0.75 ± 0.14	1.8 ± 0.25
Cu	43 ± 4.4	328.4 ± 28.4	389.4 ± 79.4	6.7 ± 2.4	16.7 ± 2.5
Fe	9432 ± 89	54326.5 ± 147	64325.5 ± 168	16.8 ± 4.2	230 ± 12
Hg, total	0.2 ± 0.007	0.29 ± 0.007	ND	22.3 ± 8.9	0.42 ± 0.08
Mn	98.5 ± 11.5	4.5 ± 0.89	3.5 ± 0.84	0.98 ± 0.14	3.4 ± 0.65
Ni	16 ± 4.2	73.9 ± 10.8	69.8 ± 11.8	3.8 ± 0.98	1.9 ± 0.87
Pb	29.4 ± 8.6	266.1 ± 18.9	325.6 ± 21.7	1.3 ± 0.75	0.89 ± 0.14
Se	12.1 ± 3.1	32.4 ± 9.5	8.9 ± 1.2	51.8 ± 11.5	0.78 ± 0.11
Zn	30 ± 12.4	465 ± 65.7	514 ± 18.6	19 ± 3.5	28 ± 6.4

As, Se, and Hg partitioning and mass balance calculations

As previously stated, Hg, Se, and As are the most volatile elements in flue gas.[77] They are important to study and understand because even though they are emitted into the gas phase they can interact with particles and heterogeneously condense or undergo surface reactions. One of the biggest issues with analyzing gas phase elements emitted from coal combustion is the methods for collecting them. There are two main categories of collection: "methods based on solid sorbents and methods that employ impingers."[77] The first method is safer and simple to use but has an inherent disadvantage of sorbent surface issues-preference canals and salt layer blocking that occur on the surface-which can impede the collection of gas phase species.[77,78] An additional issue that must be considered when collecting Hg^0 is that its collection efficiency decreases with increasing temperature.[77] With these issues addressed, Otero-Rey et. al found that Hg, Se, and As partition in the bottom ash, fly ash, flue gas, and particles associated with the gas phase. The study was conducted at *As Pontes* power station in the Northwest region of Spain, which uses 4 pulverized boiler units combusting a mixture of 50% anthracite and 50% subbituminous coal.[77] An impinger system, the Ontario Hydro Method Sampling Train, was used to collect the gas phase species, and is very similar to Figure 4.3 (same as other impinger), microwave assisted digestion was used for the solid samples, and multiple AAS techniques were used for instrumental analysis.[77] Using these techniques, the concentrations of As, Hg, Se, and Cl in coal, bottom ash, fly ash, flue gas, and particle associated to the gas phase were found, and these are shown in Table 4.2. It can be seen that Hg is the most volatile since the vast majority of the Hg emitted is in the flue gas. However, a large percentage of the As in the gas phase is associated with particles, which will be further explored later in this chapter. Both As and Se are predominately found in the fly ash with some being found in the flue gas.

Table 4.2: The concentrations in coal, bottom ash fly ash, flue Gas, and the particles associated with the gas phase for Hg, As Se, and Cl.[77]



	coal (mg kg^{-1})	bottom ash (mg kg^{-1})	fly ash (mg kg^{-1})	flue gas (μg m^{-3})	particle associated to gas phase (μg m^{-3})
As	43.9−47.6 45.7	7.1−12.1 10.4	145.4−218.0 169.6	16.2−20.9 18.4	45.4−56.9 53.0
Hg	0.15−0.17 0.16	<LOD	0.07−0.09 0.08	19.1−21.8 20.5	<LOD
Se	10.8−12.3 11.5	3.3−9.7 7.6	32.4−37.9 36.1	47.5−68.7 58.5	4.5−7.4 5.5
Cl	37.8−45.6 41.1	20.9−32.6 23.0	16.8−28.0 24.9	4.8−11.5 6.8	*a*

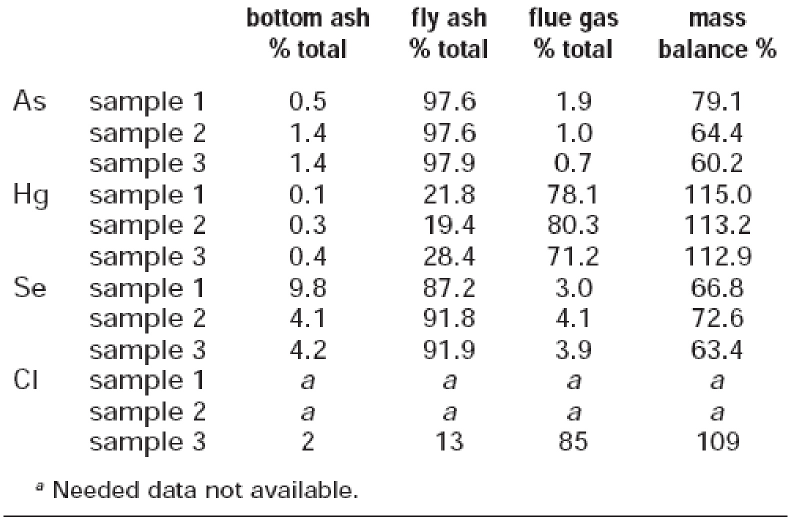
[a] Not analyzed.

To calculate mass balances of As, Hg, Se, and Cl, Equation 6 was used to see if all of the elements were being collected efficiently and accounted for from the known amount in the coal:

$$C_c * F_c = C_s * F_s + C_a * F_a + C_g * F_g, \qquad (6)$$

where F_c, F_s, F_a, and F_g, expressed in kg/kgcoal except for F_g which is expressed in terms of m^3/kgcoal, are used to determine the input/output rates for a specific element with respect to the coal, bottom ash, fly ash, and flue gas.[77] The terms C_c, C_s, C_a, and C_g correlate to the concentration of each compound, expressed in μg/kg or μg/m^3, in coal, bottom ash, fly ash, and flue gas, respectively.[77] The mass balances for Hg, Se, As, and Cl are shown in Table 4.3. The average mass balances for As, Hg, and Se are 67%, 113%, and 68% respectively.[77] These results are acceptable and much improved based on previous studies; however, gas phase Se is found at a smaller percentage then in previous measurements implying that the Ontario Hydro Method Sampling Train is not an accurate collection device for this element.[77]

Table 4.3: Mass balances for Hg, As, Se, and Cl.[77]



		bottom ash % total	fly ash % total	flue gas % total	mass balance %
As	sample 1	0.5	97.6	1.9	79.1
	sample 2	1.4	97.6	1.0	64.4
	sample 3	1.4	97.9	0.7	60.2
Hg	sample 1	0.1	21.8	78.1	115.0
	sample 2	0.3	19.4	80.3	113.2
	sample 3	0.4	28.4	71.2	112.9
Se	sample 1	9.8	87.2	3.0	66.8
	sample 2	4.1	91.8	4.1	72.6
	sample 3	4.2	91.9	3.9	63.4
Cl	sample 1	*a*	*a*	*a*	*a*
	sample 2	*a*	*a*	*a*	*a*
	sample 3	2	13	85	109

[a] Needed data not available.

Arsenic partitioning

There are three main forms of arsenic present in coal: pyritic (the most abundant), arsenate, and organic.[79] The pyritic form is very important because the increase in pyrite, which contains sulfur and is directly related to As, increases the concentration of As found in the coal, which increases the amount released in the vapor phase upon combustion, shown in Figure 4.4.

Even though arsenic is mostly emitted in the vapor phase upon combustion, it still has pathways to form particles from the vapor. Also, two of the arsenic gaseous forms, As_2O_3 or the dimer As_4O_6 (the most predominant form), that exist at the temperatures where selective catalyst reduction (SCR) occurs-reducing the oxides from nitrogen-are thought to deactivate the catalyst.[80] Coals with high calcium concentration can lower these effects because calcium oxide reacts with gaseous arsenic oxide to form $Ca_3(AsO_4)_2$-the most thermodynamically stable calcium arsenic compound; however, higher ranked coals typically do not contain enough calcium for this reaction pathway to occur.[80] Another issue with As_4O_6 forming is that post-combustion interactions with the fly ash can occur. The interactions are reliant upon the "gas temperature profile and the size and composition distribution" of the ash, and two pathways

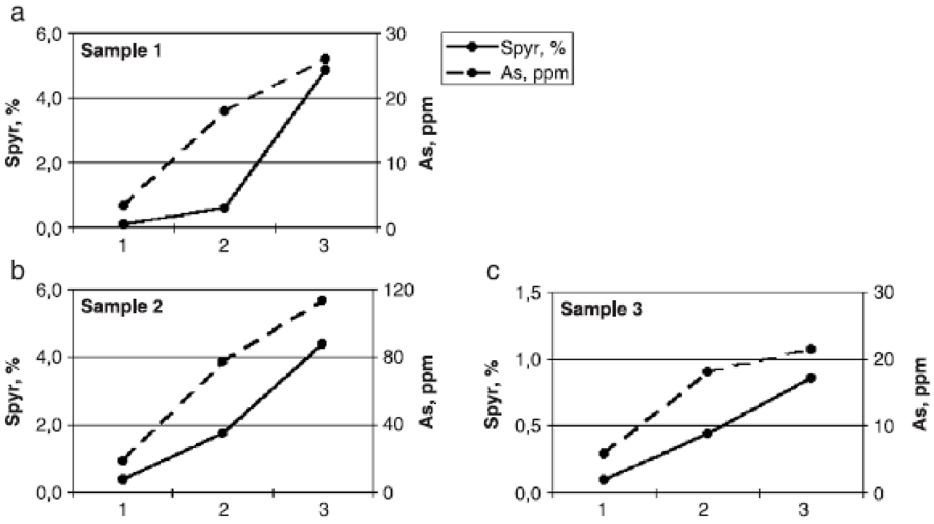


Figure 4.4: "Selected data of the As content in density fraction of three samples of Spanish anthracites. Plotted after the data from (Martinez-Tarazona et al, 1997, p. 399)." S_{pyr}% is the percent of sulfur contained in the pyritic form.[79]

exist: surface reaction to the particle and heterogeneous condensation, which are assumed to not occur at the same time.[80]

By observing the trend of the logarithm of vapor pressure vs. temperature by Senior, C.L. et. al in Figure 4.5 of As_4O_6, condensation will occur at very low temperatures and high concentrations of arsenic in the vapor phase.[80] The reaction rate of the vapor phase of As to the particle is based on the arsenic concentration, the fraction of the active surface area, which directly correlates to the calcium content, the particle size, and an Arrhenius-based reaction constant due to the spherical and nonporous characteristics of the particle.[80] Calcium cations at the particle surface are important because the surface reaction with arsenic can extract it from the vapor phase into the particle, so calcium content must be included in the model.[80] Any arsenic that is not vaporized via combustion is assumed to be uniformly distributed onto the particle.[80] Depending on the conditions post-combustion, this will determine which pathway the gaseous arsenic will take. If the temperature is above 1200^{o}C, then condensation or surface reactions will not occur.[80] When characterizing the equations for the model, Senior et al. took into account

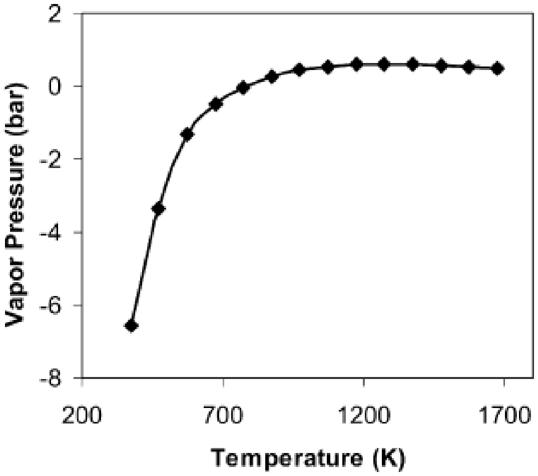


Figure 4.5: The logarithm of the equilibrium vapor pressure logarithm (bar) of $As_4O_{6(g)}$ vs temperature (K).[80]

the gas-phase transportation regimes, which are based upon free molecular-submicrometer size range-and continuum-supermicrometer size range.[80] To have surface reactions occur, the bulk partial pressure must be less than the equilibrium vapor pressure; whereas to have heterogeneous condensation occur, the equilibrium vapor pressure must be less than the surface pressure-bulk pressure for the free molecular regime.[80] The reaction rate constant for surface reaction for both regimes is given in Equation 7 taken from work done by Helble et al:

$$k_r = k_o e^{(-E(act)/RT)} \tag{7}$$

where k_o (8.8 m/s for these experiments) is a pre-exponential factor and E(act) (19.3 kJ/mole) is the activation energy for the reaction.[80] Another effect that had to be considered when modeling the arsenic reactions from the vapor phase was the SO_2 present in the flue gas can also react with the calcium (CaO) in the ash to form calcium sulfite, which then oxidizes to form $CaSO_4$.[80] This competition for calcium reduces the reactivity of arsenic towards the ash, which in turn reduces the amount of arsenic captured from the vapor phase to the particle.[80]

For the experimentation portion of the study, a cascade impactor was used for particle collection.[80] The particle size distribution is important because the aforementioned reaction types, heterogeneous condensation and surface reaction, are dependent upon this.[80] The fly ash size distribution is shown in Figure 4.6 for coal from six varying regions: Illinois (bituminous), Pittsburgh (bituminous), Ohio (bituminous), Kentucky (bituminous), Wyodak (subbituminous), and North Dakota (lignite).[80] The peak at smaller size fractions is dependent upon the part of the ash that is vaporized in the high temperature char burning, and the larger peak at higher sizes is due to the residual ash particles. The process that occurs postcombustion is the supersaturation of the ash vapor followed by condensation due to cooling of the gases.[80] The ash vapor then homogeneously agglomerates to form ash fume.

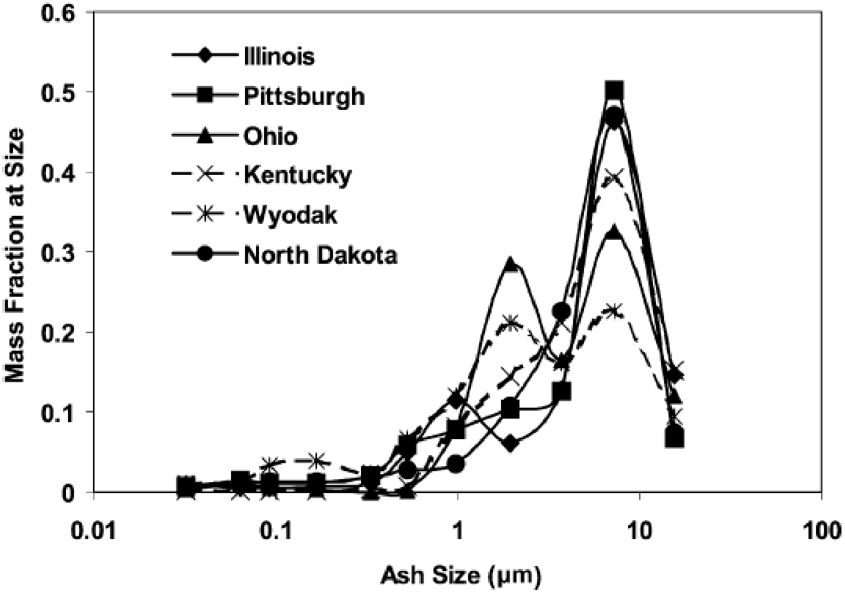


Figure 4.6: Mass fraction at size vs. ash size distribution (µm) for six coals at the postcombustion stage.[80]

In the study, Senior et al. also compared arsenic vaporization to the combustion type and coal type because as previously stated in chapter 2, the amounts of metal emitted varies based on these two parameters. The amount of arsenic vaporized varies from 55 to 98% as seen in Figure

4.7. By looking at the trends, a cyclone boiler, due to the higher firing temperature, yields larger amounts of arsenic in the vaporization phase, whereas tangential and wall fired units (both pulverized type boilers discussed in chapter 2) do not emit as much arsenic into the vapor phase. The higher ranked coals, bituminous, also lead to a larger percentage of arsenic being emitted in the vapor phase.[80]

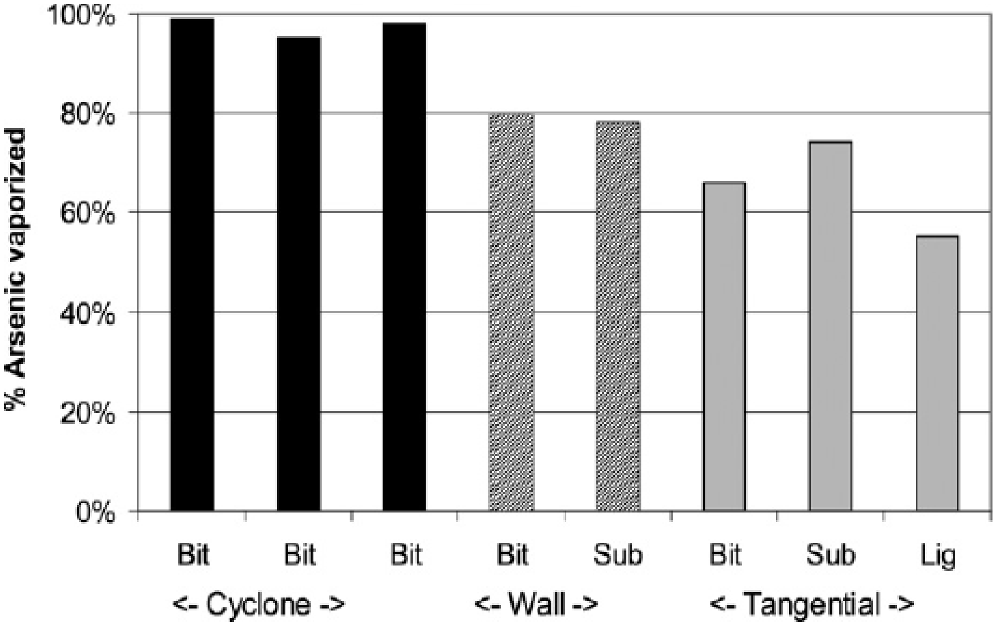


Figure 4.7: Vaporization of arsenic compared to boiler type and coal type from DOE toxic assessment program from eight different power plants.[80,81]

The experimental data was then compared to the model created to note any inconsistencies. The residence times of the sample, temperature, and percentages of arsenic vaporized and varying fly ash sizes is shown in Table 4.4. The coals with high Ca/As ratios and low sulfur levels-Wyodak and North Dakota-show an increased amount of arsenic laden particles in the size range < 0.1 μm. The effect of sulfur on the concentration of arsenic at varying sizes was also characterized and is shown in Figures 4.8 and 4.9. The only difference between the two figures is the region the coal was extracted from and the percentage of CaO in the fly ash. At

Table 4.4: Comparison of calculated and measured arsenic partitioning in ash and vaporization conditions.[80]

	Illinois bitum.	Pittsburgh bitum.	Ohio bitum.	Kentucky bitum.	Wyodak subbit.	North Dakota lignite
			Experimental conditions			
Residence time to sampling point (s)	3.5	2.9	3.2	2.9	6.6	9.44
Peak flame temperature (°C)	1292	1292	1357	1387	1197	1152
Sampling temperature (°C)	792	792	797	947	687	596
			Quantities calculated from data			
% As vaporization in flame	72.6%	94.8%	77.7%	62.9%	56.3%	36.3%
% As captured by fly ash	37.9%	37.2%	14.1%	5.7%	100.0%	100.0%
% As in fly ash <1 μm	44.3%	94.3%	59.8%	24.4%	54.1%	26.1%
% As in fly ash <0.1 μm	0.9%	1.3%	2.6%	2.3%	16.2%	7.3%
			Quantities predicted by model			
Conc. As in flame (ppbv)	16.3	29.2	111.1	19.6	11.0	55.8
Conc. As at sampling (ppbv)	10.2	18.4	95.0	18.5	0.0	0.0
% As in fly ash <1 μm	47.6%	83.6%	20.7%	12.5%	60.6%	32.4%
% As in fly ash <0.1μm	9.5%	23.3%	1.9%	2.1%	38.6%	17.3%

smaller particle sizes, a definite sulfur dependence on arsenic concentration is observed in both Figures 4.8 and 4.9. As SO_2 in the flue gas is increased, the concentration of postcombustion arsenic in the ultrafine size is decreased.[80] When comparing Figure 4.8 and 4.9, CaO has a huge impact on the concentration value of arsenic that is added to the particles via surface reactions. Figure 4.9, using the Kentucky coal (2% CaO in fly ash), definitely illustrates that decreased levels of Ca in the coal, which leads to decreased levels of CaO in the fly ash, inhibits arsenic from reacting at the surface of the particle so less arsenic is in the particle phase. This study not only gave an accurate model to predict portioning of arsenic via coal-fired combustion, but it also provides insight into the fate of arsenic after combustion.

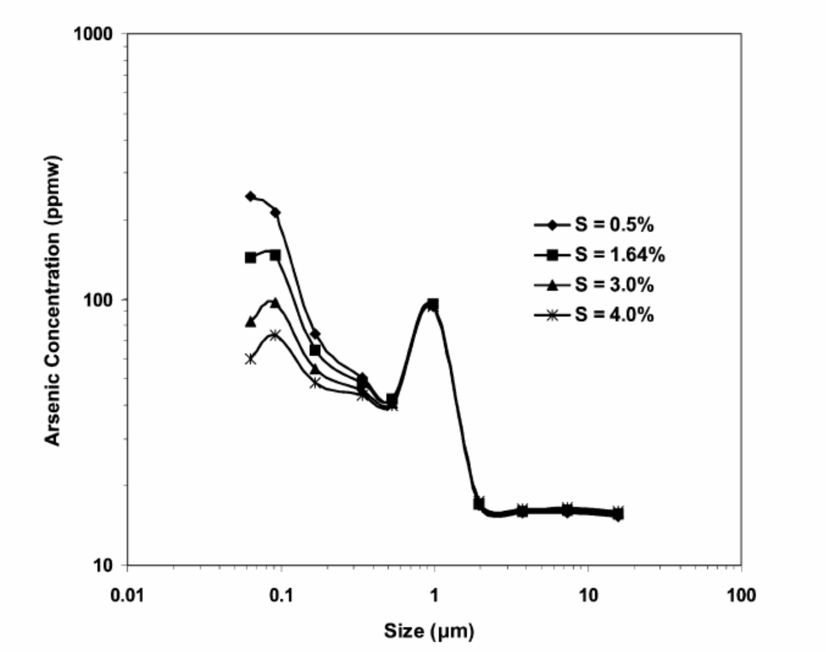


Figure 4.8: Arsenic concentration as a function of size and sulfur content using Pittsburgh coal (4.6% CaO in ash).[80]

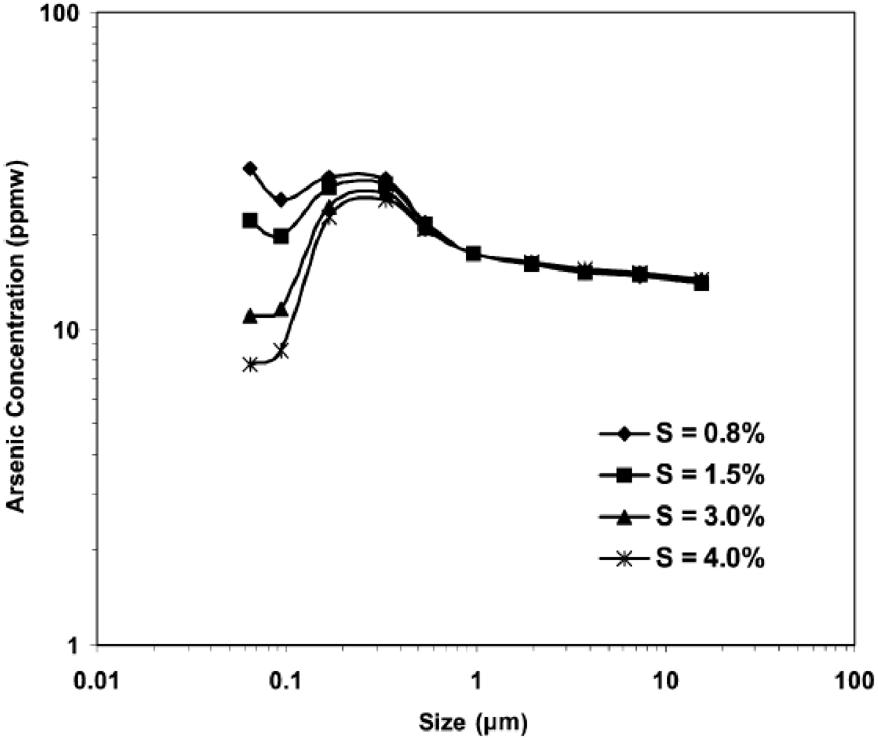
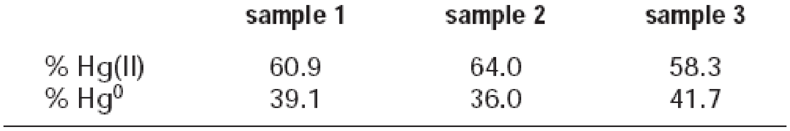


Figure 4.9: Arsenic concentration as a function of size and sulfur content using Kentucky coal (2% CaO in ash).[80]

Mercury partitioning and surface reactions to fly ash particles

As stated in the previous study by Otero-Rey et. al, Hg is predominately emitted into the gas phase upon coal combustion. The two forms it is emitted into the flue gas are Hg^0 and Hg^{II}, and the percentages, 38.9 and 61.1% respectively, were determined, as seen in Table 4.5.[77] As observed from previous studies, gaseous $HgCl_2$ has been found in the flue gas emission, but the mechanism of its production was not previously known.[82] Upon examination of the Hg emissions chemistry by Schofield, the cooler regions of the flue gas further from the combustion zone allowed the formation of solid $HgSO_4$ to condense onto any surface within a specific temperature range; however, if there is gaseous HCl present, it immediately scavenges the Hg on the particle in the form of $HgSO_4$ to form $HgCl_{2(s)}$.[82] Once this is accomplished, $HgCl_{2(s)}$ then evaporates so $HgCl_2$ ends up in the gas phase.[82]

Table 4.5: Percentages of Hg^0 and $Hg^{\ II}$ in flue gas.[77]



	sample 1	sample 2	sample 3
% Hg(II)	60.9	64.0	58.3
% Hg^0	39.1	36.0	41.7

Schofield's study has opened the door for other researchers to examine the effects of retention of Hg onto fly ash. Multiple studies have proposed that for mercury to be formed onto a particle, certain characteristics must be considered: unburned content, surface area, and morphology.[83] However, little is known about the Hg-fly ash and Hg-inorganic components interactions.[83] In the next study by Lopez-Anton et. al, the interaction of mercury with fly ash that was mainly composed of inorganic materials with a small portion of non combusted particles that were heated under three gas atmospheric conditions with mercury: inert, an environment simulating coal gasification, and an environment simulating coal combustion.[83] The coal combustion atmospheric environment will be the focus of the following discussion.

CTA, CTSR, and CTP were the three fly ash samples analyzed.[83] CTA was collected from anthracite coal that was combusted in a pulverized boiler, CTSR was collected from bituminous coal that was combusted in a pulverized boiler, and CTP was collected from mixtures of coal that have a high mineral content that was combusted in a fluidized bed boiler.[83] The experimental device used to create the aforementioned atmospheric environments is shown in Figure 4.10. Gaseous Hg was created at 190°C from the evaporation of solid mercury in the elemental form.[83] The experimental device consisted of a test tube that contained an external tube that was heated by the furnaces, an internal tube that consisted of the "sorbent bed", and an inner tube that contained the source of the element, mercury.[83] The experiment was developed in this manner to monitor the collection of mercury into the "sorbent bed" and to capture any element in the gas phase into the impingers.[83] Microwave acid digestion was used for sample preparation, and AAS was used to determine the elemental concentration of mercury.[83] The results of the mercury retention in a combustion process onto coal fly ash is

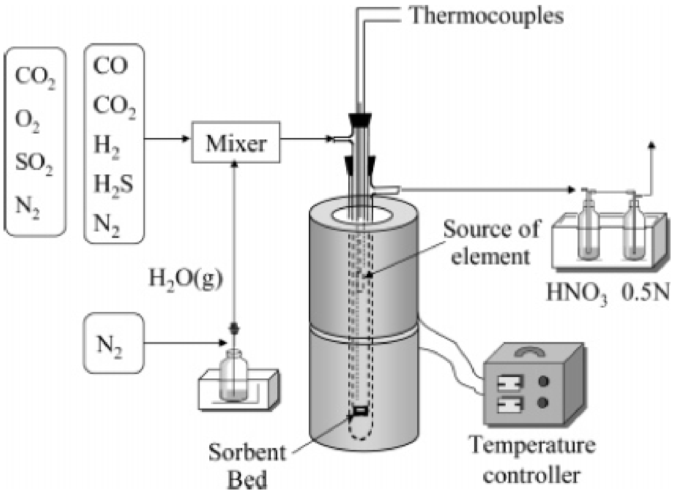


Figure 4.10: Schematic of the experimental device used to create the environmental atmosphere and study the retention of Hg onto fly ash.[83]

observed in Figure 4.11.[83] The retention capacity of the fly ash is significantly larger than compared to the carbon sources analyzed in the study.[83] It would seem, then, that mercury retention is not dependent upon carbon content, but in fact when comparing the different fly ash samples, more mercury was retained with increasing carbonaceous material.[83] So when analyzing fly ash, an increase in carbon content directly correlates to an increase in retention of mercury. Another notable difference was the mercury in the gas phase was found only in the Hg^0 form for gasification and inert atmospheres, whereas mercury can be found in the form Hg^{II} when coal fly ash is introduced into the system.[83] The oxidation of mercury could cause additional interactions with the fly ahses.[83] In this study, the reaction atmosphere was very simple and did not include the multiple complexities that exist when coal is combusted on a power plant scale (ie chlorines, sulfur oxides, and nitrogen oxides were not introduced).

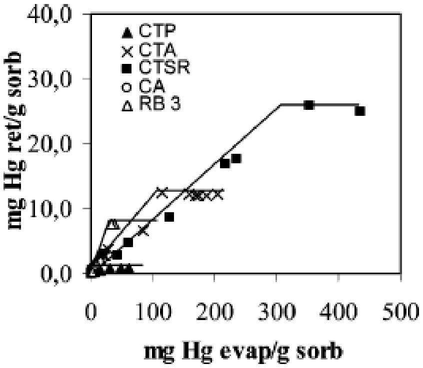


Figure 4.11: The combustion products of coal fly ash to measure the retention of mercury.[83]

Selenium surface reaction

As stated above, post-combustion zone interactions of metals released into the vapor phase with particles emitted is a topic that must be further explored. In the study by Seames et. al, Se, Cd, and As (semi-volatile metals) were analyzed to find the partitioning of these metals under laboratory simulated time and temperature combustion conditions and post-combustion conditions for two coals, and to deduce mechanisms and rates by analyzing samples collected in the combustion zone and immediately down stream from this zone.[18] It has been shown that semi-volatile metals have a tendency to be enriched onto submicron aerosols as compared to supermicron.[18] It has been hypothesized that for supermicron particles chemical reactions on or within the particle between trace metals and species on the particle results in an environmentally non-toxic form of the metal; however, surface condensation can create particles that are water soluble which has huge implications to the environment.[18]

Seames et. al simulated boiler coal combustion conditions by using a furnace in a laboratory setting that simulated the time and temperature of a commercial setting, yet allowing a well characterized flow stream for rate and mechanistic studies.[18] A sampling probe was used to collect the particles and route them through a Berner Low Pressure Impactor.[18] Two sample collection sites were used: 0.5 resident seconds after the burner and 2.2 residence seconds downstream from the burner.[18] Two samples of coal were used from a Illinois and Pittsburgh seam, but the specific type of coal was not stated.[18] INAA was used to determine the concentration of the particulates.[18]

The first comparison observed was the effect of particle size distribution of Se, Cd, and As between the two types of coal and the two varying residence times.[18] When comparing the Pittsburgh coal to the Illinois coal, there does not seem to be a significant difference, but there is a more pronounced decrease in the particle number for longer residence samples for Illinois coal compared to the Pittsburgh sample.

The study focuses on submicron particle enrichment, which can occur by vaporization followed by homogeneous nucleation, vaporization followed by heterogeneous condensation onto the particle surface, or vaporization followed by heterogeneous reaction with surface chemicals or chemicals in the particle.[18] It has been proposed that heterogeneous transformations are the dominant mechanism compared to homogenous nucleation for trace metals.[18] To compare the metals, a normalizing condition, the enrichment factor, must be established to remove the effect of differences in the furnace sampling. The enrichment factor can be found by comparing the ratio of ash mass sampled on a given sampling stage to the average mass of all the stages from the impactor combined, as seen in Equation 8:

$$E_{fa,x} = \text{ash on stage x (mg)/average ash on all stages (mg)}.^{18} \qquad (8)$$

To compare the metals at different residence times, Equation 9 is used to develop an understanding of elemental partitioning onto submicron surfaces:

$$\Delta E_{fa,\,x,\,2.2\text{-}0.5} = E_{fa,\,x,\,2.2} - E_{fa,\,x,\,0.5}.^{18} \qquad (9)$$

Figure 4.12 shows the enrichment factor of submicron particles for selenium. An enrichment of selenium is shown for the Illinois coal (triangles) but not for the Pittsburgh coal (circles).[18] The preferential mechanism for selenium enrichment post-combustion seems to be heterogeneous transformation onto the particle.[18]

In light of these studies, it has been demonstrated that not only the metal particulates emitted upon combustion need to be analyzed, but the transformations post-combustion must also be analyzed to have a complete understanding of the partitioning effects of coal-fired power plant emissions. The transformations include re-volatilization of metals from the particle into the vapor phase and metals that are volatile or semi-volatile partitioning onto the particle by a

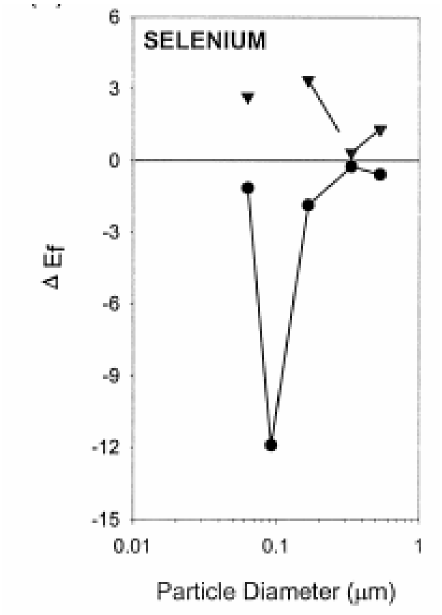


Figure 4.12: Enrichment factor comparison of varying particle sizes for selenium the circles are Pittsburgh coal and the triangles are Illinois coal.[18]

variation of mechanisms. Both of these transformations post-combustion are important because the emission control devices are less efficient for ultrafine particulates, and emission control devices for metals in the vapor phase are essentially non-existent.

CHAPTER 5

SUMMARY AND FUTURE PROJECTS

Summary

As the leading energy source in the United States, approximately 50%, and the vast majority of other countries in the world, coal-fired plant emissions are of concern to the international community. Several factors must be considered when trying to quantify and understand the metals emitted in the particulate form: health effects, fate and transport, environmental effects, coal type used, combustion process, emission control devices, sample collection and preparation, instrumental techniques, and partitioning of the metals upon combustion.

The particulate size range most detrimental to humans upon inhalation is ≤ 2.5 μm.[1] Another concern with particles at this small size is that emission control devices' efficiencies decrease.[2] The health effects range from minor respiratory inflammations for small exposure times to major respiratory conditions such as fibrosis and severe damage on the cellular and DNA level, which can eventually lead to cancer at prolonged exposure times. To understand humans' contribution to trace metals in the atmosphere, biogenic and anthropogenic sources are monitored. Biogenic sources range from wildfires to volcanoes to windblown dust, and anthropogenic sources include coal and oil incineration and metal manufacturing.[4,10] Coal emissions account for a large portion of the worldwide anthropogenic sources of metals: 84% of Mo, 58% of Hg, 47% of Se, 37% of Sb, 37% Cr, 29% of Mn, 25% of Ni, and 15% of Sn.[10]

After combustion of coal, there are three main forms of the combustion by-products of concern: bottom ash, fly ash, and flue gas.[12] The bottom ash, although not emitted into the atmosphere, can leach into the surrounding soil or water supply at the storage site on the plant premises or at the landfill where the waste will eventually be moved. The fly ash environmental impacts include contamination to the atmosphere, transportation from the plant site by meteorological conditions, and wet and dry deposition into the surrounding soil and water supplies. Flue gas, although in the vapor phase in the combustion zone, can condense, coagulate, or nucleate to form particles in the post-combustion zone of the plant or once released from the plant stack.[16] The vapor phase combustion by-products are of great concern because the emission control devices technology is limited.

The concentrations of the metals upon emission can vary due to the coal type and the incineration process used. The four types of coal listed in increasing rank are: lignite, subbituminous, bituminous, and anthracite.[13-15] Virtually every element in the periodic table is present in coal. The lower ranked coal, lignite, has the highest moisture content, a smaller amount of carbon content, and more lignite is required to produce the same amount of energy as a higher ranked coal.[13] The highest ranked coal, anthracite, has the largest carbon, lowest moisture, and lowest volatile matter content, which leads to a higher ignition temperature for combustion.[14] These trends are observed because of the age of the coal, which directly relates to the amount of heat and pressure applied-lignite is the youngest and anthracite is the oldest. When incinerated, bituminous releases the smallest amount of metal particulates, subbituminous releases more, and lignite releases the most.[4]

Another variable to consider is the boiler used to incinerate the coal. There are three main types of boilers that release metals, listed by increasing concentration: pulverized, cyclone, and stoker.[4] Stoker boilers are used only in industrial settings to produce power on a smaller scale, so it's overall contribution is less than the mass scale power plant boilers, cyclone and pulverized.

Analyzing particulate emissions at an anthropogenic source site is a daunting task because of the multiple phases that must be considered. The most important phase is properly collecting the samples over the ultrafine, fine, and coarse particle range. The most commonly employed techniques to collect particles are impactors: cyclone, plate, and virtual. All of these techniques use inertial effects to collect the particles based on size.

Filters are also commonly employed separately or in conjunction with an impactor to collect the particles for analysis. There are two main classes of filters used: fibrous mat and membrane.[37] The type of filter employed warrants careful consideration with what type of instrumentation is used. The filter needs to have a low blank value, must not have surface reactions, and must not contain metals of interest that will alter the values obtained from the instrument.[37,38,43] The filter holder used for the filters is of the utmost importance. There are two types used, open-face and in line, and open-face must be used for sampling with coal-fired emissions.

After collection of the particles, sample preparation is the final step before instrumental analysis. There are three main methods: extraction, conventional digestion, and microwave digestion. All of the methods use a mixture of acids, HNO_3, HCl, HF, or $HClO_4$, to extract or digest (with heat) the materials on the filter.[36]

The four techniques discussed, INAA, AAS, ICP-MS, and single particle TOF-MS, provides means for analyzing the vast number of metals contained in particulates emitted from coal combustion. The advantage of INAA, TOF-MS and ICP-MS compared to AAS is that multiple elements are analyzed simultaneously, whereas AAS can only measure one element at a time.[36] The vast majority of ambient sampling employs multiple techniques to measure all of the metals of interest. INAA, although advantageous because of high sensitivity, exclusion of matrix effects, and determination of sub-ppm concentrations for most metals, has inherent disadvantages: usage of a nuclear reactor, long sampling times on the order of months, and high expense.[43,55,56,59] ICP-MS has several advantages over INAA: shorter analysis time, interfacing with other analytical techniques, and less expense; however, the filter sample is completely destroyed during analysis.[35,38] The greatest advantage of single particle TOF-MS is that each individual particle can be chemically characterized, and the aerodynamic size can be obtained without sample preparation.[69]

The studies presented have shown that the particles' concentration decreases from the emission site to distances away from the emission site.[59] Also, the metals' concentrations are lower for dry deposition at the source site compared to the wet deposition.[59] The seasonal effects to the metal particulates are also negligible.[64] With AAS, it was found that for Mo and As as the particle size decreased the enrichment factor of these two metals onto the particles increased.[68] Correlation studies between ICP-MS and INAA by Bettinelli et. al showed a high degree of correlation between the two instrumental methods for V and Ni; however Maenhaut et. al have shown that ICP-MS consistently underestimates the metal concentration compared to INAA.[36,54]

The partitioning effects of the metals (classified in chapter 1) were confirmed by a computer model study and laboratory experiments.[75,78] The computer model showed that interactions in both oxidizing and reducing conditions can lead to the formation of metal oxides, sulfates, arsenates, and halogens as well as metal-metal interactions.[75,78] It has also been shown that semi-volatile metals tend to be enriched onto submicron particles compared to supermicron particles.[18]

Metals in the vapor phase were not the focus of the paper, but they must be considered when characterizing combustion zone partitioning as well as post-combustion interactions. As, Se, and Hg can be found in both the fly ash and flue gas; however, Hg is predominately emitted in the vapor phase, whereas Se and As are predominately found in the fly ash.[77]

The release of As in the vapor phase consists of two forms, As_2O_3 and As_4O_6 (the predominant form), and these gases in the combustion zone can lead to condensation of the gas onto fly ash particles at low temperatures and high concentrations.[80] A higher content of calcium in coal was also directly linked to increased scavenging of As from the vapor phase to the particle surface.[80] However, at temperatures above 1200°C, condensation and surface reactions were negligible for As.[80] It was also found that the As emitted in the vapor phase has a direct correlation with the pyrite sulfur content found in coal; as the sulfur content increases, the arsenic in the vapor phase increases.[80]

The two forms of elemental mercury emitted into the gas phase are Hg^0 and Hg^{II}.[77] Gaseous $HgCl_2$ is also found via the formation of solid $HgSO_4$, which condenses onto the particle surface, but solid H_2SO_4 is immediately scavenged by HCl to form solid $HgCl_2$, which immediately vaporizes.[82]

Future projects

Since INAA, ICP-MS, and AAS have been used in the field of coal-fired emission characterization for decades, the novel approach of ATOF-MS has huge implications for advancing the field due to the rapid analysis and omission of sample preparation. One future project to begin the advancement of ATOF-MS into the coal emission field for trace metal particulates is to initiate correlation studies between ATOF-MS and INAA or ICP-MS of known standards of coal fly ash. If a direct correlation between the techniques is observed, then laboratory studies must be conducted to simulate combustion zone conditions and post-combustion zone conditions to characterize particle size and the number of particles in both regions as a function of temperature.

Once a general understanding of the size fractions of particles formed in a lab setting with increasing residence times from the combustion zone, field studies must be implemented to measure these effects on site at a power plant. The effects of dry deposition and wet deposition at the site as well as distances from the site must be conducted to determine individual particles composition in real time. By slowly combining the pieces of the puzzle, a better understanding of partitioning, post-combustion interactions, fate, transport, and effects of boilers and coal types on emissions will increase clarity of trace metal particulates in the atmosphere from coal-fired combustion.

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