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Evaluation of Capillary Electrophoresis Combined with a
Modified European Community Bureau of Reference (BCR)
Sequential Extraction for Determining the Distribution of Fe,
Zn, Cu, Mn and Cd in Airborne Particulate Matter

By

Meghan Kelly, B.Sc.

A Thesis submitted to the Faculty of Graduate Studies and Research in Partial
Fulfillment of the Requirement for the Degree of Master of Science

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Submitted by
Meghan Kelly, B.Sc.

in partial fulfilment of the requirements for the degree of Masters of Science

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Glossary

AAQD	Analysis and Air Quality Division
AAS	Atomic Absorption Spectrometry
BCR	European Community Bureau of Reference
BGE	Background Electrolyte
CE	Capillary Electrophoresis
CPA	Corrected Peak Area
DAD	Diode Array Detector
EK	Electrokinetic (injection)
EOF	Electroosmotic Flow
ERMD	Emissions Research and Measurement Division
ETC	Environmental Technology Centre
FAAS	Flame Atomic Absorption Spectrometry
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
HGAFS	Hydride Generation Atomic Fluorescence Spectrometry
IC	Ion Chromatography
ID	Inner Diameter
IS	Internal Standard

LOD	Limit of Detection
NAPS	National Air Pollution Surveillance (Network)
NIST	National Institute of Standards and Technology
<i>o</i> -phen	1,10-phenanthroline
PM	Particulate Matter
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SRM	Standard Reference Material
UV	Ultraviolet
XRF	X-Ray Fluorescence

Abstract

This work evaluated the potential of a capillary electrophoresis (CE) method to determine the distribution of Fe, Zn, Cu, Mn and Cd in an airborne particulate matter (PM) after a sequential extraction based on the European Community Bureau of Reference (BCR) protocol. The CE experimental conditions were optimized for sensitively measuring trace metals ion the BCR extractants. Limits of detection were at low- $\mu\text{g/l}$ ($\mu\text{g/g}$) levels and mid- $\mu\text{g/l}$ (tens of $\mu\text{g/g}$) levels using electrokinetic and pressure injection, respectively. The other focus of this work was to speed up the BCR sequential extraction procedure by using ultrasonication in place of mechanical stirring. The reliability and applicability of the accelerated extraction scheme were evaluated using a Standard Reference Material, NIST 1648 Urban Air PM. The accelerated method had good precision (relative standard deviation typically below 10%) for all metals in all fractions, and the results were reasonably comparable to those obtained using the conventional method. The overall operating time was reduced from 51 hours (conventional method) to 2 hours (ultrasound-accelerated method). The studied analytical methodology was also applied to some actual filter-collected $\text{PM}_{2.5}$ samples from two source types: urban ambient air and a highway tunnel (the latter representing an anthropogenic-rich source as vehicle emissions). Conclusions were drawn about the metals themselves, and, in general, the metal distributions between the two source types were similar, indicating that the urban air is characteristic of an anthropogenic-rich PM.

Acknowledgements

I would like to thank my supervisor, Dr. Ewa Dabek, for her tremendous support and guidance throughout this research.

I wish to express my sincere gratitude to my co-supervisor, Dr. C.L. Chakrabarti, for his valuable advice and input, and for lending me the use of his GFAAS instrument.

A great thanks to Dr. Heidi Chen for her input and assistance with some of the experimental work, and for her editorial work on this thesis.

Thank-you to the members of the Inorganic Lab of the AAQD at Environment Canada for performing the IC analyses.

I would also like to thank the students of Dr. C.L. Chakrabarti's lab for their advice and guidance and for their assistance with running the GFAAS.

Finally, I would like to thank my family for all of their support and encouragement.

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1 INTRODUCTION

1.1 Background

Air pollution has been an area of environmental interest and concern, as is evidenced by the quantity and variety of atmospheric programs initiated in the past three decades to comprehend and evaluate different airborne pollutants. Specifically, it has become important to determine both the types and sources of various pollutants, as it is relevant to a number of important air quality and atmospheric chemistry issues including health effects of airborne particulate matter (PM) and closely related gaseous air pollutants.

Particulate air pollution has risen drastically because of increased anthropogenic activities such as coal combustion, oil and gasoline combustion, ore smelting, and waste incineration [1-4]. There are also natural sources of airborne PM, mainly weathering and mechanical uplifting of surface soils and dust, but also from other sources such as volcanoes, sea spray, and wild fires [5-8]. However, in many parts of the world, particularly in urban areas, the anthropogenic sources generate quantities of airborne PM and toxic constituents that are above the natural background levels [9]. This poses ecological and health threats because airborne particles contain toxic substances that can be released into ecosystems through atmospheric deposition or can be absorbed in the lungs during breathing [10, 11].

Thus, the characterization of airborne PM is of great importance to many

scientific fields, such as epidemiology and toxicology in health research [12-17]. In atmospheric sciences, an understanding of airborne PM is important for modeling atmospheric processes and for environmental control purposes. However, the actual components of PM that adversely affect human health have not yet been clearly identified. What appears to be of greatest concern are potentially toxic species that, upon inhalation of the particles containing them, can dissolve in lung fluids and enter the body via the bloodstream. Such toxic species may be either organic or inorganic in origin. For this reason, a great deal of research has focused on the chemical composition of atmospheric PM, including heavy metals, which are common pollutants in airborne PM samples. In addition to this, there is ample evidence that the chemical speciation, and hence bioavailability, of trace metals associated with the respirable particulate matter depend on the oxidation state and how the elements are distributed among the various components of the particle matrix. Thus, simple measurements of a metal's total concentration, commonly used in monitoring programs, may not be indicative of its potential to participate in processes deleterious to health. Therefore, the ability to determine the chemical forms (chemical speciation) of heavy metals in airborne PM is becoming increasingly important.

1.2 Airborne Particulate Matter

The term "particulate matter" refers to all microscopic airborne solid and liquid particles (aerosols), except pure water. PM is classified by particle size, or

more correctly, aerodynamic particle diameter, which accounts for irregularities in particle shape (i.e., non-spherical shapes). Aerodynamic diameter is the equivalent diameter of a spherical particle that has the same settling velocity as that of the collected particles. Particle diameters can range from about 0.005 μm to 100 μm , but the airborne portion generally consists of particles less than 40 μm . Much of the concern and interest, however, are focused on particles in the smaller size range (up to 10 μm) because larger particles are generally not inhaled into the lungs. As such, PM in the size range of interest is classified into two groups: particles less than 2.5 μm in diameter constitute fine PM ($\text{PM}_{2.5}$), and particles from 2.5 μm to 10 μm in diameter constitute coarse PM ($\text{PM}_{2.5-10}$) [9] (Figure 1(a)).

Because airborne PM is not defined according to its chemical composition like other atmospheric substances are, it can include a wide range of chemical constituents, such as elemental and organic carbon compounds; oxides of silicon, aluminium and iron; trace metals; sulphates; nitrates, and ammonium (Figure 1(b)).

The size and composition of PM depend on the nature of the source and the processes by which the particles are formed. There is generally a connection between particle size and the type of source of the airborne particulates. Coarse particulates are predominantly of natural origin, whereas fine particulates tend to come from anthropogenic sources [1, 5, 7]. Furthermore, particles can be formed as either primary or secondary. The former are particles that are emitted

(a)

(b)

Figure 1. Airborne PM size distributions in terms of (a) major sources and (b) composition

directly into the atmosphere, whereas the latter are those that are formed in the atmosphere through physical and chemical processes. Both primary and secondary particles can come from either natural or anthropogenic origins; however, secondary particles tend to be of the fine PM fraction and hence tend to be mainly anthropogenic in origin.

The matrices of airborne particles consist of different substrates or phases to which the metals are bound. These phases hold the metals with different strengths, thereby affecting the potential mobility and bioavailability of the metals [18-20]. The different source types (natural versus anthropogenic) give rise to important characteristic traits in the distribution (strength of association) of metals in anthropogenic versus natural PM: anthropogenic PM generally contains higher amounts of potentially mobile and bioavailable (loosely bound) metals while natural PM metals are typically largely immobile and non-bioavailable (strongly bound). This is due to a fundamental difference in the nature of the processes by which these two types of sources generate airborne PM. Many anthropogenic processes involve high temperatures in which metals are volatilized and then, as the temperature falls, undergo condensation and are adsorbed onto the surfaces of particles. These surface-associated metals are loosely bound, and can be released into a surrounding medium (e.g., lungs, ecosystem) relatively easily. Natural sources of PM are generally low temperature processes, and the conversion and redistribution of metals among phases does not occur. Consequently, the metals in natural PM tend to be more matrix-associated (strongly bound), and are not easily removed from the particles [1, 7, 21].

1.2.1 Health effect studies

A number of epidemiological studies have provided evidence that the health effects are largely or entirely attributable to the respirable fractions of airborne PM, especially those fractions that are less than 10 μm (PM_{10}) and more recently, less than 2.5 μm ($\text{PM}_{2.5}$) [9, 22, 23]. $\text{PM}_{2.5}$ has been found to be associated with health problems in urban areas, such as increases in daily respiratory-related mortality [24] and in the occurrence of asthma [25]. For example, in a study that investigated associations between daily hospital admissions for respiratory problems (in Toronto) and levels of PM, $\text{PM}_{2.5}$ was found to have the strongest association, followed by PM_{10} , and then total suspended particles with the weakest association [11]. This is reasonable because the degree of respiratory penetration and retention is a function of the particle size, with particles less than 2.5 μm being deposited in the alveolar regions of the lung where trace elements are absorbed more efficiently [26]. Furthermore, fine particles tend to contain higher proportions of potentially harmful and loosely bound metals such as Fe, Cd, Mn, Zn, Cu, Cr, Ni, Pb, V compared to coarse particles [9, 27]. If present in elevated concentrations in ambient air, these metals can pose a significant risk to human health.

Despite what the epidemiological studies show, the underlying biological causes of the health effects of fine particle exposure remain unclear; it is not known which factor of mass, size, composition, or a combination of these three factors, contribute most significantly to the health effects [1, 28].

It is known, however, that the particles can contain considerable amounts of various transition metals, which have the capacity to support electron exchange and catalyse free radical production. The generation of free radicals results in lung injury, inflammation, and alterations in the pulmonary defence system [29]. For example, Cartel et al. [28] reported that toxic responses were produced when normal human bronchial epithelial cells were exposed to residual oil fly ash containing high levels of several transition metals. Furthermore, these toxic responses were inhibited by the inclusion of a metal chelator or a free radical scavenger, indicating that the toxic responses were induced by the free radicals, and hence, that metals present in the residual oil fly ash may be responsible for the toxic responses. This has also been supported by findings in other toxicological studies using other types of PM, including coal fly ash, diesel and gasoline exhaust particles, and ambient air particles [30-32].

There is also evidence from toxicological studies indicating that, of the total contents of metals present in airborne PM, it is primarily the soluble (loosely bound) metals that cause the toxic responses and, hence, the health effects attributed to metals in PM [33, 34].

So, although there is no evidence to pinpoint any single feature or component of PM as the cause(s) for the observed epidemiological effects, it does seem apparent that metals contribute, at least in part, to the adverse health effects associated with exposure to airborne PM.

1.2.2 Characterization of metals in airborne particulate matter

Various approaches have been proposed for estimating the behaviour and fate of atmospherically associated trace metals and for obtaining information on their specific sources. These include appropriate selective sampling methods and advanced analytical techniques, such as single element determinations, surface-sensitive methods, and sequential leaching experiments.

The application of selective sampling to obtain particle-size distribution of airborne PM is of interest for several reasons: (i) particle sizes relate to different sources and, when properly distinguished, the information can be used to differentiate between the sources and quantify their relative contributions, vis-à-vis, submicron particles (the respirable fraction), which are formed as condensation nuclei in high temperature processes, such as combustion, and are from motor vehicles; micron particles are fugitive emissions from industrial processes, while 'supermicron' large particles arise from grinding and abrading operations, and from soil and street dust entrainment in local air currents, etc.; (ii) small particles can remain airborne for longer periods and disperse further than large particles which sediment more rapidly and deposit locally, typically within about 1 km of the emission source as dust fall, contributing to surface soil contamination and future wind re-entrainment; (iii) the microcomposition and speciation of respirable submicron particles is of particular importance in environmental health because these smaller particles tend to contain relatively high levels of potentially mobile and toxic metals [35].

Several conventional analytical techniques for metals, such as X-ray fluorescence (XRF) spectroscopy, proton-induced X-ray emission spectrometry (PIXE), instrumental neutron activation analysis (INAA), atomic absorption spectroscopy (AAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES) or inductively coupled plasma-mass spectrometry (ICP-MS), are used for the determination of total metal concentrations in atmospheric particles [36]. These methods differ with respect to detection limits, sample preparation, and cost [37]. XRF and PIXE are the most commonly applied methods because they quantify more than 40 detectable elements, they are non-destructive, and are relatively inexpensive. AAS, ICP-AES, and ICP-MS are also appropriate for quantitative determination when particles are extracted in deionised water.

Although these determinations supply valuable information about the overall pollution levels, it is often necessary to quantify specific metallic forms (species) since bioavailability, solubility, and metal cycles largely depend on physical-chemical speciation, including how the elements are partitioned among the various PM matrix components [38-41]. Therefore, determining the total metal concentrations may not be sufficient to provide a true indication of the potential threats to health. Consequently, the ability to determine the chemical forms of heavy metals (i.e. chemical speciation) in airborne PM is becoming increasingly important. Furthermore, chemical speciation information is also important in source apportionment investigations. Source apportionment is an important aspect in determining the relative responsibility, and hence, also the means for amelioration, of various anthropogenic contributors to the degradation

of ambient air quality. Chemical speciation, therefore, offers a way to determine the real metal activity in the environment and provides a new perspective for analytical control [41]. There is, however, no known universal analytical technique capable of identifying and quantifying the metal species present in airborne PM. Furthermore, owing to the chemical complexity, extremely small particle sizes, and typically small total sample size (often no more than a few milligrams) of ambient PM samples collected on filters, PM samples can pose significant problems for analysis, especially for determination of the inorganics [42].

Chemical speciation is a term denoting a variety of approaches [43]. One of them is specific speciation, which is the more traditional approach, involving the determination of actual chemical forms (e.g., oxidation states). If the scope is limited to the direct analysis of solids, a method such as Auger electron spectroscopy distinguishes the oxidation state of the element while X-ray photoelectron spectroscopy specifies the nature of the bonds in given molecules. Another technique that has significant potential for specific speciation of PM is the synchrotron-based technique of X-ray absorption fine structure (XAFS) spectroscopy, which provides information on the form of occurrence of an element in the material. Finally, mass spectrometric methods, such as laser microprobe mass spectrometry, offer the potential to generate and detect ions containing the initial analyte molecules as a whole. To some extent, this can be considered as speciation at the highest possible information level. However, spectroscopic techniques are expensive (e.g., the synchrotron-based technique

of XAFS spectroscopy), or are difficult to use routinely for large numbers of samples [42].

Another approach to chemical speciation is the fractionation of metals according to the different phases with which they are associated in the solid material. This is done using different reagents or extractants, and the fractionation of each metal depends on the extractants and operating conditions with which the extraction is carried out (hence the name “operational speciation”). Speciation in this sense is used in accordance with recent IUPAC recommendations, i.e. the determination of the distribution of an element among defined chemical species (or phases) in a sample [43]. In environmental analysis, therefore, chemical fractionation of trace content has become the dominant approach for estimation of environmental hazard [44].

1.2.3 Chemical fractionation (Operationally-defined speciation)

Many different sequential extraction schemes have been proposed in the environmental analysis [44], covering a wide range of extractants and experimental conditions. Extractions can be done either singly or sequentially, depending on the amount of information desired. Single extractions involve only one step, and thus, the results will return information about the metal content of one fraction. Sequential extractions, on the other hand, involve multiple steps in which the sample is treated sequentially with a series of different reagents, each one attacking and releasing the metals from a different fraction of the sample [38, 44]. In general, the extractant is made more reactive from one step to the next,

therefore, high contents of an element in the first fractions correspond to high mobility, and the environmental availability decreases with increasing fraction number. Thus, unlike the single-phase information obtained from single extractions, sequential extraction results give information about the distribution of metals in multiple fractions, and it can be used to distinguish between the environmentally mobile and immobile contents of metals, which is necessary for assessing the potential ecological and health threats.

A variety of terms that are used to identify the different extraction steps are found in the literature. Typically the terms refer to the phases of the solid material that are targeted by the extraction steps. The phases targeted by solutions containing salts or buffers in the neutral pH range (e.g., MgCl_2 , NH_4Ac) and weak acids (e.g., acetic acid, oxalic acid) are referred to as “exchangeable” and “carbonate-bound”, respectively. Often these two fractions are extracted in one step using a weak acid. Metals associated with “Fe and Mn oxides” are usually extracted by reducing agents such as hydroxylamine hydrochloride in the presence of either nitric or acetic acid to prevent precipitation of the extracted metals. Metals that are “bound to organic matter” are usually extracted under oxidizing conditions, most commonly H_2O_2 and heat, to degrade the organic matter that so strongly complexes the metals. Finally, complete digestion with HF and oxidizing acids is required to release the metals from the “refractory” phase [39, 45, 46].

These are the most commonly used terms for labelling the different extraction steps. However, in the light of concerns about the exact phase

selectivity of some extraction reagents, the use of more operationally based terms, relating to the nature of the metals targeted by the extractant, is considered more appropriate. For example, “exchangeable and acid soluble” for carbonate-bound metals, “reducible” for metals associated with Fe and Mn oxides, and “oxidisable” for metals bound to organic matter. The last category is still appropriately called refractory or residual [47].

Among the variety of sequential extraction methods that have been proposed, the five-step procedure designed by Tessier et al. [46] is one of the most widely used schemes, especially for soil and sediment characterization. This scheme partitions metals into five fractions: (1) “exchangeable”(1 mol/l MgCl_2 , pH 7); (2) “carbonate bound” (1 mol/l NaAc, pH 5.0); (3) “Fe-Mn oxide bound” (0.04 mol/l HAHCl in 25% (v/v) acetic acid; (4) “organic bound” (3.2 mol/l NH_4Ac after oxidation by 8.8 mol/l H_2O_2) and (5) “residual” (HF-HClO_4).

The large variety of sequential extraction schemes that exist today make it difficult or impossible to compare between the results from one method to the other. In the interest of harmonizing fractionation schemes, the European Community Bureau of Reference (BCR), now called the Standards, Measurements and Testing Programme (SM&T), developed a three-stage sequential extraction method [48], which has been widely accepted and used for metal partitioning in sediments [38, 49], soils [40, 50], sewage sludge [51], bottom ash [39], and fly ash [40]. The BCR procedure fractionates metals into (1) “easily exchangeable and acid-extractable” (0.11 mol/l acetic acid), (2) “reducible” (0.1 mol/l HAHCl acidified to pH 2.0 with HNO_3), and (3) “oxidisable”

(1 mol/l NH_4Ac after oxidation by 8.8 mol/l H_2O_2) fractions. This is the sequential extraction scheme that was focused on in this work.

This sequential extraction method offers a number of benefits. As mentioned above, the intention behind it was to provide a common sequential extraction protocol to allow comparability between different sets of results reported in the literature. In addition to this, the extraction conditions in each step have been established for optimum extraction efficiency and adequate phase selectivity. The method has been tested and thoroughly scrutinized by many different research groups to ensure that it is reproducible [38, 49, 51]. Efforts have also been underway to use the BCR protocol for the certification of a sediment reference material (CRM 601) for its extractable, rather than total, metal contents [52].

1.2.3.1 Effect of operational conditions

The order in which the extractants are applied in a sequential extraction scheme is very important for maintaining the selectivity of the extractants for the particular fractions of the sample. As described earlier, the steps begin with extractants to release the most loosely bound metals, and move progressively to stronger extractants to release the more strongly bound metals. For instance, an acidified HAHCl solution that is intended for extraction of the reducible phase will also extract metals from both the easily exchangeable and acid soluble fractions. Therefore, the exchangeable and acid soluble fraction must be extracted prior to the reducible fraction [45]. Similarly, depending on the type of information

desired, the easily exchangeable and acid-soluble metals may be extracted separately by first applying a very mild extractant (e.g., water or a neutral pH salt solution) to target the water-soluble fraction, followed by a weak acid (e.g., acetic acid) to target the acid-soluble fraction.

Besides the selection and order of the extractants, there are various other conditions that must be considered for a sequential extraction method. The duration of each extraction step is important as it relates to the kinetics of the species between liquid and solid phases. If the extraction time is too short then some species will remain entrapped in that fraction of the solid sample and the extraction will not be complete. But after longer extraction times processes that are detrimental to the extraction results may occur, such as readsorption onto the solid phase or precipitation [19]. Thus, development of an extraction method usually involves an investigation of the change in the amount extracted over time. Often, where more than one species are of interest, a compromise has to be made in the extraction time, as different species equilibrate between liquid and solid phases at different rates.

The liquid (extractant) to solid (sample) ratio is another variable. Not only can the liquid to solid ratio influence the rate of extraction, but it also determines the resultant concentration of metals in the extracted solution to be analysed. A greater volume of extractant can speed up the extraction, and even increase to a certain extent the final amounts of metals extracted [19]. On the other hand, it also may be undesirable to use such excessive volumes as to yield extracts of very dilute concentrations of already trace-level metals. The liquid to solid ratio

may also affect the precision of the extraction results. In a study to evaluate the reliability of a sequential extraction method, it was found that precision was poorer at lower liquid to solid ratios [47].

The pH and ionic strength of the extractants will also affect the extraction results. Decreasing the pH or increasing the ionic strength of the extractant will increase the amounts extracted, but in both cases, certain limits must be upheld because of the risk of attacking other fractions [45, 19].

The temperature at which the extraction steps are carried out must also be considered. The first few fractions (exchangeable, acid soluble, and reducible) are generally extracted at room temperature, while heat is usually required for the oxidisable and residual fractions [45].

1.2.3.2 Current applications in PM characterization

Although sequential extraction methods have primarily had widespread application to the study of terrestrial and aquatic solid materials, such as soils, sediments and sludge [39, 44, 46, 49, 53], there has been a growing interest in the application of sequential extractions to trace metal speciation, or distribution, in airborne particulate matter [21, 41, 54-68]. However, the methods that have been used vary widely in their operating conditions, and hence the results, and some of the studies have been restricted to only one metal [60-63]. In general, most of the schemes used for airborne PM are derived from others employed for soils and sediments.

As mentioned before, the protocol developed by Tessier et al. [46] is one

of the most widely used sequential schemes for the fractionation of metals in a variety of matrices, including airborne particles. As an example, Lum et al. [56] and Dreetz and Lund [55] applied a modified Tessier scheme to the Standard Reference Material, NIST 1648 Urban Particulate Matter, and dust from a filter cassette, respectively. Another study [35] reported the use of such a scheme to estimate the metal distribution in a sewage sludge incinerator ash from two hospitals. More recently, Fernandez et al. [54] adopted Tessier's scheme to investigate if operational metal speciation is capable of determining and characterizing the principal pollution sources in an area using statistical analyses of pattern recognition. In the following study, Fernandez et al. [41] modified the procedure, employing less aggressive conditions in order to extract the chemical forms from fine urban particles that can be biologically available to the respiratory tract of the human body. The reported four-stage sequential procedure fractionated metals between (1) "soluble and exchangeable" (water), (2) "carbonates, oxides and residual metals" (0.25 mol/l HAHCl, pH 2), (3) "bound to organic matter, oxidisable and sulphidic metals" (2.5 mol/l NH_4Ac extraction after oxidation by 8.8 mol/l H_2O_2), and (4) "residual metals" ($\text{HNO}_3/\text{HCl}/\text{HClO}_4$).

Other reported sequential leaching schemes utilized a modified version of the method developed by Chester et al. [21], which is apparently a shorter and more simplified procedure than others, consisting of only three stages. The fractions of metals separated by the above method are applied to establish the distribution of metals between (i) "environmentally mobile", (1 mol/l NH_4Ac , pH 7.0); "bound to carbonates and oxides" (1 mol/l HAHCl with 25% acetic acid), and

(iii) “environmentally immobile – bound to silicates” (HNO_3/HF). Using this technique Chester et al. [21] showed that some trace metals (e.g. Al, Fe and Mn) had speciation signatures that were generally similar in both urban-rich and crust-rich aerosols, but others (e.g. Cu, Zn and Pb) had considerably higher fractions of their total concentrations in exchangeable associations in urban-rich samples. On the basis of their fractionation data, Chester et al. [21] introduced the concept of the “potential environmental mobility” for a trace metal in an aerosol, in which the exchangeable metals are the most mobile and those associated with the refractory fraction are the least mobile. This three stage sequential leaching procedure was also applied to the determination of the distribution of trace metals in filter-collected PM at two cities in Hungary [59] as well as in NIST 1648 Urban PM [68].

In some cases, extraction schemes have been developed and applied to only one metal. For example, a special chemical fractionation procedure was designed for nickel distribution in airborne dust, which apportions the airborne nickel species into four fractions: (1) “water soluble” (0.1 mol/l ammonium citrate), (2) “sulphidic” (H_2O_2 -citrate), (3) metallic” (bromine-methanol), and “oxidic” ($\text{HNO}_3/\text{HClO}_4$) [60]. Another study [63] reported a mild sequential extraction procedure for speciation of arsenic species in urban aerosol samples. The aerosols were collected by sequential filtration through membrane filters. Part of each filter was investigated by INAA for the total amount of As. Another part of the filters was treated by a sequential extraction procedure to differentiate between water-extractable, phosphate-extractable and refractory chemical form.

Water-soluble forms were further differentiated into anionic As species by HPLC-HGAFS.

Other strategies that have been employed involved single extraction with or without acidification. For example, Lindeberg and Harris [57] used selective extraction to determine water-soluble and acid-soluble Cd, Zn, Mn and Pb trace metals in PM collected at forested sites in PM of different particle sizes. It has been reported that a substantial fraction (around 50% or greater) of the acid leachable metals are soluble in water. This water-soluble fraction generally increased with decreasing particle size and with increasing frequency of atmospheric water vapour saturation during a sampling period. The pattern of relative solubilities ($Zn > Mn \cong Cd > Pb$) was similar to the general order of the thermodynamic solubilities of the most probable salts in continental aerosols with mixed fossil fuel and soil sources. In another study [64], simple and efficient extraction procedures using filtration with water and 0.1 mol/l HCl were recommended for obtaining information about the dissolution behaviours of various elements in airborne PM. The method was successfully applied to the characterization of $PM_{2.5}$ and $PM_{10-2.5}$ aerosols collected in Kofu City, Central Japan, and it was also proposed as a useful approach for the source apportionment studies.

Single extraction methods may be also developed with more physiological aspects in mind. Voutsas and Samara [69], for example, used a synthetic serum solution to determine the bioavailable fractions of Cd, Mn, Ni, Pb and Zn in

airborne particles collected at various urban and industrial sites in the Greater Thessaloniki area, N. Greece. Using the metal bioavailable fraction, daily respiratory uptakes of heavy metals were also calculated and compared with the literature data.

The extracted metals from each stage in a sequential extraction have usually been determined without further separation of species, using flame or/and graphite AAS or inductively coupled ICP-MS. Although these analytical techniques offer considerable applications in geosciences, problems and disadvantages connected with matrix, drift and interferences have to be controlled [70]. In addition, the use of spectroscopic detection methods can be problematic because of the small volumes of extracts obtained with the small PM sample sizes.

A possible alternative to these methods is to use separation techniques, such as high performance liquid chromatography (HPLC) or, as reported recently, capillary electrophoresis (CE). CE can perform fast and efficient separations of various species, and operates with simple instrumentation and very low running costs, making it a very attractive technique in the general sense [71, 72]. In the specific case of analyzing trace metals in extracts of airborne PM samples, CE is very advantageous because it requires only small volumes of sample, making it well suited for the analysis of very small volumes of extracts obtained from such small sample sizes of PM collected on filters. This use of only small volumes of extractants for small sample sizes is important in order to have extractant-to-mass ratios (typically about 40 to 50 ml/g), and therefore

extraction results, that are somewhat similar to those reported in the literature. Thus far there have been some examples of applications of CE to the determination of metals extracted from airborne PM. For instance, Fung et al. [66, 67] reported the use of CE for the determination of water-leachable and acid-leachable metal ions in airborne particulate matter. In another study, Dabek-Zlotorzynska et al. [68] investigated the feasibility of using CE for the determination of the distribution of selected metals in particulate matter after a three-stage sequential extraction procedure based on the Chester et al. [21] method. The developed analytical procedure was validated by applying it to a Standard Reference Material, NIST 1648 Urban Particulate Matter.

1.3 Capillary electrophoresis

1.3.1 Principles and theory

Electrophoresis is a technique that separates the components of a mixture based on the differences in the rates at which they migrate under the influence of an applied electric field. Originally, electrophoresis was carried out on a thin flat layer of a porous semisolid gel containing an aqueous buffer solution within its pores, and the analysis was carried out in a manner similar to that of thin-layer chromatography [73]. In capillary electrophoresis, this process takes place in a narrow bore fused silica capillary. The earliest precursor to CE dates back to the work of Hjerten in 1967, using a 3-mm inner diameter (ID) capillary that rotated along its longitudinal axis to minimize thermal convection gradients [74]. Later

developments, especially during the 1980s, lead to the use of smaller (sub-millimetre) ID capillaries without the need for rotation for heat dissipation [75]. The main components of a CE instrument are shown in Figure 2.

The inlet and outlet ends of the capillary are each inserted into separate reservoirs, which are filled with a background electrolyte (BGE) solution. Platinum electrodes, connected to a high-voltage power supply, are also inserted into the BGE reservoirs. The capillary is also filled with the BGE solution. For sample introduction, the inlet end of the capillary is inserted into a reservoir containing the sample solution and then placed into the inlet BGE reservoir. When a high dc potential is applied the analytes migrate through the capillary for eventual detection, which is typically optical detection through the capillary wall.

The capillaries used in CE are narrow bore fused silica capillaries, typically 25 to 100 μm ID and 40 to 100 cm in length. With such small diameters these capillaries have efficient heat dissipation, so band broadening due to thermal convective diffusion is minimized. The efficient heat dissipation also permits the use of high voltages (up to 30 kV), which makes for fast separations.

Figure 2. Basic components of a CE instrument.

1.3.1.1 Electrophoretic mobility and velocity

The movement (migration) of a charged species under the influence of an applied field is characterized by its electrophoresis mobility, μ_{ep} , which has units of $\text{cm}^2/\text{sec}\cdot\text{V}$

The electrophoretic mobility is expressed as:

$$\mu_{ep} = q / 6\pi\eta r \quad (1)$$

where q is the ionic charge, η is the viscosity of the medium, and r is the hydrated ionic radius of the analyte. Note that μ_{ep} is positive for cations, negative for anions, and zero for neutrals.

The electrophoretic velocity, v_{ep} , (that is the direction and speed of travel), in turn, depends upon the electrophoretic mobility and the electric field strength, E :

$$v_{ep} = \mu_{ep} E \quad (2)$$

From equation (1) it can be seen that ions have different electrophoretic mobilities due to differences in their charge to size ratios (q/r), and therefore, as equation (2) dictates, they migrate at different velocities.

The electric field strength is determined by the magnitude of the applied voltage, V , and the total length, L_t , of the capillary:

$$E = V/L_t \quad (3)$$

Combining equations (2) and (3), one obtains

$$v_{ep} = \mu_{ep} V/Lt \quad (4)$$

This relationship shows that higher voltages are desirable for achieving rapid separations because the electrophoretic velocities are more rapid.

1.3.1.2 Electroosmotic flow

Besides the electrophoretic mobilities of the analytes, there is another driving force that moves the analytes in CE. When a fused silica capillary is filled with an electrolyte solution and a voltage is applied, a process called electroosmotic flow (EOF) occurs, which is the migration of the electrolyte solvent in the capillary towards the cathode end. EOF results from the formation of an electric double layer at the inner surface of the capillary. When the pH is sufficiently high (above pH 3), the silanol groups of the fused silica capillary surface are ionized, and the capillary surface acquires a negative charge. This surface charge is referred to as the zeta potential. Cations in the BGE congregate at the negative surface in two layers: a compact inner layer and a diffuse outer layer. The cations of the diffuse outer layer are attracted toward the negative electrode and, because they are dissolved in solution, their movement drags along the bulk solution in the capillary (Figure 3(a)).

The velocity of EOF is expressed as

$$v_{eof} = \mu_{eof} \cdot E \quad (5)$$

where μ_{eof} is the electroosmotic mobility, which is a function of the zeta potential,

ζ , the dielectric constant, ϵ , and the viscosity of the electrolyte:

$$\mu_{\text{eof}} = \zeta \cdot \epsilon / \eta \quad (6)$$

The zeta potential is governed by the surface charge on the capillary, which in turn is strongly dependent on pH, so the velocity of the EOF varies with the pH of the BGE. As the pH increases so does the extent of ionization of the silanol groups, which translates to an increased zeta potential, and thus, a greater EOF velocity. The velocity of EOF also varies with the ionic strength of the BGE. Increased ionic strength results in the compression of the electric double layer, a decreased zeta potential, and a reduced EOF velocity.

The actual electrophoretic velocity of a solute in CE is a function of both the electrophoretic mobility of the solute and the electroosmotic mobility of the EOF. The expression for the actual electrophoretic velocity of a solute in CE is

$$v_{\text{act}} = (\mu_{\text{ep}} + \mu_{\text{eof}}) E \quad (7)$$

Since electrophoretic mobility is negative for anions, positive for cations, and zero for neutrals, in the absence of EOF anions would remain at the inlet end, neutrals would not migrate at all, and only cations would migrate past the detector to the outlet end (or the other way around if the polarity is reversed). The velocity of the EOF, however, is typically greater than those of the solute species, so it forces all species to migrate toward the outlet end (Figure 3 (b)).

Another important feature of the EOF is its relatively flat flow profile, as opposed to the gradient flow profile of hydrodynamically pumped systems such

as liquid chromatography. With a flat flow profile the velocity component exerted on the solute species by the EOF is the same throughout the cross section of the capillary. So, while the gradient flow profile contributes to band broadening the flat flow profile does not.

Figure 3. (a) Electroosmotic flow and migration of ions through the capillary; (b) net migration velocities of anions, neutrals, and cations in CE.

1.3.2 Operation modes of capillary electrophoresis

Based on different separation mechanisms, there are different operating modes of CE. The variety of methods encompassed by CE includes free solution capillary electrophoresis (FSCE), also called capillary zone electrophoresis (CZE), capillary gel electrophoresis (CGE), capillary isoelectric focusing (CIEF), capillary isotachopheresis (CITP), micellar electrokinetic capillary chromatography (MECC), and capillary electrochromatography (CEC). The mode of CE that is used depends on the nature of the analyte(s), and switching between different modes is more convenient than doing the equivalent in HPLC, because in CE this simply involves changing the BGE.

Capillary zone electrophoresis is the simplest and most commonly used operating mode of CE, and it was the mode that was used in this work. It can be used to separate almost all ionic compounds that are soluble in an electrolyte solution, such as small inorganic ions (including both anions and cations simultaneously), large biomolecules, and, when nonaqueous BGEs are used, water insoluble compounds. CZE operates by the principles described earlier, where the capillary is filled with a BGE, and separation of the analytes is effected by the different rates of migration due to their different electrophoretic mobilities. Neutral species are not separated from each other, and migrate at the same rate as the EOF (Figure 3(b)).

1.3.3 Detection techniques

Several different detection systems have been employed in CE, including photometric, fluorescence, electrochemical, and mass spectrometry (MS). Photometric detection (UV and UV/Visible) takes place on-capillary at a section of the capillary where the protective outer polyacrylamide coating is removed (the “detection window”). This form of detection is simple and it does not interfere with the electrophoretic process, making it a very attractive detection method in contrast to other methods. For this reason, UV-VIS absorbance detectors are still the most popular detection systems for CE, and are supplied with almost every commercial CE system. For analytes that absorb UV or visible light sufficiently, direct UV-VIS detection can be used. However, most inorganic ions are UV-transparent, and consequently, the vast majority of CE applications relating to environmental samples utilise indirect UV detection. In this approach, a highly absorbing co-ion (known as the visualizing reagent) is added to the BGE to create a large background absorbance signal. When the non-absorbing analytes are present, they displace the visualizing reagent, causing a decrease in absorbance as they pass by the detector. The resulting detector signal is a negative peak [76].

Alternatively, direct UV or visible light absorbance detection of UV/VIS-transparent ions can be accomplished by derivatisation of the analytes using a suitable chromophore prior to separation [71, 72, 76-78]. This was employed in this study and will be discussed in more detail below.

1.3.4 Capillary electrophoresis of metals

The separation of small metal ions is definitely an area where CE is gaining popularity [71, 72, 76-78]. Analysis of metals by CE often involves complexation with a complexing agent for one or both of two reasons: to enhance selectivity and/or to enable direct UV/VIS detection.

The distinctive feature of metal cations, metal-complexed ions and metal oxoanions is their high charge-to-size ratio and, hence, large electrophoretic mobility. In CE, this leads to rapid separations. However, inadequate selectivity is often encountered because, many metal cations are of nearly identical charge and hydrated ionic radius, so the differences in mobility are not great enough to provide sufficient separations. Special measures to circumvent this problem, to enhance the separation selectivity, typically involve selective complexation of the sample cations. This is basically achieved through the addition of a complexing reagent, either to the background electrolyte and/or to the sample, that complexes a group of metal cations, partially or completely, and provides them with much larger differences in electrophoretic mobility. In the former case, when the partial complexation is established within the capillary, it is the formation of metal complexes of different composition, and thereby an average effective charge, that allows for modulating the resolution in a broad range. The most commonly employed weak complexing agents are various carboxylic and hydroxycarboxylic acids, such as 2-hydroxyisobutyric acid (2-HIBA) [79], lactic acid [80], citric acid [81], oxalic acid [82], and tartaric acid [83]. In most cases,

indirect UV detection is used because significant amounts of the metals remain in uncomplexed (and therefore, non-UV-absorbing) form.

The other reason for using metal complexation in CE is to facilitate direct UV/VIS detection by complexing the otherwise non-absorbing metal ions with a ligand that absorbs UV or visible radiation strongly. This requires the use of strong complexing agents, so that the complexes that are formed will remain intact throughout the separation process until detection. The strong complexing agents that are used are typically organic ligands, such as 2,2'-bipyridine [84], 4-(2-pyridylazo)resorcinol (PAR) [85], ethylenediaminetetraacetic acid (EDTA) [86], and 8-hydroxyquinoline-5-sulphonic acid (HQS) [87]. Recently, another multi-dentate ligand, 1,10-phenanthroline (*o*-phen), has been successfully employed in the CE analysis of metals [67, 68, 84]. *o*-Phen has been shown to form strong, positively charged complexes with a large number of metals, and it has a strong chromophore that makes it well suited for direct UV detection [68].

1.4 Research objectives

This project was a continuation from the previous study [68] on the potential of using capillary electrophoresis in conjunction with sequential extraction schemes to estimate the distribution of metals in an airborne particulate matter. In this study, a three-stage sequential extraction procedure following the BCR protocol was selected [48]. The first objective of this research was to optimize and validate the CE procedure, including detection sensitivity, for measuring trace metal concentrations in the presence of the BCR extractants.

Since the extraction procedure is quite lengthy (51 hours), the second goal of the present work was to speed up the conventional BCR sequential extraction scheme, and thereby improve sample throughput, by using sonication in an ultrasonic bath instead of mechanical stirring, as is done in the conventional BCR method. Acceleration of metal fractionation by means of ultrasound has been reported as a useful alternative to the conventional BCR procedure [88].

The proposed combination of the BCR sequential extraction and CE analysis method was evaluated using a Standard Reference Material, NIST 1648 Urban Air PM. The method was eventually also tested on real samples of filter-collected airborne PM_{2.5} from two source types, urban air and a highway tunnel.

2 EXPERIMENTAL

2.1 Instrumentation

The CE system used in this work was a Beckman P/ACE 5510 (Fullerton, CA, USA). It was equipped with a high voltage power supply (-30 kV to +30 kV), a diode array detector (DAD), and an autosampler. Polymicro (Phoenix, AZ, USA) fused silica capillaries with an inner diameter of 75 μm , an outer diameter of 366 μm and a total length of 57 cm (50 cm to the detection window) were used. The capillary temperature was maintained at 30.0 ± 0.1 $^{\circ}\text{C}$ by means of a fluorocarbon liquid being continuously circulated through the cartridge. A GOLD software station was used to acquire data and control operating variables.

For the BGE and rinsing solutions 4-ml glass vials were used, while analyte solutions were put into polypropylene micro-vials (500 μl), which were held up in the 4-ml vials with a spring.

All weighings were made with a Mettler AT400 analytical balance (Mettler-Toledo Inc., Highstown, NJ). Measurements of pH were made with a Radiometer-Copenhagen PHM93 pH meter (Radiometer-Copenhagen, Copenhagen, Denmark).

For some metal extractions, as well as any heating/evaporation steps, a Reacti-Therm III^{TM} Heating/Stirring Module (Pierce, Rockford, IL, USA) was used. For other extractions and for degassing, an ultrasonication bath at 43 KHz

(Fisher Scientific, Ottawa, ON, Canada) was used. Mechanical shaking for the water rinsing between extraction steps was done with a Thermolyne Type 51399 Roto Mix mechanical horizontal shaker (Canadawide Scientific, Ottawa, ON, Canada) at a speed of 200 rpm. Centrifugation was carried out at 6000 rpm in a microcentrifuge (Cole-Parmer Instrument Co., Vernon Hills, IL, USA).

The total contents of metals and other elements in filter-collected PM samples were determined by X-ray fluorescence (Kevex Analyst 770 and EDX 771, Kevex, Redwood City, CA). Water-soluble inorganic anions and cations were determined by a Multi (3) Ion Chromatography System (Dionex, Sunnyvale, CA, USA).

AAS analyses were done on either a Varian Zeeman SpectrAA 880 Graphite Furnace AAS (Varian Canada) or a Perkin Elmer 3100 Flame AAS (Perkin Elmer).

2.2 Chemicals and reagents

Metal standards and the Standard Reference Material, NIST 1648 Urban Particulate Matter, were purchased from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA).

Table 1 shows the certified contents of the NIST 1648 PM used in this work. All other reagents were purchased from either Sigma-Aldrich (Oakville, ON, Canada) or Fisher Scientific (Ottawa, ON, Canada) in the highest purity form available and used without further purification. Deionized water (18 M Ω /cm) was

used for the preparation of all solutions, background electrolytes and standards.

Table 1. Certified content of the studied metals and some other elements in the NIST 1648 Urban PM Standard Reference Material.

Element	Total certified content [%]	Element	Total certified content ($\mu\text{g/g}$)
S	5.0 *	Fe	39100 ± 1000
Mg	0.8 *	Zn	4760 ± 140
Cl	0.45 *	Cu	609 ± 27
K	1.05 ± 0.01	Mn	786 ± 17
Na	0.425 ± 0.002	Cd	75 ± 7

* Contents of these elements are not certified

2.3 Airborne PM samples

In the present work two sets of filter-collected fine airborne PM were used. The first set included samples collected at different urban sites by the Canadian NAPS (National Air Pollution Surveillance) air quality-monitoring network [89]. The second set of samples was selected from the Cassiar Tunnel study [90]. For the purpose of testing out the extraction and CE method studied in this work on some real PM samples, the samples were selected based on the PM mass and metal content on the filters. As such, seven samples of urban PM (from the

NAPS sites) and six samples from the Tunnel Study were selected.

2.3.1 NAPS samples

Samples were collected over 24-hour sampling periods on a six-day sampling schedule using a dichotomous sampler (Graseby Andreson G241). These devices size-fractionate the particles by means of virtual impaction into a fine ($< 2.5\text{-}\mu\text{m}$) and a coarse ($2.5\text{-}10\text{ }\mu\text{m}$) fraction. Larger particles were excluded by an appropriate aerosol inlet. The samplers were operated at a total flow rate of 16.7 l/min . Particles were collected on Teflon discs (37-mm diameter) with a polyethylene support ring using the dichotomous samplers. The samples that were selected for this work, along with the sampling dates and locations, are listed in Table 2.

Table 2. Site locations and collection dates for urban $\text{PM}_{2.5}$ samples from the NAPS network

City	Location	Site Type	Sampling Date
Calgary	611-4th Street S.W.	Commercial (C)	Jan-2-02
Winnipeg	65 Ellen Street	Commercial (C)	Oct-22-01
Québec City	600 Rue Des Sables	Industrial (I)	Nov-15-01
Toronto	Evans & Arnold Ave	Industrial (I)	Nov-2-00
Toronto-2	Judson	Residential (R)	Aug-23-01
Montréal	7650 Rue Châteauneuf	Residential (R)	Oct-10-01
Montréal-2	11111 Notre-Dame Est	Residential (R)	Aug-23-01

2.3.2 The Cassiar Tunnel Study samples

The Cassiar Tunnel is a twin-bore tunnel (a southbound bore and a northbound bore), located on the TransCanada Highway on the eastern border of the City of Vancouver, B.C. The tunnel is approximately 750 m long, 7 m high, and each bore is about 14 m wide. The two bores are completely separated by a wall. They are also ventilated, independently of each other, by roof mounted turbine fans that direct flow along the tunnel axis in the same direction as traffic. Only the northbound bore was used for the collection of samples in the study. To reduce dilution, the fans in the northbound bore were turned off during the sampling periods, so the only ventilation in the northbound bore during sampling periods was from the effect of the traffic moving through the tunnel. Traffic flow in the northbound bore was from south (inlet) to north (outlet).

PM samples were collected on Teflon filters (47-mm diameter) at the inlet end and at the outlet end of the tunnel using URG cyclones and filter packs [90]. Sample collection at the inlet end was done at the control room access hatch, situated over the northbound bore, 220 m from the inlet, and about 1 m from the inside separation wall. Sample collection at the outlet end was done at the very end of the tunnel, about 1 m down from the tunnel roof. The PM samples were collected at sampling periods of three hours each, three times a day, for seven consecutive days starting on Thursday, August 9th, 2002. Sample collection was conducted during periods representative of different traffic patterns – morning rush (06:30-9:30), mid-day (11:00-14:00), and afternoon rush (15:30-18:30).

Five weekday and two weekend days were sampled in total.

2.4 Procedures

2.4.1 Conventional and accelerated BCR extraction procedures

2.4.1.1 NIST 1648 PM Standard Reference Material

In the accelerated BCR extraction method, ultrasonication in an ultrasound bath was used for the extractions in place of the mechanical stirring used in the conventional BCR procedure. The temperature of the bath was controlled by means of ice packs, placed in the bath during ultrasonication, and monitored with a temperature probe. In the description of the extraction procedures given below, the extraction time in each step for stirring was the time used in the original BCR method, while the extraction time for ultrasonication was determined in this work from experiments to select the optimum ultrasonication extraction time.

For all work done with the NIST 1648 PM, a portion of the bulk material was taken and placed on a Teflon surface to be dried overnight in an oven at 105 °C. Extractions were performed on 0.01 g samples of the dried NIST 1648 PM, and carried out in 2-ml polypropylene centrifuge tubes, which were also used for centrifugation to minimize possible loss of sample in the centrifuge-washing steps.

The sequential leaching experiments were carried as follows:

Step 1 (Fraction F1: water & acid soluble phase associated with soluble salts and carbonates): To each vial (including blanks), 100 μ l isopropanol and then 1 ml of 0.11 mol/l acetic acid (E1) were added. Extractions took place at room temperature, by either magnetic stirring for 16 h or ultrasonication for 15 min. Then the vials were centrifuged at 6000 rpm for 15 min, and the supernant liquid was removed with a clean, dry pipette, taking care not to remove any of the solid residue, and transferred to another clean, dry polypropylene vial. The residue was then washed by adding 0.5 ml of deionised water and shaking continuously, on a mechanical shaker, for 15 min. The vials were centrifuged as above, and the supernant liquid was removed by pipette and discarded.

Step 2 (Fraction F2: reducible phase associated with oxides): 1 ml of 0.1 mol/l HAHCl (E2), adjusted to pH 2 with HNO₃ was added to the residue (and blanks) from step 1. The extractions were then carried out as above with either 16 h of magnetic stirring or 45 min of ultrasonication, followed by centrifuging to remove the liquid, and subsequent water-washing and centrifugation.

Step 3 (Fraction F3: oxidisable phase associated with organic matter and sulphides): For the conventional BCR (stirring) method, 0.5 ml of 8.8 mol/l H₂O₂ was carefully added to the residue from step 2. The vials were left, with occasional manual shaking, at room temperature for 1 h with covers just partially closed (to allow gas to escape and avoid bursting). Then, they were heated at 85 °C in a heating apparatus (temperature monitored by a probe in a separate vial

filled with water), with covers just partially closed, for 1 h, with occasional manual shaking. With the vial caps completely open, the liquid was evaporated to one half of its volume. After cooling, another 0.5 ml aliquot of 8.8 mol/l H_2O_2 was carefully added. The vials were partially covered and heated at 85 °C for 1 h with occasional manual shaking, and then evaporated (completely uncovered) to near dryness. After cooling, 1 ml of 1 mol/l NH_4Ac (E3) adjusted to pH 2 with HNO_3 was added, and the mixtures were stirred for 16 h at room temperature. Separation by centrifugation to obtain the liquid was performed as described above.

In Step 3 for the accelerated BCR (ultrasonication) method, 0.5 ml of 8.8 mol/l H_2O_2 was carefully added to the residue from step 2. The vials were then ultrasonicated, at room temperature, for 2 min. The liquid was evaporated in the heating apparatus, as in the conventional method, to one half its volume. After cooling, another 0.5 ml of 8.8 mol/l H_2O_2 was added to the vials, followed by 2 min of ultrasonication at room temperature. The vials were then evaporated to near dryness. After cooling, 1 ml of 1 mol/l NH_4Ac adjusted to pH 2 with HNO_3 was added, and the mixtures were ultrasonicated for 60 min at room temperature. Separation (by centrifugation) was performed as described above.

The details of the conventional and accelerated BCR sequential extraction procedures are summarized in Table 3. Unless otherwise stated, the sequential extractions were performed in triplicate. With each batch of extractions, a blank (i.e., a vessel with no sample) was carried out through the complete procedures

in the same manner as the samples.

Table 3. Operating conditions used in the conventional and the accelerated BCR sequential extraction procedure

Step	Fraction description	Chemical reagents and conditions	Extraction time and temperature
1	Water and acid soluble (F1)	1 ml 0.11 mol/l acetic acid (E1)	a) 16 h at 25 °C b) 15 min at 25 °C
2	Reducible (F2)	1 ml 0.1 mol/l HAHCl adjusted to pH 2 with HNO ₃ (E2)	a) 16 h at 25 °C b) 45 min at 25 °C
3	Oxidisable (F3)	1) 0.5 ml 8.8 mol/l H ₂ O ₂ , then evaporation (2 times)	a) 1 h at 25 °C + 1 h at 85 °C; 1 h at 85 °C b) 2 min at 25 °C; 2 min at 25 °C
		2) 1 ml 1 mol/l NH ₄ Ac adjusted to pH 2 with HNO ₃ (E3)	a) 16 h at 25 °C b) 60 min at 25 °C

a) conventional extraction with magnetic stirring; b) accelerated extraction with ultrasonication

Metal recovery (%) was defined as the ratio: (metal content using accelerated extraction) / (metal content using the conventional BCR extraction) x 100. It should be clarified that the goal of this study was not to enhance the extraction efficiency of the conventional extraction method but rather to find ultrasonication extraction conditions that yield similar extractable metal contents within shorter treatment time.

In addition, the accelerated BCR extraction scheme was eventually modified by the inclusion of an extraction step using deionized water and 30 min of ultrasonication before the original first extraction step with 0.11 mol/l acetic acid. This modification was made in order to follow the same analysis steps employed in the AAQD inorganic lab for filter-collected PM samples, which will be explained in greater detail later on.

2.4.2 Chemical analysis of airborne PM

All samples were handled according to established operating guidelines used in the Inorganic Laboratory of the Analysis and Air Quality Division (AAQD) of Environmental Technology Centre (ETC), Environment Canada (Figure 4).

The Teflon filters were weighed before and after sample collection using a Mettler 5 Microbalance (MT-5, Mettler-Toledo Inc., Highstown, NJ), under controlled relative humidity (e.g., 40-45%) and temperature (e.g., 22-24 °C) conditions. At the end of each sampling, filters were stored in the controlled humidity and temperature room for 24 h prior to weighing in order to ensure removal of particle-bound water.

After weighing, the Teflon filters were analyzed by XRF [91] to determine the total concentrations of particle-bound trace elements and metals. Water extraction and ion chromatography were then used to analyze for water-soluble ions. The water extraction was done by first wetting the whole filter with 100 µl of isopropanol (to enable contact between the water and the hydrophobic PM), and then extracting with 10 ml of deionized water with ultrasonication for 30 min [92].

The aqueous extracts from the Tunnel Study PM were also analyzed for water-soluble organic acids by another CE method [93].

Figure 4. Flow chart outlining the different analysis steps performed by the AAQD on filter-collected PM_{2.5} samples.

2.4.2.1 Filter-collected airborne PM_{2.5}

Elements on the filters were first extracted with water for IC analysis, as described above (Section 2.4.2). A portion of the aqueous extract was then carefully transferred to a second, acid-cleaned polystyrene tube using an auto pipette, for subsequent analysis of water-soluble metals by the CE method used in this work. The filters were next placed into acid-cleaned 2-ml polypropylene vials and the metals were sequentially extracted using the accelerated BCR leaching scheme. In order to fit the filters into extraction vials, the rigid outer ring was removed by placing the filter on a clean surface, and cutting around the perimeter with a clean, stainless steel scalpel. At all times the filters were handled with clean Teflon tweezers.

Method blanks (unexposed filters) were also carried through each step of the sequential extraction procedure at the same time and in the same way as the samples were. The method blanks were, therefore, blanks for reagent, vials, and filters. The blank values were subtracted from the concentrations of the corresponding metals in the samples.

2.4.3 Cleaning of labware

All glasswares were cleaned after use by rinsing with deionised water, soaking overnight in approximately 10% HNO₃, and then rinsing several times with deionised water. Glass CE vials were air-dried before the next use, and volumetric flasks and reagent bottles were filled with deionised water and capped for storage until next use. Polypropylene items (CE micro-vials, 2-ml centrifuge

vials, and transfer pipettes) were all washed before use by soaking in approximately 10% HNO₃, then rinsing several times with deionised water, and then were allowed to air-dry. These were disposed of after a single use.

2.4.4 Capillary electrophoresis analysis

The CE procedure has been described previously [68] and is only summarized briefly here. The method uses pre-capillary complexation with *o*-phen, followed by direct UV detection at 226 nm for simultaneous quantification of the studied metals. The BGE consisted of 200 mmol/l NH₄Ac (pH 5.5), 0.5 mmol/l *o*-phen, 10 mmol/l HAHCl and 20% acetone. The addition of a small amount of *o*-phen to the BGE prevents the dissociation of metal complexes during CE analysis. The HAHCl was added to the BGE to provide a more transparent background to enhance sensitivity, and to create a reducing environment to convert Fe(III) to Fe(II), as is necessary for *o*-phen complexation (the Fe(II)-*o*-phen complex had an intense red colouration, whereas the Fe(III)-*o*-phen complex is almost colourless). Acetone was added in order to improve the resolution between Cu(II) and Mn(II) ions. The complete set of CE separation conditions are shown in Table 4.

Table 4. CE operating conditions

Parameter	Conditions
Background electrolyte	200 mmol/l NH ₄ Ac (pH 5.5 with acetic acid), 0.5 mmol/l <i>o</i> -phen, 10 mmol/l HAHCl, and 20% acetone
Separation mode	Constant voltage, + 14 kV
Hydrodynamic injection	0.5 p.s.i (70 mbar) for 10 s
Electrokinetic injection	5 kV for 45 or 20 s
Capillary treatment	New capillaries: washed with methanol (10 min), followed by water (1 min), 0.5 mol/l NaOH (10 min), 0.1 mol/l NaOH (5 min), water (1 min), and finally conditioned with BGE for 20 min. For routine use: every morning the capillary was washed with 0.1 mol/l NaOH (5 min), water (2 min), and BGE (20 min). Between injections: rinsed with BGE (1 min) At the day's end: rinsed with 0.1 mol/l NaOH (5 min) followed by water (5 min).

2.4.4.1 Preparation of BGE

The BGE solution was prepared daily from stock solutions of 500 mmol/l NH₄Ac adjusted to pH 5.5 with 1 mol/l acetic acid, 100 mmol/l HAHCl, 10 mmol/l *o*-phen, and acetone. The BGE was filtered through a 0.45 µm membrane filter and degassed by ultrasonication (20 min) before use [68].

2.4.4.2 Pre-capillary derivatization of metal ions

All mixtures of metal standard solutions were prepared by diluting appropriate volumes of the single metal stock standard solutions (200 mg/l).

For quantitative analysis of metals in the extracts obtained from the BCR sequential extractions (Table 3), the samples were prepared in the presence of 2 mmol/l HAHCl (F1 and F3) and 2 mmol/l α -phen. The preparation of F2 extracts for CE analysis did not require the addition of the HAHCl because it was already present as the extractant (E2). In preparing the samples for CE analysis, the F1 and F2 extracts were diluted two-fold (or more as required if the metal concentrations were very high), while the extracts of F3 samples were diluted 20 times. The reagent blanks without metals and the metal standard solutions that were used for making analytical calibration curves were prepared in the same manner (including the same extractant concentration) as the samples. Once prepared, all samples were allowed to stand for at least 15 min before injection.

2.4.5 Method validation procedures

2.4.5.1 Calculation of Limit of Detection (LOD)

The concentration-based limits of detection (LODs) were determined by analyzing dilute solutions of metal standards, prepared in the presence of matrix extractants. At least seven replicate analyses were performed on a sample containing the metals at concentrations about ten times higher than their respective estimated detection limits (or the concentration giving a signal-to-

noise ratio of 3). LODs were then calculated as:

$$C_{\text{LOD}} = st_{n-1} \quad (8)$$

where s is the standard deviation of the calculated concentrations and t_{n-1} is the t-statistic (one-sided), at the 99% confidence level with $n-1$ degrees of freedom [94]. Note that the standards for LOD experiments were prepared in diluted matrices, 2-fold (E1, E2) and 20-fold (E3).

2.4.5.2 Analytical calibration curves

External calibration was used as the calibration strategy for all CE analyses. For each stage in the sequential extraction, multi-element calibration standards were prepared in the same matrix as samples (appropriately diluted extractants), and run on the same day as the unknowns. Quantitative results were obtained using corrected peak area (CPA = peak area/migration time).

2.4.5.3 Accuracy

To verify the results quantified by CE, analyses of some samples using AAS and/or IC methods were performed. A quantitative difference between CE and AAS methods for studied metals was calculated in terms of the relative percentage difference (RPD) between results as follows:

$$\text{RPD (\%)} = 100 (X_{\text{CE}} - X_{\text{AAS}})/0.5 (X_{\text{CE}} + X_{\text{AAS}}) \quad (9)$$

where X_{CE} and X_{AAS} were the measurements of metal cation concentrations of the same filter extracts using CE and AAS, respectively. In addition, linear regression was used for the comparison of analysis by CE and IC methods.

3 RESULTS AND DISCUSSION

3.1 Optimization of CE operational parameters

As mentioned in Chapter 1, the first goal of this work was to evaluate the previously developed CE method [68] for the determination of Fe, Cu, Zn, Mn and Cd ions in the presence of each extractant used in the BCR leaching scheme. Thus, in the first stage of this work the suitable CE experimental conditions, including detection sensitivity, for measuring trace metals in the BCR extracts were optimized.

It is well known that detection limits and precision in CE depend on the injection mode that is used, and accordingly, this was one of the aspects investigated for optimizing the CE method. In addition to this, the effects of the sample matrix (extractants) on the performance of the CE method must also be considered. A major problem that arises in CE with samples from extraction media is that the high ionic strength of the solutions generates distorted peak shapes for the analytes and usually results in degraded separation performance [95]. Moreover, it is far more challenging to develop a CE methodology that works well for the determination of trace-level ions in samples in which the metal concentrations are often very unevenly distributed. Thus, in order to achieve the best possible combination of separation efficiency and sensitivity, the performance of the CE method for separating the studied metals in each BCR extractant was assessed and optimized. Standard metal solutions prepared in

water (E0) and each of the BCR leaching solutions (E1, E2, E3) were used to evaluate the effect of sample matrix (extractant) on the resolution and sensitivity of the analysis.

3.1.1 Selection of injection mode and conditions

Injection conditions are important for the separation and sensitivity of analysis in CE. If the sample volume that is loaded onto the capillary is too high, it will cause sample overloading, resulting in serious peak distortion and a decrease in resolution. Conversely, a loaded sample volume that is too small will cause difficulty with detection. Therefore, the best injection conditions involve a compromise between resolution and detectability.

In order to obtain the optimum sensitivity, two injection modes, hydrodynamic and electrokinetic (EK), were investigated. The initial tests were done using standard solutions prepared in water at two concentration levels (100 µg/l and 1 mg/l using EK and pressure injection, respectively).

3.1.1.1 Hydrodynamic (pressure) injection

In this injection mode, the amount of sample that is loaded is nearly independent of sample matrix effects, but does depend on the capillary dimensions, the BGE and sample viscosity, the applied pressure, and the duration of injection. However, it is limited in that increasing the sample size by more than a few percent of the capillary volume causes sample overload, which results in broad and distorted peaks [96].

Based on previously reported results [68], up to 10 s of hydrodynamic injection using a pressure of 0.5 p.s.i. (70 mbar) could be used without any major deterioration in the resolution.

3.1.1.2 Electrokinetic injection

As expected, higher sensitivities were obtained using EK injection mode. With EK injection the sample is introduced electrophoretically by applying voltage. Because the electrophoretic separation process occurs during injection, larger amounts of sample can be injected before losses in separation efficiency and resolution are seen [97]. The main advantage of this injection mode is that, without modifying the instrument, preconcentration of the sample can be obtained as a result of the sample stacking that takes place. It should, however, be remembered that the amount of analyte that is introduced into the capillary during the EK injection depends on the EOF, the conductivity and viscosity of the BGE and the sample, the applied time and voltage level, and the electrophoretic mobilities of the analytes [98]. Thus, injection bias exists, with the more mobile species being loaded to a greater extent. Furthermore, the sensitivity (amount injected) generally suffers with increasing sample conductivity; at high conductivities less sample is injected and, therefore, the LOD increases. These problems can, however, be dealt with by employing the internal standard (IS) procedure and/or by preparing the calibration standards in the same matrix concentration as that of the sample. Both of these measures were used in this study (for the IS, imidazole was used).

In order to optimize the signal response with EK injection, the effects of injection time (5-90 s) and injection voltage (2-10 kV) on both peak height and corrected peak area, as well as resolution, were investigated. First, the effect of injection time was evaluated. Figure 5 presents the relationship between the injection time and the peak height (Figure 5 (a)) and corrected peak area (CPA = peak area / migration time) (Figure 5 (b)) using injection at 5 kV for Fe, Zn and Cd as representative metal ions. As can be seen, both responses increase, although differently, with the injection time. A point can be made here about the use of peak height and peak area, and in particular, corrected peak area. Differences in the sample concentrations mean differences in the conductivity of the sample, and consequently, differences in the degree of stacking of the analyte zones. Greater sample stacking gives rise to sharper, higher peaks and vice versa. This means that peak height will not increase linearly with sample concentration, and this effect is visible in Figure 5 (a). With peak area, as it measures the overall peak size and not just the height, this does not happen. As a result peak area increases in a linearly with sample concentration. Corrected peak area (CPA) is the peak area corrected for migration time, which accounts for differences in the mobilities of the analytes. With the exception of Figure 5 (a), all of the peak measurements for the CE results were based on CPA.

Figure 5. Effect of injected sample size using different injection times on (a) peak height and (b) corrected peak area for selected metal cations at 100 $\mu\text{g/l}$ each, using EK injection at 5 kV.

The injection voltage also has an influence on peak response since the higher the voltage the greater the amount of analytes introduced into the capillary. As can be seen in Figure 6, with 45 s for the injection time, a pronounced improvement in the detection sensitivity was seen up to 5 kV of injection voltage, after which a continued increase in peak size took place at the expense of resolution (especially between Fe and Zn which migrate so closely together). On the basis of these results, the best combination, according to the resolution parameters and response sensitivity, was 5 kV for 45 s. A sample electropherogram showing the separation of metal standards with these EK injection conditions is given in Figure 7.

One must keep in mind that these optimum conditions were for samples containing only analytes in reagent water. In this scenario, sample loading apparently reached a steady state at 45 s so that any additional increase in the loading time only degraded the separation as space charge and diffusion limitations start to dominate. It was expected that samples with higher ionic strengths would probably reach this steady state at a shorter injection time since the degree of sample stacking would be reduced (because there is less difference between sample and BGE conductivities). This will be addressed in the next section.

Figure 6. Effect of the size of injected sample with different injection voltages on (a) CPA for metal cations and (b) Fe-Zn resolution, at 100 $\mu\text{g/l}$ each, with an EK injection time of 45 s.

Figure 7. A typical electropherogram for a mixture of metal standards, dissolved in water at 100 $\mu\text{g/l}$ each, with EK injection (5 kV, 45 s). CE conditions are as given in Table 4.

3.1.2 Matrix effect and sensitivity strategies

The separation efficiency and the amount injected (especially with EK injection) are influenced by the difference in conductivity between the sample and BGE, as this affects the degree of sample stacking. Samples obtained from the BCR sequential extractions inevitably contained high ionic strength extracts, especially in the third fraction with the 1 mol/l NH_4Ac . Although a BGE with high conductivity was used, it might have been necessary in addition to dilute the samples in order to have sufficient difference between the conductivity of samples and that of the BGE. Having to dilute samples will, of course, make for poorer detection, but there will also be a simultaneous improvement in detection because of the increased stacking effect during injection. If the magnitude of this increase due to stacking were greater than that of the decrease due to dilution, then it would be beneficial to dilute the samples.

Thus, in the subsequent experiments, the effect of matrix concentration on separation efficiency and sensitivity was investigated under optimized injection conditions. Although it was expected that the samples with higher ionic strengths would require shorter injection times for adequate resolution, it was found that samples dissolved in 0.11 mol/l acetic acid (E1) and 0.1 mol/l HAHCl , pH 2 (E2) were separated effectively with the optimized EK injection conditions (5 kV for 45 s) after just 2-fold dilution. Note that all samples prepared for CE analysis in this method were diluted by a factor of at least 2, simply because of the addition of the reagents for pre-capillary metal complexation. On the other hand, samples

dissolved in 1 mol/l NH_4Ac at pH 2 (E3) required at least ten-fold dilution, with pressure injections at 10 s, in order to obtain an acceptable compromise between efficiency and sensitivity of the separation. For EK injection to be used, a higher dilution factor (at least 100-fold) was required.

In the following experiments the EK injection mode was used for the analysis of the studied metals in water (E0), E1, and E2 matrices. With the E1 and E2 extractants, increasing the dilution factor (to increase the degree of sample stacking) did result in notable increases in CPAs. However, in neither case were these increases greater than the decreases than would occur due to sample dilution. Thus, for both E1 and E2, the minimum dilution factor (2-fold) was chosen for optimum sensitivity. Samples in the presence of the high ionic strength E3 solution (1 mol/l NH_4Ac , pH 2) required 20-fold dilution and the use of pressure injection, rather than EK injection. It should be noted that, in cases where the metal concentrations were very high in the actual extracts of samples (especially in the NIST 1648 PM), the samples were diluted accordingly to fit within the range of the analytical calibration curves. In such cases the standards used for external calibration were also prepared with matching matrix (extractant) concentrations.

3.1.3 Analytical Figures of Merit of the CE method

After optimization of injection conditions with the pressure and EK injection modes, the analytical characteristics of the method were investigated. The parameters evaluated were precision, linearity, detection limits and accuracy.

3.1.3.1 Precision

The precision of the method was evaluated in terms of repeatability (same day) and assessed as the relative standard deviation (RSD). Seven replicate injections of standard solutions at concentration of 100 µg/l (E0, E1, E2) and 1 mg/l (E3), made in the presence of the appropriate matrix, were used for the repeatability study. Imidazole was used as an internal standard (IS). However, it turned out that the use of the internal standard did not substantially improve the within-day precision of CPA measurements for either injection mode (data not shown). As can be seen in Table 5, both injection modes gave excellent precision of migration time with the relative standard deviation generally being less than 0.4% in E0, E2 and E3 matrices. Slightly poorer, but still adequate, migration time precision (RSD < 0.9%) was obtained in the E1 matrix. As expected, the relative migration time (RMT) precision was better for both injection modes (RSD < 0.2%) in each matrix. The precision of the CPA in all matrices is also good with RSDs generally being less than 5% for both injection modes.

3.1.3.2 Linearity

Calibration plots established from nine concentration levels of mixed standards, prepared in water (E0), 2-fold diluted E1 and E2 (using EK injection) and 20-fold diluted E3 (using pressure injection) showed good linearity in the investigated concentration range (0.01-1.5 mg/l and 0.1-2 mg/l, respectively, for EK and pressure injection) (Table 5). The linear correlation coefficients varied

Table 5. The performance of the CE method under the optimized conditions

Metal Ion	Extractant	Precision (RSD %)			Slope (CPA/ $\mu\text{g/l}$)	R^2	LOD ($\mu\text{g/l}$)
		Mt	RMT	CPA			
Fe (II)	E0	0.2	0.1	2.1	381	0.9991	0.9
	E1	0.7	0.04	0.9	145	0.9998	0.7
	E2	0.3	0.08	1.9	23.0	0.9996	11
	E3	0.06	0.07	2.1	6.70	0.9995	25
Zn (II)	E0	0.2	0.1	2.5	518	0.9996	0.4
	E1	0.7	0.05	1.0	156	0.9998	0.8
	E2	0.3	0.07	2.1	25.2	0.9990	12
	E3	0.06	0.07	2.2	6.92	0.9987	25
Cu(II)	E0	0.2	0.1	1.0	510	0.9993	1.6
	E1	0.7	0.1	1.0	166	0.9999	1.0
	E2	0.3	0.02	1.2	24.7	0.9994	3.2
	E3	0.08	0.06	2.9	6.87	0.9997	26
Mn(II)	E0	0.2	0.1	3.0	252	0.9990	2.4
	E1	0.8	0.2	1.0	97.0	0.9996	1.6
	E2	0.4	0.06	2.2	14.1	0.9997	7.0
	E3	0.1	0.03	4.8	3.17	0.9993	76
Cd(II)	E0	0.2	0.1	4.3	294	0.9992	3.4
	E1	0.9	0.2	2.2	92.3	0.9996	3.2
	E2	0.4	0.07	1.8	12.3	0.9992	11
	E3	0.1	0.03	3.7	3.32	0.9987	66

MT = migration time, RMT = relative migration time, CPA = corrected peak area

from 0.9990 to 0.9999 and from 0.9987 to 0.9995 for calibration using EK injection and pressure injection, respectively. Examples of the calibration curves are shown in Figure 8. Each point on the calibration graph corresponded to the mean value obtained from two independent CPA measurements.

Since, for each sample matrix, a separate set of calibration standards was prepared in the same diluted matrix as samples, the use of IS was not necessary to compensate for the matrix effects. Thus, external calibration was used with both injection modes.

(Continued on the following page)

Figure 8. Calibration graphs for metal standards prepared in: water, 2-fold diluted E1 (55 mmol/l acetic acid), 2-fold diluted E2 (50 mmol/l HAHCl), 20-fold diluted E3 (50 mmol/l NH_4Ac , pH2 with HNO_3).

3.1.3.3 Sensitivity and limit of detection

The sensitivity, defined as the corrected peak area (CPA) per unit concentration (i.e., the slopes of analytical calibration curves), differs, not only for the different metals, but also in the different matrices (Table 5 and Figure 8). As described earlier, this is due to differences in the ionic strengths of the matrices as it affects the degree of sample stacking that takes place. The best sensitivity was obtained for metals dissolved in water (E0), followed by metals dissolved in 2-fold diluted acetic acid (E1) and HAHCl (E2). As expected, the poorest sensitivity was obtained for metals dissolved in 20-fold diluted E3 with pressure injection.

The LODs were determined for all studied metals in each matrix under the optimized injection conditions (Table 5). Note that the standards for LOD experiments were prepared in 2-fold (E1, E2) and 20-fold (E3) diluted matrix. With EK injection (5 kV for 45 s) the Limits of Detection (LOD) were below 4 µg/l and 12 µg/l in E1 and E2 matrices, respectively, for the different metals under study. However, as expected, LODs obtained by applying pressure injection (0.5 p.s.i. for 10 s) were higher than those obtained by EK method, and ranged from 25 to 66 µg/l.

One must bear in mind that the LOD, the linear range and the linear coefficient are dependent on the conductivities of the injection solutions. A higher conductivity results in a higher LOD (a smaller stacking effect), a wider linear range and a smaller linear coefficient.

3.1.3.4 Accuracy

In order to assess the accuracy of the proposed CE methodology, the concentrations of the representative metals in three bulk fractions from BCR extractions of NIST 1648 PM (F1, F2, F3) were determined in parallel by CE and either by graphite furnace atomic absorption spectrometry (GFAAS) or by flame atomic absorption spectrometry (FAAS). Because of the small volumes of sample extracts that were available from such small-scale extractions, bulk sample solutions for the AAS analyses were prepared by combining the extracts obtained from triplicate extractions. Analyses with AAS were performed under standard conditions for each element using the standard addition method for GFAAS or external calibration for FAAS. Table 6 presents the results obtained by CE and AAS. Correlation between the two sets of data was found to be quite good. Using the matched pair t-test method [99], no significant difference was found at the 95% confidence level between the results obtained by CE and GFAAS or FAAS. In general, quantitative deviations between these methods for metals calculated in terms of the relative percentage difference (RPD) between results were found to be less than $\pm 10\%$. Worse results were, however, obtained in cases where metals were present at low concentrations, particularly Cd, which was present at very low concentrations (around 10 times the LOD).

Table 6. Comparison of CE and AAS results of the determination of the studied metal ions in BCR extracts of NIST 1648 PM

Ion (Fraction)	Concentration (mg/l)		RPD (%)
	CE	AAS	
Fe (F2)	80.4	74.5	7.6
Fe (F3)	27.0	29.2	-7.8
Zn (F1)	24.5	26.2	-6.7
Cu (F3)	1.6	1.5	6.5
Mn (F2)	1.2	1.0	18.2
Cd (F1)	0.4	0.7	-54.5

Additionally, the reliability of the CE procedure was also checked by comparing the CE and IC results for water-soluble Mn in extracts of filter-collected PM from the tunnel study. This was done only for Mn because the other metals could not be analysed by the IC method. Referring to Figure 9, the regression equation for Mn analyzed in 41 tunnel study samples was $CE = 0.997 IC - 0.034$ with correlation coefficient of 0.9297, showing an acceptable comparability of the two methods.

Overall, these values indicate a good performance in terms of the accuracy of the CE method.

Figure 9. Correlation between CE and IC measurements for water-soluble manganese in aqueous extracts of airborne $\text{PM}_{2.5}$ samples from the Cassiar Tunnel Study.

3.2 BCR sequential extraction procedure and its modification

As described in Chapter 1, the sequential extraction method proposed by the BCR provides a common protocol that fractionates metals into three fractions: exchangeable and acid soluble, reducible and oxidisable. Although The BCR method is simpler (consisting of only three stages), than other previous methods (e.g., Tessier et al.'s [46], or variations of it [100]), the overall operation time is much greater, and typically it is over twice as long. This means that it could be considered too time-consuming and tedious for routine analysis. In the interest of practicality, Perez et al. [88] investigated a way of reducing the operation time of the BCR sequential extraction procedure by applying focused ultrasound instead of mechanical agitation. This resulted in the reduction of the overall operation time from 51 hours to just 22 minutes, with virtually no difference in results compared to the conventional method.

Thus, the second goal of this work was to speed up BCR extraction by finding a set of ultrasonication conditions, using an ultrasonic bath, giving results that were similar to those of the conventional extraction method for the metals of interest. Since appropriate filter-collected particulate matter standards were not yet available, NIST 1648 Urban Particulate Matter Standard Reference Material was used for the evaluation of the ultrasonic accelerated sequential extraction procedure.

3.2.1 Optimization of sonication time

The effect of the ultrasonication time on the extraction efficiency was evaluated by comparing the metal recoveries, which were the ratios of the results obtained using the accelerated extraction to those obtained using the conventional BCR extraction. The results corresponding to the optimization of ultrasonication time are summarized in Figure 10.

(Continued on the following page)

Figure 10. Effect of duration of ultrasonication on the recoveries of the studied metals from NIST 1648 PM, extracted with (a) 0.11 mol/l acetic acid, (b) 0.1 mol/l HAHCl, and (c) 1.0 mol/l NH_4AC (after oxidation by 8.8 mol/l H_2O_2).

In the first step of extraction, subsamples of PM were leached with 1 ml of 0.11 mol/l acetic acid (E1) for 7-120 min to extract the water and acid soluble metals. With exception of Fe, the results obtained from the ultrasound accelerated procedure for 15 min or longer were in good agreement with those obtained from the conventional extraction method with stirring for 16 h (Figure 10 (a)). The slight decrease in recovery at 30 min of sonication was probably due to random error during extractions. The recovery for Fe was around 50% throughout the investigated sonication time. Although there was a small increase in the Fe recovery when the sonication time was increased to 45 min, ultrasonication for 15 min was selected for the first step of extraction.

After extraction of the water and acid soluble metals at the optimized time (15 min) in new sub-samples of NIST 1648 PM, the residues were extracted with the second extractant, 1 ml of 0.1 mol/l HAHCl, for several periods of time (Figure 10 (b)). In this fraction the leaching of the reducible metals increased up to 45 min. Longer sonication time did not result in any further significant increases in metal recovery. Therefore, 45 min of sonication was carried out throughout the rest of the experiment. The concentration of Cd in this fraction was below the detection limit.

In step three, the oxidisable metals were extracted under oxidizing conditions with H_2O_2 and heat, followed by extraction with the third extractant (E3), the pH 2 $\text{NH}_4\text{Ac}/\text{HNO}_3$ solution. The conventional BCR method includes three extractions with the H_2O_2 : one at room temperature and two at 85 °C for

one hour each, followed by the 16-h extraction with E3. For the ultrasonication method in this work, the H_2O_2 extraction was applied two times for 2 min of ultrasonication each, and then it was the E3 ($\text{NH}_4\text{Ac}/\text{HNO}_3$) extraction that was evaluated for different durations of ultrasonication (from 6 to 120 min). The results are illustrated in Figure 10 (c). The concentrations of Mn and Cd were below their detection limits. The recoveries of Cu and Zn increased with increasing sonication time in $\text{NH}_4\text{Ac}/\text{HNO}_3$ up to 15 min. After this point, the recoveries levelled off, and eventually decreased at sonication time longer than 60 min. This effect could be the result of re-adsorption of the metals onto the particles, or perhaps another process taking place, such as oxidation. The recovery of Fe, on the other hand, continued to increase throughout the investigated extraction time. Therefore, as a compromise between the recoveries of Zn, Cu, and Fe, 60 min of sonication was selected for this step.

Thus, the finalised extraction times selected for the ultrasonication method are 15 min for F1, 45 min for F2, 4 min (2 min, 2 times) for H_2O_2 , and 60 min for F3. This gives a total operating time of 124 min (excluding evaporation), which is substantially shorter than the 51 h (excluding evaporation) of the conventional method (Table 3). Although it appeared that focused ultrasonication, using a probe, offers even faster extractions (22 min, excluding evaporation time) [51], it can treat only one sample at a time. So, in cases when there are more than 6 samples to be analyzed, the ultrasonic bath extraction will definitely be advantageous.

3.2.1.1 Comparison between the percentage recovery of metals leached using conventional and accelerated BCR extractions

The ultrasonically accelerated BCR procedure from the above optimization and the conventional BCR procedure were applied for metal fractionation in the NIST 1648 PM reference material. The results, along with detection limits, are presented in Table 7. Note that detection limits are expressed in micrograms metal per gram PM, referring to the initial 0.01 g mass of the dried NIST 1648 PM and taking into account the minimum required dilution factor used in sample preparation for CE analysis. The limits of detection were at the very low $\mu\text{g/g}$ level for all metals in F1 and F2 (0.1 to 2.4 $\mu\text{g/g}$) and at the tens of $\mu\text{g/g}$ level for all metals in F3 (50 to 132 $\mu\text{g/g}$). This was to be expected since greater sample dilution and the use of pressure injection were required for the analysis of F3 samples. However, these detection limits were still at least 10 times better than those reported in the previous work [68].

With the exception of iron in F1 and F2, the results of the accelerated extraction method are reasonably comparable to those obtained from the conventional extraction procedure (Table 7). The recoveries (expressed as the percent of the conventional method results) were above 97% for Zn, Cu, Mn and Cd (F1), for Zn and Cu (F2), and for Zn (F3). Lower recoveries were, however, obtained for Mn (78%) in the second fraction, and Fe (86%) and Cu (68%) in the third fraction. Cadmium in fractions F2 and F3, and manganese in fraction F2 were not detectable. The relatively low value for iron in F1 and F2 (45.0 and 55.2%, respectively) revealed that the accelerated extraction was not as efficient

for extracting Fe as the conventional extraction was.

The precision of both BCR extraction methods (conventional and accelerated) was evaluated in terms of between-batch determinations run on different days (expressed as RSD, $n = 6$). These results are also presented in Table 7. In general, the fraction-specific experimental precision of the accelerated BCR leaching method was similar to that of the conventional procedure with RSDs lower than 10% for most of the metals in the three fractions. The poorer precision ($\text{RSD} < 20\%$) obtained for some of the elements in some fractions using both extraction methods may be due to either insufficient selectivity of the extraction step or the low concentration of the metal present in the PM matrix. As expected, the precision was worse when the concentration approached the detection limits but improved for higher concentrations. Overall, the method is reproducible enough to obtain useful information on heavy metal distribution.

Table 7. Metal fractionation ($\mu\text{g/g}$) in NIST 1648 PM with conventional and accelerated BCR sequential extractions.

Metal (Total certified)	Fraction	LOD	Mean $\pm$ sd (% RSD)*		Recovery (%)
			Conventional	Accelerated	
Fe (39100 $\pm$ 1000)	F1	0.1	504 $\pm$ 85 (16.9)	227 $\pm$ 12 (5.2)	45 $\pm$ 8
	F2	2.2	5002 $\pm$ 495 (9.9)	2759 $\pm$ 59 (2.1)	55 $\pm$ 6
	F3	50	2489 $\pm$ 296 (11.9)	2146 $\pm$ 125 (5.8)	86 $\pm$ 11
Zn (4760 $\pm$ 140)	F1	0.2	2932 $\pm$ 238 (8.1)	2930 $\pm$ 198 (6.7)	100 $\pm$ 11
	F2	2.4	181 $\pm$ 21 (11.5)	185 $\pm$ 9 (4.6)	102 $\pm$ 13
	F3	50	210 $\pm$ 20 (9.5)	209 $\pm$ 21 (10.0)	100 $\pm$ 14
Cu (609 $\pm$ 27)	F1	0.2	188 $\pm$ 16 (8.7)	195 $\pm$ 11 (5.8)	104 $\pm$ 11
	F2	0.6	94 $\pm$ 5 (5.8)	91 $\pm$ 11 (12.4)	97 $\pm$ 13
	F3	52	143 $\pm$ 15 (10.6)	97 $\pm$ 7 (7.4)	68 $\pm$ 9
Mn (786 $\pm$ 17)	F1	0.3	258 $\pm$ 21 (8.3)	249 $\pm$ 13 (5.3)	97 $\pm$ 9
	F2	1.4	64 $\pm$ 2 (2.9)	49 $\pm$ 4 (7.9)	78 $\pm$ 7
	F3	152	<152	<152	
Cd (75 $\pm$ 7)	F1	0.6	42 $\pm$ 7 (16.0)	41 $\pm$ 5 (11.3)	98 $\pm$ 20
	F2	2.2	<2.2	<2.2	
	F3	132	<132	<132	

*n = 6

3.2.1.2 Water-soluble fraction

As previously mentioned, the ultimate goal of this work was to apply the BCR sequential extraction to metal fractionation in filter collected airborne PM_{2.5} as an addition to the other analyses that are performed by the lab (XRF and IC). Since the filters would be extracted with water for major ion analysis prior to applying the BCR extractions, a further modification of the BCR method – the inclusion of a water extraction before the first BCR extraction step (with 0.1 mol/l acetic acid) – was evaluated. Because the BCR sequential extraction method was developed for the purpose of having a common procedure for the comparability of results, it was important to ensure that this modification would not alter the overall results of the extraction scheme, so that the only difference from the original method would be that the “water and acid soluble” fraction (F1) was separated into water-soluble (F0) and acid-soluble (F1’) fractions. As long as that is the case, then there would be no difference between the original F1 and the sum of F1’ and F0.

Validation of this modification was also carried out using NIST 1648 PM, because no aerosols standards on Teflon filters were available. Table 8 shows the water- and acid-soluble concentrations of the studied metals using the accelerated ultrasonic extraction. Comparison of the sums of the metal concentrations in the individual fractions F0 and F1’ with that obtained in the single F1 fraction shows good agreement for all trace metals, with ratios between them being as follows 1.29 (Fe), 0.83 (Zn), 0.8 (Cu), 0.93 (Mn) and 0.83 (Cd). Overall trace metal recoveries ranged from 83% to 129% (Table 8). Therefore,

the BCR sequential extraction could be carried out on filter collected PM samples, after water extractions for IC analysis, with confidence in the validity of the results.

Table 8. Concentrations of water- and acid-soluble metal ions in NIST 1648 PM

Fraction	Mean and standard deviation* [$\mu\text{g/g}$]				
	Fe	Zn	Cu	Mn	Cd
F0	114 $\pm$ 12	1842 $\pm$ 92	99 $\pm$ 7	206 $\pm$ 12	22 $\pm$ 0.2
F1'	178 $\pm$ 12	587 $\pm$ 43	57 $\pm$ 6	26 $\pm$ 2	12 $\pm$ 1
Sum	292 $\pm$ 20	2429 $\pm$ 147	156 $\pm$ 14	232 $\pm$ 15	34 $\pm$ 1
F1	227 $\pm$ 12	2930 $\pm$ 198	195 $\pm$ 11	249 $\pm$ 13	41 $\pm$ 5
Recovery [%]	129	83	80	93	83

*N=3

A comparison was also made of water-soluble metals determined in NIST 1648 PM in this work with those determined by Lum et al. [56] and Fung et al. [67] in this same reference material (Table 9). There is acceptable agreement between the three sets of results for most of metals. The discrepancy between the results for cadmium was likely attributable to its low content in PM. As can be seen in Table 9, significant amounts of Zn, Cu, Mn and Cd were present in

readily soluble forms. Thus, the total fraction F1 was composed of 50-60% water-soluble (the most loosely bound) forms.

Table 9. Comparison of water-soluble metal concentrations in NIST 1648 PM determined in this work and by other researchers

Metal	This work		Lum et al. [56]		Fung et al. [67]	
	[$\mu\text{g/g}$]	% Total	[$\mu\text{g/g}$]	% Total	[$\mu\text{g/g}$]	% Total
Fe	114	0.3	N/A	N/A	99	0.3
Zn	1842	38.7	1761	37.0	2037	42.8
Cu	99	16.3	97	15.9	98	16.1
Mn	206	26.2	189	24.0	N/A	N/A
Cd	22	29.3	8	10.7	15	20.0

3.2.1.3 Comparison of the results of analysis of NIST 1648 PM Standard Reference Material

The fractionation pattern of the extracted metals using both the conventional and accelerated BCR methods is illustrated in Figure 11. The results, expressed as a percentage of total metal content of the analyzed metals in NIST 1648 PM in each step, corresponded to the mean of six experiments. The residual fraction (F4) was calculated as the difference between the certified total metal content and the sum of the three extraction steps (fractions F1, F2

and F3), rather than digesting the residual remained after step 3.

As discussed above, the distribution of metals among the fractions yielded results that were reasonably comparable between the accelerated and conventional extraction procedures. As expected, different distribution patterns were observed for different metals.

Iron: About 1% of the total Fe was found in the water/acid soluble phase, about 13% was associated with reducible phase, and about 6% was associated with the oxidisable phase, while the remaining majority (~80%) of Fe was refractory in character. The iron distribution in NIST 1648 PM examined by ⁵⁷Fe Mossbauer spectroscopy [42] confirmed that the majority of Fe is present as the refractory species, such as magnetite, hematite and ferric/ferrous species in a clay mineral. Moreover, Huggins et al. [42] also reported that insignificant Fe seemed to present as sulfate species, which may explain the fact that very little Fe (0.3%, Table 9) was present in the water-soluble phase.

Figure 11. Distributions of the studied metals in the chemical fractions in NIST 1648 PM based on the conventional (C) and accelerated (A) BCR sequential extraction procedures. Standard deviations are given in Table 7.

Zinc: This element was mainly present in the water/acid soluble fraction (~62%), and secondly in the residual fraction (~30%), with lesser amounts of Zn in the reducible and the oxidisable phases (~4% each). The high concentration of Zn in the water/acid soluble is supported by X-ray absorption near-edge structure (XANES) spectrum for Zn in the same reference PM, as reported by Huggins et al. [42], indicating that zinc occurs as a hydrated sulphate species, although some other additional forms may also exist.

Copper: Copper was evenly distributed between the water/acid soluble and residual fractions (~30% each), and a significant amount of Cu was also found in reducible phase (~15%) and the oxidisable phase (~24%). The presence of Cu in the oxidisable phase indicates that a significant amount of Cu may be sulphidic and/or bound to organic ligands. However, XANES spectra suggest that the copper species are neither metallic nor sulphidic, but appear more like the hydrated copper sulphate [42]. Thus, the water-soluble (~16%, Table 9) or water/acid soluble Cu may be present as hydrated copper sulphate.

Manganese: This element was mainly present in the residual fraction (~60%), but a considerable amount of Mn (~33%) was also found in water/acid soluble fraction, and the rest (~8%) was in the reducible phase (F2). Although the reported identification of specific Mn forms in this PM reference material was not conclusive, Huggins et al. [42] did find that a significant fraction of Mn is present in higher oxidation states (Mn^{3+} or Mn^{4+}), in addition to divalent forms. It is likely that Mn (III, IV) may exist in various forms of oxides or (oxyhydro)oxides, which

contribute to both the refractory and the reducible Mn in the NIST 1648 PM.

Cadmium: Around 55% the total Cd was partitioned among water/acid soluble phase (~29% water-soluble, Table 9), while the rest was seemingly in residual phase. Concentrations found for Cd in F2 and F3 fractions were lower than its respective detection limits. Due to the similarity of the XANES spectra of Cd compounds, the actual speciation of Cd in NIST 1648 PM remains unclear [42], but Huggins et al. [42] did indicate the possible existence of cadmium sulphate or cadmium silicate, which seems reasonable from the Cd distribution results of our study.

In summary, the amount of reducible metals (F2) present in the NIST 1648 PM samples decreases in the order of $\text{Cu} \cong \text{Fe} > \text{Mn} > \text{Zn}$ (Cd was below LOD), that of oxidisable metals (F3) decreases in the order of $\text{Cu} > \text{Fe} > \text{Zn}$ (Mn and Cd were below LODs), and that of refractory metals (F4) decreased in the order $\text{Fe} > \text{Mn} > \text{Zn} \cong \text{Cu} > \text{Cd}$. On the other hand, the amount of metals released in the water (F0) or in the water/acid soluble step (F1) decreases in the order of $\text{Zn} > \text{Cd} > \text{Mn} \cong \text{Cu} > \text{Fe}$, which was in agreement with the study performed by Chester et al. [21], that more volatile elements seem to be more “loosely bound” in urban particulate matters, indicating their anthropogenic origin [55], and also suggesting that they are more environmentally mobile.

Different sequential extraction schemes have been carried out on the NIST 1648 PM by other researchers [56, 68]. The sequential extraction procedures differ from the BCR procedure in many of the operational conditions

(the number of steps, the extractants used, extraction times, etc.), so the resulting metal distributions cannot be compared directly. However, some comparisons can be made in a general sense (i.e., in terms of loosely bound and strongly bound). In this sense the results from these other studies were quite similar to the results obtained here. Fe was mostly in the more strongly binding fractions (e.g., oxides, organic, and residual), and very little Fe was loosely bound; Zn was primarily loosely bound; Cu had a more even distribution among the different fractions; Mn tended to be mainly in the most loosely bound and the most strongly bound fractions.

3.3 Chemical characterization of filter-collected airborne PM_{2.5}

After testing the accelerated BCR sequential extraction procedure with the reference material, it was tested out on some real PM_{2.5} samples collected on Teflon filters. For the purpose of this work, a few samples from each of two source types were selected: seven samples collected at various NAPS (urban) sites and six samples from the Cassiar Tunnel study. These filters were chosen based on PM mass loading on the filter and the total metal contents.

As mentioned in Chapter 2, all samples were handled according to established operating protocol used in the Inorganic Laboratory of the AAQD. PM_{2.5} mass was measured first, followed by analysis of the total concentrations of particle-bound trace elements by means of XRF and then IC analysis of the water-soluble major ions. Details of the XRF and IC methods can be found in references [91] and [92], respectively. In addition to this, the water extracts from

all of the selected filters were analysed for water-soluble metals by CE. Finally, the accelerated BCR sequential extraction, with subsequent CE analysis, was applied for the fractionation of metals. The results will be discussed below.

3.3.1 NAPS samples

The sampling locations and dates for the collection of ambient air PM samples are given in Table 2 (Section 2.3.1). All sites are located in urban areas. The sample collection stations were placed near emission sources such as industrial (I) and high traffic commercial (C) zones, as well in places with cleaner residential air (R). The selected samples were collected between August 2001 and January 2002.

3.3.1.1 General overview of urban particulate samples

3.3.1.1.1 Total concentrations of elements

The total PM_{2.5} mass and the total concentrations (in ng/m³) of selected elements determined by XRF in the samples from different NAPS stations are presented in Table 10. In general, most values are above the detection limits. In addition, Figure 12 shows the relative proportions in which these elements occurred in the ambient air PM at each sampling location.

Table 10. Concentrations of total PM and selected elements in urban air PM_{2.5} samples collected at various NAPS sites.

Element	LOD	Concentration (ng/m ³)						
		Calgary (C)	Winnipeg (C)	Quebec City (I)	Toronto (I)	Toronto-2 (R)	Montreal (R)	Montreal-2 (R)
		Jan 2/02	Oct 22/01	Nov 15/01	Nov 2/00	Aug 23/01	Oct 10/01	Aug 23/01
PM		14330	7882	39992	21954	19579	12747	10248
S	1	228	349	1284	571	2249	1013	936
K	5	96	158	186	205	75	89	111
Ca	5	316	326	76	222	91	152	148
Si	2	155	128	181	192	132	137	290
Mn	2	25	15	31	44	14	17	16
Fe	2	335	293	257	480	173	158	161
Cu	2	7	6	7	21	5	5	108
Zn	1	21	20	74	95	39	26	51
Cd	2	BDL*	BDL	BDL	BDL	BDL	10	BDL
Pb	1	BDL	5	17	14	12	14	67
Br	0.3	1.6	1.7	9.8	5.2	5.0	3.6	2.3

*below detection limit

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Figure 12. Relative proportions of elements of in the urban air $PM_{2.5}$ samples collected at various NAPS sites.

The characteristics of this fine PM generally agree with the previous report that examined the relationship among total mass of PM, PM₁₀, PM_{2.5} and inorganic constituents of PM at multiple Canadian NAPS Locations [9], with the relative abundance depending on sampling location, time (seasonal and weekday/weekend), and meteorological conditions. As can be seen in Table 10, there was considerable variability in the elemental concentrations between different urban areas, which appear unrelated to variations in the total PM_{2.5} mass. Sulphur, mostly present as sulphate ($S_{(XRF)} \equiv SO_4^{2-}{}_{(IC)} / 3$), was an overall prominent element in these PM samples, but varied considerably from one sample location to another. Total S was comparatively low in the PM samples from Calgary (C), Toronto (I) and Winnipeg (C). Higher proportions were seen in the PM samples from Quebec City (I), Montreal (R), and particularly in Montreal-2 (R) and Toronto-2 (R), where the total S constituted about 66% and 80%, respectively, of the sum of all these elements shown here.

Iron was also present at considerable levels in these PM samples. The highest Fe proportions were found in the PM from Calgary (C), Toronto (I) and Winnipeg (C), making up about 25% of the sum of all of these elements. Lower Fe proportions were present in the PM from the two Montreal (R) sites, Quebec City (I), and Toronto-2 (R), but it was still fairly well represented (6% to 12%). On the other hand, the relative percentage composition of another crustal element, silicon, was more comparable among the five cities (5% to 15%). This suggests that silicon is dominated by local sources such as roadside dust rather than inland sources. Calcium was present in noticeably greater proportions in Calgary

(C), Toronto (I) and Winnipeg (C) (12% to 27%) compared to the two Montreal (R) sites, Quebec City (I), and Toronto-2 (R) (3% to 9%). Potassium composed about 3% to 12% of these elements. These PM samples contained only very small proportions of Cu (no more than 1%), with the exception of the Montreal-2 (R) PM sample, which had 6% Cu. Zn was present in all of these PM samples (1% to 5%). Mn was a minor component in all of these samples (1% to 2%). Cadmium was detected in the samples, but at very low proportions (less than 1%). Lead occurred in all samples (1% to 4%) except Calgary (C). Similarly, bromine was present at low proportions (less than 1%). It has been reported that fine Pb comes from automotive emissions and it is associated with fine Br and fine Cl [9]. In general, the concentration of the studied metals decreased in the order $\text{Fe} > \text{Zn} \cong \text{Mn} > \text{Cu} > \text{Cd}$.

In relation to the characteristics of the stations, there were differences in the distributions of the metal species that likely reflect differences in the predominant sources in each area. Most of the metals implicated usually appear in association with traffic exhaust and industrial activity. For example, the Quebec City (I) and Toronto (I) samples are apparently richer in industry- and vehicle-related species (Fe, Mn, Zn, S, NO_3^- , Pb, Br).

3.3.1.1.2 Water-soluble major ions

Table 11 presents the concentrations of a number of water-soluble ions in these PM samples, as determined by IC analysis. Various ions, namely chloride, oxalate, sodium, potassium, magnesium, and calcium, were present in overall

minor proportions (from less than 1% to 3%, individually, of the total PM mass, and combined 3% to 7%). As in other reported cases [103], sulphate, nitrate, and ammonium were the three most prominent ions in these samples. Together, they constituted about 70% to 95% of the sum of all these water-soluble ions. The relative proportions of these three major ions are illustrated, as a percentage of the total PM mass, in Figure 13. The $\text{SO}_4^{2-}/\text{NO}_3^-/\text{NH}_4^+$ component accounts for about 15% to 50% of the fine PM mass, depending upon the site. These values are within the average range reported by Brook et al. [9] for the NAPS network. In general, all fine sulphate and nitrate were likely in the form of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 [9].

Table 11. Concentrations of major water- soluble ions in urban air PM_{2.5} samples collected at various NAPS sites

Ion	LOD	Concentration (ng/m ³)						
		Calgary (C)	Winnipeg (C)	Quebec City (I)	Toronto (I)	Toronto-2 (R)	Montreal (R)	Montreal-2 (R)
		Jan 2/02	Oct 22/01	Nov 15/01	Nov 2/00	Aug 23/01	Oct 10/01	Aug 23/01
PM		14330	7882	39992	21954	19579	12747	10248
Cl ⁻	7	164	34	334	36	35	35	34
SO ₄ ²⁻	14	545	837	6485	1894	7145	3201	2840
NO ₃ ⁻	7	1448	128	9414	1421	168	255	88
Oxalate	7	BDL*	49	329	180	232	120	142
Na ⁺	1	327	39	220	79	69	107	66
NH ₄ ⁺	5	194	248	4009	840	2324	1068	885
K ⁺	2	62	102	245	106	82	68	86
Mg ²⁺	1	29	45	13	26	19	BDL	12
Ca ²⁺	2	272	247	95	129	79	128	131
Mn ²⁺	1	9	7	15	26	9	8	7

*below detection limit

Figure 13. Relative proportions of the major water-soluble ions in the urban air $PM_{2.5}$ samples collected at various NAPS sites.

3.3.1.2 Chemical fractionation results

The metal contents in each BCR fraction (including water-soluble) for the selected NAPS ambient air PM samples are shown in Table 12. These concentrations are expressed as ng/m³ of sampled air. Note that the concentration in the residual fraction was calculated by subtracting the sum of all the other fractions (F0-F3) from the total concentration determined by XRF. With exception of iron, the metal concentrations in the oxidisable fraction (F3) in all of these samples were below their respective detection limits. The metal distributions among the BCR fractions in the ambient air PM samples, expressed as a percentage of the total metal concentration determined by XRF, are shown in Figure 14.

Table 12. Distributions of metals in the fractions of urban air PM_{2.5} samples collected at various NAPS sites

Metal	Location (zone type)	Concentration (ng/m ³)					
		Total	F0	F1'	F2	F3	F4
Fe	Calgary (C)	335	5.9	7.2	30	32	259
	Winnipeg (C)	293	8.7	5.6	66	BDL*	213
	Quebec City (I)	257	37	6.1	14	24	176
	Toronto (I)	480	44	12	38	28	359
	Toronto-2 (R)	173	45	4.4	4.4	BDL	119
	Montreal (R)	158	11	4.0	9.9	24	109
	Montreal-2 (R)	161	17	14	4.7	BDL	126
Zn	Calgary (C)	21	10	4.5	1.8	BDL	4.9
	Winnipeg (C)	20	11	3.5	0.2	BDL	5.2
	Quebec City (I)	74	39	4.7	0.8	BDL	29
	Toronto (I)	95	63	6.9	6.7	BDL	19
	Toronto-2 (R)	39	11	0.6	9.9	BDL	17
	Montreal (R)	26	3.4	1.0	1.2	BDL	20
	Montreal-2 (R)	51	17	3.8	0.9	BDL	29

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Metal	Location (zone type)	Concentration (ng/m ³)					
		Total	F0	F1'	F2	F3	F4
Cu	Calgary (C)	7	0.3	2.9	0.6	BDL	3.2
	Winnipeg (C)	6	0.2	0.5	0.9	BDL	4.4
	Quebec City (I)	7	2.5	0.9	1.5	BDL	2.2
	Toronto (I)	21	1.9	2.2	1.0	BDL	16
	Toronto-2 (R)	5	2.7	1.3	0.1	BDL	0.9
	Montreal (R)	5	0.5	0.2	0.1	BDL	4.3
	Montreal-2 (R)	108	31	6.1	3.5	BDL	37
Mn	Calgary (C)	25	11	0.9	0.6	BDL	13
	Winnipeg (C)	15	7.5	0.7	1.0	BDL	2.8
	Quebec City (I)	31	17	0.6	1.5	BDL	12
	Toronto (I)	44	28	1.0	1.1	BDL	14
	Toronto-2 (R)	14	10	0.4	0.3	BDL	3.2
	Montreal (R)	17	9.4	0.7	0.1	BDL	6.8
	Montreal-2 (R)	16	5.3	0.4	3.5	BDL	6.9
Cd	Montreal (R)	10	8.1	0.5	BDL	BDL	1.3

*below detection limit

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Copper

Manganese

(Continued on following page)

Figure 14. Distributions of metals in urban air PM_{2.5} samples collected at various NAPS sites.

There were notable differences in the distributions of the different metals in these PM samples (Table 12 and Figure 14). Furthermore, there were also some differences in the metal distributions between different stations. Since atmospheric particles at a given sampling site usually originate from a diversity of sources with varying mineralogical composition and relative contribution, the fractionated distribution of heavy metals is expected to vary from one site to another.

Iron: Water-soluble Fe was only minor in the Calgary (C) and Winnipeg (C) samples, but greater proportions were seen in the other five samples (Montreal-2 (R), Quebec City (I), Toronto (I), and Toronto-2 (R)). The higher solubility of iron in such samples was probably associated with high contents of sulphate, nitrate and oxalate compared to the others. These samples had relatively little Fe (< 5% of the total) in the acid-soluble fraction. The distribution of Fe in the reducible and oxidisable fractions varied from one location to another. Reducible Fe was found in all samples at relatively low levels (~2-10%), except in the Winnipeg (C) sample where it constituted about 23% of the total Fe content. Oxidisable Fe (~6-15%) was detectable in four samples: Toronto (I), Quebec City (I), Calgary (C), and Montreal (R). This suggests that some Fe was probably associated with Fe-Mn oxides (reducible) and, to a lesser extent, organic matter (oxidisable). In all seven samples, the majority of Fe (~68-78%) was refractory in character, which means that much of the total Fe would be environmentally immobile. This is in agreement with other works [54, 59], reporting a greater distribution of Fe in the more environmentally immobile

fractions, as is typical for a crustal-dominated element.

Zinc: Substantial portions of the total Zn were present in the water-soluble fraction (the lowest being ~13% in the Montreal (R), while the others had ~30% - 66%), and lesser amounts in the acid-soluble fraction (~1%-21%). These first two fractions combined accounted for about 30% to 73% of the total Zn content, which indicates that Zn had significant environmentally mobile character in these PM samples, and also suggests that it probably comes largely from anthropogenic sources [18]. The amount of reducible Zn was relatively minor (less than 10%), with the exception of the Toronto-2 (R) sample, which had about 25% of the total Zn in the reducible fraction. The concentrations of Zn in the oxidisable fraction (F3) were lower than its corresponding detection limit in all samples. The remainder was in the residual fraction, which represented the other significant proportion of Zn in these PM samples (~23% - 78%).

Copper: The distribution of Cu varied considerably from one sample to the next. The majority was generally divided between the water-soluble and acid-soluble fractions (~3-57% and ~3-41%, respectively) and the residual fraction (~18-86%). The relative proportions of water-soluble and acid-soluble Cu varied among these samples. In some cases (Montreal (R), Montreal -2 (R), Quebec City (I), and Toronto-2 (R)) there was more Cu in the water-soluble fraction than in the acid-soluble fraction. In other cases (Calgary (C), Toronto (I), and Winnipeg (C)) it was just the opposite. This differs from the distributions of the other metals in these two fractions, which were quite consistently removed more by the water-soluble step than the acid-soluble step. This could suggest

that the Cu in these three samples is more significantly associated with acid-soluble components, such as carbonates and oxides, compared to the Cu in the other samples. Some Cu was detected in the reducible fraction of all samples (~1-21%). Again, the concentrations in the oxidisable fraction were below the detection limit in all studied samples.

The obtained results were generally consistent with those reported by other researchers. Copper in urban particles has been found in easily available forms such as carbonates and oxides [54, 56]. Other studies have reported differing distributions of Cu from sequential extractions of airborne PM; Hlavay et al. [59] reported Cu to be mostly in the residual phase and Varga et al. [45] reported that Cu was mainly associated with “oxides and sulphides”. Although the sequential extraction methods used in each case differed, it does appear that Cu can exhibit varying distributions in PM from different sources and/or locations. Overall, however, the Cu in most of these PM samples did exhibit high environmentally mobile character as well as environmentally immobile character, which may indicate that both anthropogenic and natural sources are significant contributors to Cu.

Manganese: Mn was distributed almost exclusively between the water-soluble (~33-72%) and residual fractions (~23-52%). No oxidisable Mn was detected in any of these PM samples, and only small amounts of Mn were present in the reducible fraction of the samples, with the exception of the Montreal-2 (R) PM, which had a more significant reducible component (~22%). Acid-soluble Mn was relatively low in all cases (less than 5%), but significant

amounts of water-soluble Mn indicates that a lot of the Mn in these PM samples would be environmentally mobile. Similar mobile character was found in other studies where the Mn distribution was determined in ambient PM [41, 54].

Cadmium: Cd was detected in only one of these samples (Montreal (R)), which makes sense because this sample contained much more total Cd than the others based on the XRF results. The Cd in this sample was mainly present in the water-soluble fraction (~81%). This highly mobile character of Cd in urban PM is consistent with data reported by others [41, 54, 56] where this metal appeared to be almost exclusively in soluble-exchangeable forms, and was often removed mostly in the first step of sequential extractions. This is in agreement with reports that cadmium tends to be more concentrated on the surface of particles produced by combustion processes, and thus, it would be loosely bound [101, 102].

3.3.2 The Cassiar Tunnel samples

The on-road transportation sector is the largest local source of smog-causing pollution, including fine particles, in urban areas. On-road vehicles emit combustion-generated particles directly from the tailpipe, and they also generate particles from brake and tire wear and also uplift dust from the roads as they move – even on paved roads. Therefore, in order to estimate the contribution of automobile emissions to ambient air PM and assess its associated potential health hazard, it is imperative to carry out many field measurements from different source points. One such field measurement was performed by

Environment Canada in a highway tunnel in Vancouver, in August 2002 [90].

As described in Chapter 2, PM samples were collected on filters at the inlet (south) end and at the outlet (north) end of the Cassiar Tunnel in Vancouver. They were collected at sampling periods of three hours each, three times a day, for seven consecutive days starting on Thursday, August 9th, 2002. All filters were analysed according to the protocol of the Inorganic Lab of the AAQD for PM mass, total elemental concentrations by XRF and major water-soluble ions by IC. In addition to this, the water extracts from all the filters were analyzed for water-soluble metals by CE. Six filters were later selected for further characterization using the accelerated BCR sequential extraction scheme and CE analysis of the fractionated metals.

3.3.2.1 General overview of the tunnel PM_{2.5} samples

3.3.2.1.1 Total concentrations of elements

Table 13 presents the total concentrations of elements (in ng/m³), determined by XRF for the six selected filters, along with detection limits, and the total PM mass on each filter. The measured concentrations of PM_{2.5} varied with sampling period and with tunnel position (inlet versus outlet). These changes may be related to changes in traffic conditions, such as number of vehicles, speed, or type of vehicles. For example, the concentrations of various elements and PM were lower in samples collected on Saturday morning, when traffic was lower (4418 vehicles) in comparison to other higher traffic sampling periods, such as on Friday mid-day (7022 vehicles) or Monday morning (7813 vehicles). The

general increases in concentrations from inlet to outlet of the tunnel were probably due to changes in the driving speed of vehicles, which causes differences in the emission rates, and/or to the flow of air from inlet to outlet that is generated by the movement of traffic in that direction.

Figure 15 illustrates the relative proportions in which these different elements occurred in each sample. In general, sulphur and iron were the most abundant elements. There were also significant amounts of silicon in the PM, with somewhat lesser amounts of Mn, Cu, Zn, Ca, and K. Only very small proportions of Pb and Br occurred in all of these samples, and Cd was not detected in any of them.

Sulphur (most likely as sulphate) has been reported to be more prominent in fine PM than in coarse PM [90]. This is consistent with sulphur existing as sulphate in the particulate phase – from either secondary particle formation or direct (primary particle) emission. In a study to characterize vehicle PM emissions done by Cadle et al. [103], sulphur was attributed to the fuel (gasoline and diesel) and the motor oil. As part of the Cassiar Tunnel study, various fuels and motor oils were analysed for their elemental contents. Significant concentrations of sulphur were present in gasoline and diesel fuels, and even higher concentrations of sulphur were present in the motor oils [90]. Thus, it seems that the sulphur found in these PM samples came from the fuel and oils in the vehicles.

Table 13. Concentrations of total PM and selected elements in PM_{2.5} samples collected from the Cassiar Tunnel study

Element	LOD	Concentration (ng/m ³)					
		Aug-10-02 Fri Mid-Day (7022)*		Aug-11-02 Sat AM (4418)		Aug-13-02 Mon PM (7813)	
		Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
PM		64400	107800	39100	57300	63400	98500
S	8	1866	1658	689	1373	2515	2575
K	30	75	84	102	146	BDL	155
Ca	40	189	417	89	192	113	236
Si	20	921	171	199	383	484	855
Mn	20	124	143	74	89	176	187
Fe	20	1020	1971	740	1251	1076	2591
Cu	20	91	95	BDL	113	55	148
Zn	8	108	172	89	93	92	121
Cd	6	BDL**	BDL	BDL	BDL	BDL	BDL
Pb	10	12	13	3	12	11	18
Br	3	BDL	3	3	5	8	BDL

*number of vehicles

**below detection limit

Friday, August 10, Mid-day: Inlet

Friday, August 10, Mid-day: Outlet

Saturday, August 11, AM: Inlet

(Continued on following page)

Figure 15. Relative proportions of elements in $PM_{2.5}$ samples collected from the Cassiar Tunnel Study.

As described in the report by Graham [90] concentrations of elements commonly associated with crustal material and re-entrained road dust (Fe, Ca, and Si) decrease as the particle size decreases. Iron is commonly a representative crustal element, but if a major source of Fe at this site is motor vehicles, it could be emitted in large particles from the rusting of metal parts (e.g. exhaust system and undercarriage) and as small particles due to wear of the engine. Similarly, one of the sources of Ca – also a typical crustal element – in fine PM could be vehicular emission since Ca, a detergent additive in motor oil, was reported to be present as a major elemental component in the motor oils analysed [90]. An additional possible source of Ca could be the concrete walls of the tunnel itself, as concrete contains limestone (calcium carbonate). Silicon is another crustal element [1, 103], but it is also a motor oil additive, which may account for its presence in PM_{2.5}. Silicon was found in motor oils as a minor elemental component [90], however, the Si content of motor oils does vary widely from one brand to the other, often leading to difficulties in clearly identifying the likely sources of Si [103].

Zinc is added to motor oil as an anti-wear and anti-oxidant in the form of zinc dithiophosphate [103], which is a probable partial source for vehicle-derived Zn. Zinc was indeed present as a major elemental component of motor oils [90], It has been suggested, however, that the wear of brake linings [104] and the wear of tires [105] also likely contribute to Zn in PM from vehicle sources.

Copper has also been attributed to vehicle emissions [103, 104]. Cu comes mainly from the wear of brake linings [104], but it also seems likely that

some Cu comes from motor oil, because it is an anti-oxidant additive to motor oil [103], and was found as a minor elemental component in the motor oils analysed for the Tunnel Study project [90].

Manganese can be emitted in the same way as Fe associated with larger particles. Small particles are emitted independently due to the use of MMT (methylcyclopentadienyl manganese tricarbonyl) in gasoline to increase the octane rating [90]. Used in Canada since the late 1970s, MMT has seen a substantial increase in utilization over the last few years, and has now completely replaced tetraethyl lead in gasoline.

Although tetraethyl lead is no longer used in gasoline in North America, there could still be some Pb emitted due to re-suspended lead that accumulated in the exhaust pipes of older cars while leaded gasoline was in use [105]. The other potential source for vehicle-derived Pb is the wear of brake linings [106].

Cadmium has been linked with vehicle emissions [104], however it was below the detection limits in all of these samples.

3.3.2.1.2 Water-soluble major ions

The results and detection limits for water-soluble ions in ng/m^3 by IC analysis for the selected filters are presented in Table 14. All detected ions showed an increase in concentration from entrance (inlet) to exit (outlet) of the tunnel, as did the total PM emissions, likely due to different traffic speeds from inlet to outlet, and perhaps also due to the air flow generated by the movement of vehicles from inlet to outlet. As with the urban ambient air PM samples,

sulphate, nitrate and ammonium were the dominant ionic species, comprising about 85 to 93% of the sum of all these ions in these PM samples. Other ionic species such as chloride, oxalate, sodium, potassium, magnesium and calcium were also present, but at relatively low concentrations (< 1% individually, of the total PM mass, and about 1-2% combined).

The relative proportions of the three major ions are illustrated, as percentages of the total PM mass, in Figure 16. The $\text{SO}_4^{2-}/\text{NO}_3^-/\text{NH}_4^+$ component accounts for about 7% to 27% of the fine PM mass, depending on the traffic volume. These values are lower than those determined for the urban ambient air PM samples from the NAPS network. This indicates that other components of PM, such as combustion-generated organic carbon/elemental carbon, tend to dominate in these types of samples. From correlation data between ammonium and sum of sulphate and nitrate prepared for the Tunnel Study report (data not shown), it appears that the ammonium present in the particle phase is associated with either sulphate or nitrate [90]. As stated in the report [90], the slope of the regression was greater than 1 and there was a positive intercept, indicating that there was a slight excess of sulphate and nitrate ions. If these were present as the corresponding acids this would lend to the particles being acidic. This is in agreement with the measured pH of these PM samples, which varied from 4.5-6.5.

Table 14. Concentrations of major water-soluble ions in PM_{2.5} samples collected from the Cassiar Tunnel Study

Ion	LOD	Concentration (ng/m ³)					
		Aug-10-02 Fri Mid-Day (7022)*		Aug-11-02 Sat AM (4418)		Aug-13-02 Mon PM (7813)	
		Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
PM		64400	107800	39100	57300	63400	98500
Cl ⁻	8	47	42	59	61	165	155
NO ₃ ⁻	9	863	1072	2571	2115	6472	6099
SO ₄ ²⁻	9	3797	4325	2010	2387	6406	7029
Oxalate	4	393	429	344	471	544	583
Na ⁺	10	104	170	101	90	179	197
NH ₄ ⁺	9	1502	1946	1503	1493	3997	4255
K ⁺	8	185	234	110	117	147	163
Mg ²⁺	5	26	45	20	30	40	70
Ca ²⁺	10	199	273	107	149	96	180
Mn ²⁺	7	66	74	31	56	124	140

*number of vehicles

Figure 16. Relative proportions of the major water-soluble ions in $PM_{2.5}$ samples collected from the Cassiar Tunnel study

Approximately 81% of the sulphur found in the six selected PM_{2.5} samples is present as water-soluble sulphate. This is in agreement with findings by Cadle et al. [103], reporting the occurrence of about 90% SO₄²⁻/S in the vehicle exhaust PM. Based on the IC and XRF results it was found that approximately 50% and 60% of total calcium and manganese, respectively, were present as water-soluble ions.

3.3.2.2 Chemical fractionation results

The concentrations of metals in the BCR fractions for the selected six Cassiar Tunnel PM samples are given in Table 15. Again, the concentration of each metal in the residual fraction was calculated by subtracting the sum of all the extracted fractions (F0-F3) from the total concentration determined by XRF. With exception of iron, the metal concentrations in the oxidisable fraction (F3) in all of these samples were below the detection limits. Mn was also not detected in reducible fraction (F2), and Cd was not detected in any fractions for any of these samples.

Table 15. Distributions of metals in the fractions of PM_{2.5} samples collected from the Cassiar Tunnel Study

Metal	Date, time	Position	Concentration (ng/m ³)					
			Total	F0	F1'	F2	F3	F4
Fe	Friday Aug-10, MD	Inlet	1020	20	13	88	198	701
		Outlet	1971	36	15	155	201	1565
	Saturday Aug-11, AM	Inlet	740	5	4	26	105	600
		Outlet	1251	2	1	87	124	1037
	Monday Aug-13, PM	Inlet	1076	38	9	64	174	791
		Outlet	2591	143	7	83	463	1895
Zn	Friday Aug-10, MD	Inlet	108	38	2	1	BDL*	67
		Outlet	172	98	4	45	BDL	26
	Saturday Aug-11, AM	Inlet	89	23	3	2	BDL	61
		Outlet	93	65	1	14	BDL	13
	Monday Aug-13, PM	Inlet	92	32	3	27	BDL	30
		Outlet	121	81	2	19	BDL	19

(Continued on following page)

Metal	Date, time	Position	Concentration (ng/m ³)					
			Total	F0	F1'	F2	F3	F4
Cu	Friday Aug-10, MD	Inlet	91	25	17	18	BDL	31
		Outlet	95	6	6	4	BDL	78
	Saturday Aug-11, AM	Inlet	ND**	ND	ND	ND	ND	ND
		Outlet	113	6	2	BDL	BDL	105
	Monday Aug-13, PM	Inlet	55	28	4	4	BDL	20
		Outlet	148	68	7	BDL	BDL	72
Mn	Friday Aug-10, MD	Inlet	124	38	3	BDL	BDL	83
		Outlet	143	57	3	BDL	BDL	84
	Saturday Aug-11, AM	Inlet	74	36	2	BDL	BDL	36
		Outlet	89	25	2	BDL	BDL	62
	Monday Aug-13, PM	Inlet	176	127	2	BDL	BDL	47
		Outlet	187	112	2	BDL	BDL	72

* below detection limit

** no data (XRF)

The metal distributions among the BCR fractions, expressing the metal content of each fraction as a percent of its total concentration in these PM samples, are illustrated in Figure 17. Each metal showed a different distribution pattern.

(Continued on following page)

Figure 17. Distributions of metals in the PM_{2.5} samples collected from the Cassiar Tunnel Study

Iron: Iron had a fairly consistent distribution among the six samples. There was very little Fe in the water-soluble and acid-soluble fractions (< 6% and < 2%, respectively). Slightly greater amounts of Fe were present in the reducible fraction, the highest being about 9%, and even more in the oxidisable fraction, in which the highest was approximately 20%. By far, the majority of the total Fe was in the residual fraction (~69-83%). This means that, in these Tunnel Study PM samples, Fe would be largely environmentally immobile.

Zinc: The Zn distribution varied between different filters. Overall, Zn was very prominent in the water-soluble fraction (~26%-70%), leaving only small amounts of Zn being extracted in the acid-soluble stage (~1%-4%). This indicates that substantial amounts of the total Zn in the Tunnel Study PM samples would be highly environmentally mobile. The distribution of Zn in the reducible fraction varied from approximately 1% to 30%. No oxidisable Zn was detected in any of these filters. The remainder of the Zn was in the residual fraction, which ranged from about 14% to 69%.

Copper: The distributions of Cu very different among the filters. It should be kept in mind that only a few samples were selected for the purpose of testing out the BCR extraction and CE analysis method, and therefore, it is uncertain as to whether these differences in the distribution of Cu were due to some experimental error or whether there is an actual reason for them. No Cu was detected in the oxidisable fraction for any of these filters. In the Friday mid-day sample, collected at the outlet of the tunnel, Cu was quite evenly distributed between the four fractions (F0, F1', F2, F4). In the corresponding inlet sample

(Friday mid-day), some Cu was present in each of the water-soluble, acid-soluble, and reducible fractions, but most was present in the residual fraction (~82%). The filters from the outlet end, Saturday morning contained small amounts of water-soluble and acid-soluble Cu, with the majority in the residual fraction (~93%). There were no XRF data for Cu in the corresponding inlet end filters, so this one could not be included in the graph. The Cu distributions in the inlet and outlet samples collected on Monday afternoon were relatively similar to each other, with the exception that a small quantity of reducible Cu was present in the outlet PM but none in the inlet PM. Both inlet and outlet had significant amounts (about 45-50%) of the total Cu in the water-soluble fraction, small amounts in the acid-soluble fraction, and the considerable remainder in the residual fraction.

Manganese: As is evident in, the manganese in all of these filters was almost entirely distributed between the water-soluble fraction (~28-72%) and the residual fraction (~27-70%). The only other fraction in which Mn was detected was the acid-soluble fraction, which contained only minor amounts. These results suggest that a considerable proportion of the Mn in these Tunnel Study PM samples would be environmentally mobile.

3.3.3 Urban versus anthropogenic-rich PM_{2.5} samples

To compare the metal distributions in the two types of airborne PM, Figure 18 illustrates the average distributions of the studied metals observed in the urban PM_{2.5} and the PM_{2.5} collected in the highway tunnel. The metal

distributions are fairly similar. The fact that the tunnel study PM represents an anthropogenic-rich source (vehicle emissions) suggests that the average trace metal fractionation signature of studied urban PM_{2.5} is characteristic of anthropogenic-rich sources.

Iron was essentially refractory in character in both types of PM samples. However, Fe had more water-soluble character in the urban ambient air PM compared to the tunnel study PM. This may be due to the higher proportions of sulphate and/or a complexing agent such as oxalate that were present in the urban air PM. There is also evidence of increasing Fe solubilities in urban aerosols after acidic cycling, a process that the tunnel study PM did not undergo. Airborne aerosols are typically exposed to about 10 condensation/evaporation cloud cycles before removal by rain, and as a result of the uptake of H₂SO₄ and HNO₃ and SO₂ oxidation, cloudwater pH can be very low. It has been proposed that organic complexation may play a role in this process by holding Fe that would have solubilized at low pH in solution at high pH [58]. In general, Zn, Cu and Mn were partitioned between the exchangeable (water- and acid-soluble), reducible, and refractory fractions. All three of these metals had high proportions of their total concentrations in the exchangeable fractions in both types of aerosols, indicating that anthropogenic sources, such as vehicle emissions, are the dominant sources of Cu, Zn and Mn in urban PM. Cadmium was also dominant in the exchangeable fraction, and therefore, seemingly has significant anthropogenic origins, but it was found in only one sample of urban air PM. Despite the variations, the average partitioning of metals into exchangeable

fractions of PM_{2.5}, and hence their degree of environmental mobility, decreased in the order: Zn > Mn > Cu > Fe (Cd is excluded because it was detected only in the urban air PM in only one sample).

In summary, the results showed that, in both kind of investigated particulate matter, the different metals are distributed differently among the various compounds or phases of the atmospheric particles, and are therefore, bound with different strengths. Thus, their potential mobility and bioavailability are strongly dependent upon their chemical (operational) speciation. It has been reported that metals that are prominent in the easily exchangeable (loosely bound) forms have the potential for being highly mobile and bioavailable via inhalation into the lungs [54, 69]. In addition, metals bound to organic matter (F3) can also easily pass through lung tissues [54].

On the basis of the present data it may therefore be concluded that zinc, copper, manganese and cadmium are the most potentially hazardous metals due to their substantial presence in loosely bound forms (water and acid soluble) in both kinds of studied PM_{2.5}. Consequently, these metals would be the most easily available to ecosystems via atmospheric deposition and to the human body through breathing.

Although only a small number of filter samples were selected for the purpose of testing out the studied BCR extraction and CE analysis method, the metal fractionation patterns observed in these results were quite consistent with results reported in the literature, and also seem to make sense in relation to the

different source types. Thus, this seems to have been sufficient to demonstrate the feasibility and usefulness of applying the BCR sequential extraction method with CE analysis for the determination of fractionated metals in filter-collected airborne PM samples.

Figure 18. Average distributions of metals in (a) urban air PM_{2.5} and (b) highway tunnel PM_{2.5}

4 FUTURE WORK

As discussed in Chapter 1, the bioavailable fraction of heavy metals present in airborne PM can be estimated by using various leaching solutions such as water, weak acids, or salt solutions. However, these solutions are obviously quite different from the make-up of lung fluids, which would be encountered by the particles upon inhalation. Recently, Voutsas and Samara [69] reported an interesting study in which a synthetic serum was used for estimating the bioaccessible metal fractions in fly ash. A mild neutral solution, simulating serum, was selected for the study to avoid difficulties and expenses associated with the use of normal serum as well as to achieve more realistic leaching under biological conditions than those provided by the more conventional solutions (e.g., water or weak acids). Thus, future work could be done to investigate the use of a synthetic serum for extracting the potentially bioavailable metal fraction in filter-collected PM_{2.5}. Furthermore, the results obtained from such studies could be compared with those obtained in this work.

In addition, it would be useful to study the distribution, and thus, the potential bioavailability, of other toxic metals present in airborne PM, such as Ni, V or Cr. For example, it has been reported, that inhalation exposure to Ni and V salts produce a variety of toxic responses, including acute lung injury, inflammation, emphysema, fibrosis and cancer [107]. Other separation and/or detection methods with adequate sensitivity, such as ICP-MS, could also be investigated.

Future research could be further expanded to include the chemical characterization of ultrafine particles (those with diameters smaller than $0.1\ \mu\text{m}$), which are present in the atmosphere at very high particle number concentrations but at low mass concentrations, and may be particularly harmful [108]. To date, there are limited data in the technical literature that document the chemical composition of atmospheric ultrafine particles. Having information of the characterization of ultrafine PM, in addition to fine PM, would lend to a better and more detailed understanding of the sources and potential health threats of airborne PM.

5 SUMMARY

The potential for capillary electrophoresis combined with a BCR sequential extraction scheme to determine the distribution of selected metal ions in airborne particulate matter was evaluated in the present work. The studied BCR extraction scheme differentiates between metals in three fractions: “exchangeable and acid-extractable”, F1 (0.11 mol/l acetic acid), “reducible”, F2 (0.1 mol/l HAHCl acidified to pH 2.0 with HNO₃) and “oxidisable”, F3 (1.0 mol/l NH₄Ac extraction after oxidation by 8.8 mol/l H₂O₂). Simultaneous quantification of Fe(II), Zn(II), Cu(II), Mn(II) and Cd(II) ions in extracts of airborne PM was obtained using 1,10-phenanthroline as a pre-capillary derivatisation reagent for direct UV detection in CE.

In the first part of this work, suitable CE experimental conditions including detection sensitivity for measuring the trace metals in the BCR extracts were optimized. In the interest of obtaining the best possible sensitivity, two injection modes, hydrodynamic (pressure) and electrokinetic, were investigated. Electrokinetic injection gave better sensitivity results and could be used (5 kV, 45 s) for determining metals in water, E1, and E2, with no more than 2-fold dilution (the necessary dilution because of the addition of other reagents for pre-capillary derivatisation). For metals in E3, pressure injection (0.5 p.s.i., 10 s) had to be used and the samples had to be diluted at least 20-fold because of the high ionic strength of the E3 solution. The limits of detection were determined for all studied metals in each matrix under these optimized injection conditions. With

EK injection (5 kV for 45 s) the detection limits were below 4 µg/l and 12 µg/l in two-fold diluted E1 and E2 matrices, respectively. LODs of the metals dissolved in 20-fold diluted E3 matrix, using pressure injection (0.5 p.s.i. for 10 s), ranged from 25 to 66 µg/l. The analytical performance in terms of linearity and precision was quite good. The correlation coefficients for linearity for the five metals in the different matrices were between 0.9987 and 0.9999. Precision (expressed as % RSD) for corrected peak area (CPA) and migration time were less than 5% and 1%, respectively, for all metals in all matrices. The method was also validated with respect to accuracy by comparisons with other analytical techniques (AAS and IC), from analyses of selected samples that were also analysed by CE. Overall, the results indicated a good performance of the CE method.

The second part of this work dealt with the BCR sequential extraction method. In an effort to speed up the process and improve sample throughput, the BCR sequential extraction scheme was modified by using ultrasonication in an ultrasonic bath instead of the mechanical stirring that is used in the conventional BCR method. The performance of the accelerated BCR sequential extraction method, in comparison with the conventional method, was evaluated using a Standard Reference Material, NIST 1648 Urban Particulate Matter. Based on experiments to determine the optimum extraction times for each step in the accelerated method, the following extraction times were selected: 15 min for F1, 45 min for F2, and 60 min for F3. This was a considerable reduction in the overall operating time compared with the conventional method. In fact, the total extraction time was shortened from 51 hours (excluding the evaporation time) to

2 hours (excluding the evaporation time). There were some differences in the extraction results between the accelerated and the conventional method, but overall they were reasonably comparable, especially in light of the significantly reduced operating time. The precision of both the conventional and the accelerated BCR extraction scheme were below 10% RSD for most metals in the three fractions. In a few cases, precision was poorer (RSD less than 20%), probably because of either inadequate selectivity of the extraction step or the low concentration of the metal present in the PM.

The distribution of metals in the NIST 1648 Urban PM decreased in the order $Zn > Cd > Mn \cong Cu > Fe$ in the water/acid soluble fraction; $Cu, Fe > Mn > Zn$ (Cd was below its LOD) in the reducible fraction; $Cu > Fe > Zn$ (Mn and Cd were below their LODs) in the oxidisable fraction; and $Fe > Mn > Zn \cong Cu > Cd$ in the residual fraction (calculated for each metal by the difference between the total certified content and the sum of the extracted fractions).

The finalised method was then tested out on some real filter-collected $PM_{2.5}$ samples from two different source types, urban ambient air $PM_{2.5}$ and $PM_{2.5}$ samples from a highway tunnel. In order to follow the analytical protocol used in the Inorganic Laboratory of the AAQD, the original BCR method was further modified to include water extraction before first BCR extraction step with acetic acid, because the filter-samples were extracted with water for IC analysis of water-soluble ions prior to performing the BCR sequential extraction for metal fractionation. Based on experiments done with the NIST 1648 PM, there was no

significant difference between the extraction results in the original F1 fraction and the sum of the new F0 (water) and F1' (acetic acid) fractions.

The metal distributions observed in the urban $PM_{2.5}$ and the $PM_{2.5}$ collected in the highway tunnel were found to be fairly similar. Since the tunnel study PM represents an anthropogenic-rich source (vehicle emissions), it seems that the urban $PM_{2.5}$ is characteristic of anthropogenic-rich sources.

Additionally, the results showed that Zn, Cu, and Mn were generally present at significant levels in loosely bound forms (water/acid extractable), indicating they would be highly mobile and potentially bioavailable. Cadmium also fitted into this group, but it was only detected in one sample. Consequently, these metals would be the most easily available to ecosystems via atmospheric deposition and to the human body through breathing. Iron in these samples was largely refractory, which was consistent with it being primarily a crustal element. As such it would not be very mobile/bioavailable. In general these findings are consistent with other reported studies.

Although the metal distribution was only determined in a few real $PM_{2.5}$ samples using the studied analytical methodology, it can be concluded that the application of the sequential leaching scheme to airborne PM samples provides chemical fractionation data that reflect the general sources and potential health hazards of these metals. This type of information is valuable in understanding possible consequences of human exposure to airborne PM, as well as in identifying the sources and (hopefully) finding ways to reduce them.

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