THE UNIVERSITY OF CENTRAL OKLAHOMA
Edmond, Oklahoma
Jackson College of Graduate Studies

Forensic Analysis of Cigarette Ash: Brand Determination through Trace-metal Analysis

A THESIS

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE

by

Anja C. Groth

Edmond, Oklahoma

2013

Forensic Analysis of Cigarette Ash: Brand Determination through Trace-metal Analysis

By

Anja C. Groth

A THESIS

APPROVED FOR THE FORENSIC SCIENCE INSTITUTE

JULY 2013

By _____

Thomas H. Jourdan, Ph.D.   Committee Chairperson

_____

Fakhrildeen Albahadily, Ph.D.   Committee Member

_____

Cynthia K. Murray, Ph.D.   Committee Member

Acknowledgements

Table of Contents

List of Tables

List of Figures

Abstract

Although cigarette ash is frequently encountered at crime scenes, it has largely been ignored in a forensic context (Fisher, 2004). Few efforts have been made to utilize the information present in the form of trace-metal concentrations even though these could indicate the brand the ash originated from which could potentially help place suspects at crime scenes or assess how many people may have been present at a scene (Peréz-Bernal et al., 2011).

The focus of this study is to distinguish cigarette brands based on the trace-metal concentrations in their ash in a forensic context. The study included commercial cigarettes procured in America, as well as American and foreign brands purchased in different countries. Cigarettes were ashed, or "smoked", using a variable-pressure peristaltic pump, mimicking various smoking parameters reflecting the range of human smoking habits. The ashed samples were digested in a mixture of nitric acid and hydrochloric acid using a microwave digestion system and then analyzed using inductively coupled plasma-mass spectrometry (ICP/MS). From the elemental data collected various statistical models were then created using principal component analysis (PCA) to detect intrinsic differences between brands and partial least squares-discriminant analysis (PLS-DA) to discriminate between brands. Results showed that brand classification yields good sensitivity and specificity results as does the distinction between cigarettes originating from the U.S. or internationally. Varieties within one brand, however, are not as easily distinguished. This study concluded that varying smoking parameters did not have any effect on the classification of ash samples.

Introduction

More than six trillion. That is how many cigarettes are sold worldwide each year (Shafey, Eriksen, Ross, &Mackay, 2009). Thus, it is not surprising that cigarette litter is one of the most common forms of trash. Cigarette butts alone constitute 20-50% of the litter items found in streets and are the single most frequently collected item during beach clean-ups. However, streets and beaches are only two examples of where the 5.6 trillion cigarette butts which are being tossed into the environment worldwide every year wind up (Healton, Cummings, O'Connor, & Novotny, 2011; Smith & Novotny, 2011).

Cigarette butts, along with the accompanying ash, are also truly ubiquitous items of trash in the United States. Being one of the top five cigarette consuming countries in the world with over 300 billion sold annually, the United States are indubitably affected by the issue of cigarette-related littering (Centers for Disease Control and Prevention [CDC], 2012). This is confirmed by the 2009 Visible Litter Study, commissioned by the Texas Department of Transportation, according to which 43% of all pieces of litter found on or along Texas highways are tobacco-related.

Crime scenes are no exception in this regard. Cigarette-related litter is frequently encountered at sites of any kind of criminal activity. Cigarette butts, which can potentially carry the smoker's DNA and indicate the brand of the cigarette, have been extensively explored and have long played an important role in criminal investigations (Fisher, 2004). However, according to theories surrounding the so-called *CSI Effect* criminals are becoming increasingly aware of the significance of the evidence they leave behind and take measures to reduce the amount of potentially individualizing items, such as cigarette butts (Durnal, 2010). What stays behind is cigarette ash, which has largely been ignored in a forensic context (Fisher, 2004).

Although a common occurrence at crime scenes, little effort has been made to evaluate the information present in cigarette ash in the form of trace-metal concentrations which can potentially point to the brand the ash originated from. For example, in cases where no cigarette butts are present yet ash is found, the ash could be a valuable tool to gather information on potential suspects or the number thereof.

Statement of the Problem

The hypothesis of using cigarette ash as a forensic tool has several aspects. First, it is necessary to link the theoretical basis of cigarette-brand distinction based on the trace-metal concentrations in the ash to the experimental exploration of the issue. The next problem is the lack of an established procedure for this type of analysis and lastly, it has not been determined whether such an analysis could be meaningfully employed in a forensic context. These three problem areas will be outlined in more detail in the following.

The basis for any analysis determining the brand of a cigarette based on the trace-metal concentrations of its ash is dependent on the existence of a significant difference between intra-brand and inter-brand variations of trace-metal distributions. Any assessment of the intra-brand-inter-brand difference needs to be based on thorough knowledge of tobacco growing practices and cigarette manufacture since it is here that the trace-metal content of every cigarette brand is determined. Hence, there is a need to link an experimental investigation of whether this distinction is possible to an understanding of the origin of trace metals in cigarettes which, to the knowledge of the author, has not been done.

The examination of this distinction is invariably linked to the development of an established procedure, including a standard manner of sample preparation, a routinely used analytical technique, and a recognized method of data analysis. The possibly most critical issue

in this regard is the establishment of the smoking regime since this is one of the aspects which determine whether the developed procedure can be meaningfully applied in the context of forensic science. For reasons discussed later on, commercial smoking machines which are utilized in different areas of research involving cigarettes have been severely criticized for not mimicking real-life smoking behavior and it is uncertain to what extent this influences the concentrations of volatile components in smoke and thus in ash (International Organization for Standardization [ISO], 2005). If individual variations in smoking topography have a significant influence on the trace-metal yields in ash, it has to be determined if any of the elements considered for analysis are sufficiently non-volatile to be unaffected by different smoking parameters. If this is not the case, it might not be possible to use this analysis in a forensic context even if it is theoretically possible to distinguish cigarette brands based on their trace-metal concentrations.

This relates to another common issue in the field of forensic science, comparability. With forensic science being a comparative science, samples collected at crime scenes or from suspects are only limitedly useful if they cannot be compared to each other or to reference materials. This is true for every sub-discipline including but not limited to DNA analysis, toxicology, drug analysis, firearm and toolmark examinations, and latent fingerprints. Therefore, databases such as the Combined DNA Index System (CODIS) for DNA profiles or the Integrated Ballistics Information System (IBIS) for firearms have been established in order to facilitate the comparison of newly collected samples to either profiles already in the system or to reference data regarding class characteristics. However, no such database exists for trace-metal profiles in cigarette ash and thus, if ash samples were collected at a crime scene they would be of little value at this stage even if their trace-metal profiles could be reliably determined. In order to

utilize such a database with the aim of determining the brand of an unknown sample, it is necessary to develop a classification tool which is capable of placing an unknown ash sample which has been analyzed as to its trace-metal contents in the correct class (brand).

All these factors point towards the general problem that limited research has been conducted in this area. As such, there is a fundamental need to address the three problems outlined above in order to utilize the information present in cigarette ash which can potentially provide helpful clues in criminal investigations as will be discussed later on.

Background

There have been a number of peer-reviewed studies which are scientifically relevant to the hypothesis outlined above. A short summary of the relevant literature is provided to orientate the reader to this study and its purpose within current forensics research.

Data on the origin of tobacco used in American cigarette brands demonstrates that there is a great variety of cultivation areas (Geiss & Kotzias, 2007; Philipp Morris, 2011). The soil in each one of these areas has distinct natural trace-metal concentrations which are influenced by a number of factors (Moermann & Potts, 2011). Moreover, one needs to take into account that the natural trace-metal concentrations in the soil do not directly translate into the trace-metal concentrations in the tobacco plant. There are several variables which influence the ability of a plant to take up trace metals from the soil it is cultivated in (Golia, Dimirkou, & Mitsios, 2007¸ Golia, Dimirkou, & Mitsios, 2009; Moermann & Potts, 2011; Swami, Judd, & Orsini, 2009). Given these findings and the fact that cigarette manufacturers aim to keep the taste of a cigarette brand consistent by using specific formulations for every product offering there is reason to believe that the trace-metal profiles of different cigarette brands are sufficiently distinct to serve as a means of differentiation.

With the exception of two previous studies which will be discussed in detail, research on the trace-metal composition of cigarettes has primarily been carried out in the field of environmental studies and health sciences. The goal in this context is typically to determine the concentrations of specific metals and whether these amounts are detrimental to human health or the environment (Çevik et al. 2003; Moermann & Potts, 2011; Ryan & Clark, 2011; Wang & Finlayson-Pitts, 2003; Zulfiqar, Shabbir, Ishaq, Shaukat, & Sarwar, 2006). The only prominent forensic application of trace-metal determinations in cigarettes has been the distinction between genuine and counterfeit products (Giordani, Rizzio, & Brandone, 2005; Swami et al., 2009). While some of these studies involve trace-metal determinations in ash, they mainly focus on the concentrations in cigarettes prior to smoking or in the smoke. However, these previous studies provide valuable information on the advantages and disadvantages of different sample preparation procedures and analytical methods. The analytical techniques used in the context of cigarette and cigarette-ash analysis include energy dispersive x-ray fluorescence (EDXRF), instrumental neutron activation analysis (INAA), atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP/AES), and inductively coupled plasma-mass spectrometry (ICP/MS) (Çevik et al., 2003; Giordani et al., 2005; Zulfiqar et al., 2006; Moermann & Potts, 2011; Ryan & Clark, 2010; Wang & Finlayson-Pitts, 2003; Swami et al., 2009). Various sample preparation protocols have likewise been tested and evaluated.

With regards to the forensic applicability of trace-metal based cigarette distinction, two studies need to be reviewed more closely. Giordani et al. (2005), using NAA to distinguish between genuine and counterfeit Italian cigarettes, demonstrated that for their sample distinguishing cigarette brands is possible based on the trace-metal profiles of the tobacco. Peréz-Bernal, Amigo, Fernández-Torres, Bello, & Callejón-Mochón (2011) focused more

closely on this specific hypothesis by discriminating between Spanish cigarette brands by analyzing the ashes after smoking. This is the only study which directly focuses on this hypothesis and yet, the concept of cigarette-brand determination was only a secondary thought rather than the main purpose of the study. This preliminary study only took Spanish cigarettes into consideration and thus it is not certain whether the distinction can be applied to all cigarette brands produced around the world.

Neither the study by Pérez-Bernal et al. (2011) nor any of the other studies measuring trace-metal contents in ash, evaluate the effect of different smoking regimes on the trace-metal concentrations. The need for this evaluation becomes apparent when looking at the extensive body of literature on the ongoing controversy surrounding smoking machines and whether such a construct as a "standard" regime can be established at all considering the unique smoking patterns of each individual (ISO, 2005). There have been several studies which have been carried out with the goal of establishing how different smoking regimes reflect human smoking behavior with regards to the uptake of tar and nicotine. These studies have demonstrated that there are numerous factors which influence smoking topography and that this has an influence on the distribution of volatile components between the gas and the particulate phase (i.e. ash). Defenders of standard smoking machine regimes claim that this is not a problem since studies involving these regimes are solely designed to enable a comparison between different brands of cigarettes with regards to toxic contents. These studies have stated that the purpose is not to measure the actual amounts of toxic substances taken in by humans during the process of smoking (Baker, 2002; ISO, 2005; Kassel et al., 2007; Purkis, Troude, Duputié, & Tessier, 2010; Veilleux et al., 2011). Analogously speaking, thus far only the general comparison has been shown to be possible by Pérez-Bernal et al. (2011) (and only for Spanish samples) while the real-

life application is still questionable. This is because some of the elements of potential interest in ash analysis are volatile to varying extents and hence partition between the particulate phase and the gas phase in different ratios which could be influenced by the smoking parameters. These elements include As, Se, K, Cr, Zn and possibly others (Iskander, 1986).

As mentioned previously, analytical results are of little value without a database to compare them to in order to identify the source material. Nowhere in the literature is there an indication as to the existence of a trace-metal profile database for cigarette ash. However, Peréz-Bernal et al. (2011) provide useful information with regards to the development of a discriminant model which can be developed using a database and which can then be employed in order to carry out the classification of the ash. Pérez-Bernal et al. (2011) developed such a tool using partial least squares-discriminant analysis (PLS-DA) and obtained satisfactory results for both sensitivity and specificity, however, a step-wise approach first classifying tobacco samples as blond or black (mainly being composed of Virginia or dark tobacco) was employed and other possible models were not explored. Taking these findings from literature into consideration, a study to address the problems previously outlined was designed.

Purpose of Study

The purpose of this study is to test the hypothesis that trace-metal content in cigarette ash can be used in forensic investigations. This encompasses grounding the actual analysis in a strong theoretical basis by consolidating knowledge on the tobacco growing process, cigarette manufacture and the rationale behind specific cigarette formulations.

The experimental portion of the study investigates whether it is possible to strengthen the results obtained by Pérez-Bernal et al. (2011) by demonstrating that inter-brand variation is significantly larger than intra-brand variation in cigarette brands available in the U.S. These

brands will be distinguished based on their trace-metal profiles in a similar manner as it has been shown for Spanish products. This study will expand the early accomplishments of Pérez-Bernal et al. (2011) by examining whether cigarettes of the same brand produced in different countries can likewise be differentiated using their trace-metal profiles and whether products only available in their specific countries of origin, in this case outside of the U.S., are sufficiently different to be distinguished. Another aspect is to compare and evaluate techniques which have been used in this context in order to establish an analytical procedure which can be used as the standard for this kind of analysis.

Another purpose of this study is to address the forensic applicability of employing relatively volatile elements, such as Br, Cd, and Pb and exploring the influence of different smoking parameters. The launch of a database of cigarette ash trace-metal profiles including the most popular U.S. brands and their variations as well as foreign samples of the same brands and the most popular foreign brands is also part of the objective of this study since it is a prerequisite for the use of this technique in criminal investigations. The overall purpose is to use the data from the constructed database to develop a discriminant model capable of determining the brand an unknown ash sample collected at a crime scene could have originated from.

Scope of Study

The scope of this study is bounded by the following three areas:

1. The purpose of this study is not to develop a model to determine the lot number of the pack of cigarettes or where exactly or at what point in time a pack of cigarettes which a particular ash sample originated from was purchased. Thus, it will not be possible to back-track the ash to the person who purchased it based on the results of this study.

2.   It is not the goal of this research to establish a smoking regime which mimics "average"

        human smoking topography. The idea is rather to determine in how far trace-metal

        profiles are influenced by the fact that there may not be such thing as "average" human

        smoking behavior.

3.   The study does not attempt to create a database comprising all cigarette brands

        commercially available in the U.S. or all varieties of every brand. Neither is it within the

        scope of this study to compare cigarettes of the same brand from all over the world with

        each other. This part of the present study is rather exploratory and should be considered

        as the basis for further research. Moreover, neither self-rolled cigarettes nor cigars whose

        ash seems to fall into the same trace-metal-concentrations range as that of cigarettes were

        taken into account (Verma, Yadav & Singh, 2010). Efforts assessing the metal contents

        of these types of tobacco products should be included in further research.

Significance to the Field

There is no indication as to the existence of a forensically-used analysis which takes

advantage of the information present in cigarette ash. This information, however, can be

valuable in instances where ash is encountered without the corresponding cigarette butt. There is

a range of scenarios in which knowledge of the cigarette brand derived from the trace-metal

concentrations in the ash could prove useful. For instance, it could assist in placing a suspect at a

crime scene. If an ash sample from a crime scene is analyzed and its brand, which is determined

using the trace-metal profile database, coincides with the brand the suspect is known to smoke,

this is corroborating evidence. Moreover, known and unknown ash samples can be directly

compared with regards to their trace-metal concentrations. If a sample collected at a scene yields

a profile which is distinctly different from those already in the database, this would be an

indication that the perpetrator smokes an uncommon brand. If the ash encountered originated from a foreign brand this could be evidence of connections abroad or of recent travel to a foreign country. This information can be used in cases where there is already a suspect (as outlined above), in cases where there are a number of suspects, in which case it could help narrow the number of suspects down, and in cases where there is no suspect, in which case information derived from the ash could provide new clues. Ash could also assist in presumptively establishing the number of people who were present at a scene if ash from more than one brand of cigarettes is detected. The ability to analyze ash samples paired with access to a database could thus provide investigators with new leads and additional information regarding possible suspects.

Literature Review

The literature review will address different areas of research related to the analysis of trace-metal profiles in cigarette ash. The first issue addressed is the theoretical trace-metal-based distinction of cigarette brands which will be grounded in a review of tobacco growing and cigarette manufacture. The second section will discuss studies related to analytical protocols used in cigarette analysis whereas the last section will focus on research related to the forensic applicability of trace-metal analysis of cigarette ash.

Theoretical Distinction of Cigarette Brands Based on Elemental Composition

A sufficient difference between inter-brand and intra-brand variations in trace-metal contents of ash is the premise for the proposed analysis. In order to determine whether inter-brand variation is sufficiently larger than intra-brand variation it is necessary to take a closer look at the origin of tobacco and the trace metals contained in it. Since the manufacturing process also has an influence on the final trace-metal concentrations, it is necessary to take this

into account as well. An assessment of how distinct the trace-metal profiles of different brands can possibly be considering the origins of the tobacco used and the formulations utilized during manufacture will thus be possible. Exploration of this phenomenon will facilitate a thorough assessment of the theoretical feasibility of trace-metal-based cigarette brand distinction in the context of this study.

Origin of tobacco. There are several different types of tobacco, three of which are of particular interest to the current cigarette study: Bright (also known as flue-cured/Virginia, 40% of tobacco production worldwide), burley (11% of production worldwide), and oriental (also known as Turkish, 16% of production worldwide). The main producers of bright tobacco are China, the U.S., Brazil, India, and Zimbabwe, while the U.S., Italy, Korea, Brazil, and Mexico are leading in the production of burley. Russia, Turkey, Bulgaria, Greece, Serbia, Romania, and Italy are the primary producers of oriental tobacco. American blends typically consist of a mixture of bright, burley, and oriental tobacco, with bright tobacco constituting approximately 50% of the blend, burley about 37%, and oriental roughly 13%. In contrast, German-blend cigarettes have a higher percentage of oriental tobacco while English-blend cigarettes consist almost exclusively of bright tobacco. The bright and burley tobacco used in the manufacture of American-blend cigarettes is grown in the U.S. Bright tobacco is primarily grown in Virginia, the Carolinas, Georgia, Alabama, and Florida while burley is principally grown in Kentucky and Tennessee. Additional bright tobacco cultivation sites include North Carolina, Virginia, West Virginia, Indiana, Ohio, and Missouri. Oriental tobacco is, for the most part, imported from Mediterranean countries (Geiss & Kotzias, 2007; Philipp Morris, 2011).

Trace-metal uptake during the tobacco growing process. Regardless of where the tobacco is grown, it takes up some concentration of trace metals. The amount of trace metals

that a tobacco plant takes up depends on a number of environmental and plant-genetic factors

which are outlined below. While metals can also be taken up by air deposition, the prime source

of trace metals is the soil the plant is cultivated in. The amount of trace metals present in the soil

is not necessarily consistent in different regions but can be influenced by several factors such as

cultivation practices and industrial activity in the vicinity of the fields. In terms of cultivation

practices, one of the most important factors is the use of fertilizers and pesticides which alter the

natural metal concentrations of the soil stemming from the underlying bedrock (Moermann &

Potts, 2011; Swami et al., 2009).

Apart from the total concentration in the soil, it is also important to consider the amount

of trace metals available for uptake by certain plants. The tobacco plant, *Nicotiana tobaccum,*

absorbs metals from the soil at unusually high concentrations (Swami et al., 2009). As an

extensive six-year study by Golia et al. (2009) has shown, the pH of the soil has the most

significant impact on the fraction of trace metals which is actually available for uptake. Metal

concentrations and pH are negatively correlated meaning that the bioavailability of metals in soil

is higher in an acidic environment. A positive correlation exists between the amounts of metals

available for uptake by the plant and the concentrations in the leaves meaning that those

concentrations can be roughly predicted using a regression model. In this context it is important

to note that the metals are not evenly distributed throughout the tobacco plant. Lower leaves

("first priming") exhibit greater levels of trace metals than upper leaves ("second priming")

which can be explained by the low mobility of metals in the plant. This tendency holds true for

burley, Virginia, and oriental tobacco and for a range of metals. In an earlier study, Golia et al.

(2007) also observed that burley tobacco generally had a higher concentration of metals, possible

reasons for which include different reactions to an accumulation of metal, or the increased use of

fertilizers in the cultivation of burley tobacco as opposed to Virginia and oriental tobacco. It is,

however, important to note that the metals examined in both studies were limited to Zn, Cu, Ni,

Cd, Fe, and Mn, and Zn, Cu, Cd, and Pb, respectively (for full names of all elements mentioned

see Table 7). Thus, not all potential metals of interest in the analysis of cigarette ash were

included. Moreover, since this study was conducted in Greece the specific values of metals

measured in soil and tobacco leaves cannot necessarily be transferred to U.S. soil, however, the

general tendencies are likely to hold true for tobacco cultivation regardless of the location.

Additionally, it is important to note that different metals exhibit varying degrees of

mobility indicating that heavy metals such as Cd, Pb, and Zn are preferentially taken up by

plants. Metal-interactions likewise play a role. For instance, cadmium uptake is higher in the

presence of lead (Verma et al., 2010).

The influence of the manufacturing process. The amounts of trace metals which are

accumulated in the plant during its cultivation are not equivalent to the final amounts of trace

metals present in the finished cigarette product. There are many steps involved in the processing

of tobacco and the manufacture of cigarettes, all of which have different degrees of influence on

the final trace-metal concentrations (Iskander, 1992; Baker, Pereira da Silva, & Smith 2004b¸

Baker, Pereira de Silva, & Smith, 2004a). After the tobacco is harvested, the leaves are cured in

order to reduce the moisture and to eliminate the chlorophyll. Different curing techniques are

applied in the processing of different types of tobacco. Bright tobacco is generally flue-cured

while burley is air-cured. There is no evidence that the curing process significantly alters the

amounts of metals present and it will thus not be discussed in more detail (Geiss & Kotzias,

2007). Previous researchers have demonstrated that tobacco processing as a whole augments the

trace-metal concentrations since both cigars and cigarettes exhibit higher levels of trace metals than tobacco which is used in self-rolled cigarettes (Verma et al., 2010).

Traces of certain metals are also introduced through additional components of the cigarette which can include the wrapping paper (Iskander, 1992), and the casing (Baker et al. 2004b). The addition of flavorings and additives does not seem to have a significant influence on the amount of metals present in the tobacco (Baker et al., 2004a).

Due to the fact that U.S.-branded cigarettes are a blend of various types of tobacco grown in different regions within and outside of the U.S. it is impossible to trace the metals back to a particular area of land without knowledge of the exact formulation of a cigarette brand. Since these formulations are proprietary, it is not likely that access will be granted easily. However, considering that customers expect a certain consistency in the quality, taste, and strength of their cigarettes, formulations are very detailed with regards to the exact tobacco blend, the paper, filter and even the printing on the paper. They are designed to assure that the taste associated with a specific brand will be available on a long-term basis (British American Tobacco [BAT], 2011). In addition, one has to bear in mind that a number of elements are involved in the proposed analysis which are present in varying amounts in different soils and which are individually affected by the factors listed. Therefore, it is reasonable to hypothesize that the inter-brand differences with regards to trace-metal concentrations are larger than the intra-brand differences which is the condition for the development of an effective discriminant model.

Analytical Methods Used in the Trace-Metal Analysis of Cigarettes

Having established that cigarettes can theoretically be distinguished based on their trace-metal concentrations, one can now move on to assess what sample preparation methods and analytical procedures are most suited to carry out such an analysis. As previously mentioned, the

bulk of the research concerned with determining trace-metal amounts in the context of cigarettes

has focused on metals impacting health and environment while single studies have examined the

distinction of genuine and counterfeit cigarettes. These studies have measured the trace-metal

concentrations in cigarettes prior to smoking, the concentrations in the smoke produced during

the combustion process, the concentrations in cigarette butts after smoking and the

concentrations in the ash. Some of these studies will be discussed more thoroughly here,

specifically with regards to the methods utilized.

Since this study focuses on the trace-metal concentrations in ash, it is necessary to define

what ash actually is and how it is produced during the combustion process in order to set it apart

from other cigarette by-products. Ash is the residue left when a cigarette is burnt resulting in

white, grey, and black powder. Ash particles are typically in the order of 2µm in size. During

combustion, the region of the cigarette where the tobacco is present typically experiences

temperatures up to 400°C between puffs and up to 900°C during a puff (Zulfiqar et al., 2006;

U.S. Department of Health and Human Services [DHHS], 2010).

One of the most basic studies examining ash is that by Wang and Finlayson-Pitts (2003).

The purpose of the study was simply to devise an ICP/MS experiment with a real-life application

for undergraduate instrumental analysis laboratory courses. The concentrations of Zn, Fe, and Cr

were measured in Camel tobacco, Marlboro tobacco, and their respective ashes as well as in a

Marlboro filter before and after smoking.

With regards to sample preparation, Wang and Finlayson-Pitts (2003) used pipette bulbs

to draw air through the cigarettes and thus "smoke" the cigarette in order to procure the ash

samples. This is a deviation from the frequently-used method utilizing smoking machines which

will be discussed in greater detail. Two different ash digestion methods were considered in this

study. The first method dissolved the ash sample in concentrated nitric acid at room temperature for 30 minutes. The second method employed heating the ash and nitric acid solution to 100°C for two minutes. In both cases the mixture was subsequently diluted with nanopure water and filtered. No significant difference was found between the two extraction methods with regards to efficiency. The analytical technique of choice was ICP/AES which has several advantages such as the possibility of measuring multiple elements simultaneously, a large linear dynamic range, low limits of detection and a rapid analysis.

Ryan and Clark (2010) set out to confirm the results obtained by Wang and Finlayson-Pitts (2003) pointing to the relevance of their analysis in the context of health concerns. This study likewise used ICP/AES to measure trace metals in the same samples chosen by Wang and Finlayson-Pitts (2003) (Marlboro and Camel tobacco and ash, Marlboro filter before and after smoking) . Targeting As, Cr, Zn, and Fe, they slightly broadened the range of elements examined. Ash samples were produced by "smoking" the cigarette using a pipette bulb and sample preparation followed the same steps outlined in the study discussed previously. The results were not consistent between trials or with those obtained by Wang and Finlayson-Pitts (2003). The authors stated that values for some of the elements had to be extrapolated since they fell outside the concentration range of the standard solutions used. Additional reasons could simply be inherent differences in the cigarettes used. This does not necessarily mean that intra-brand variation is too large to allow for brand determinations since only a small number of elements were measured and the accuracy and precision of the results cannot be determined due to the low number of trials in both studies. Moreover, it is noteworthy that the results still fall within the range of concentrations reported by Iskander (1986) for unspecified "American" cigarettes.

Zulfiqar et al. (2006), analyzing ash samples with a view to determining both the impact on human health and the environment, chose a slightly different range of elements (Ni, Cr, Zn, Cd, Pb, Cu). The concentrations of these elements were measured in the ash of 15 different Pakistani brands as well as 15 different foreign brands including both Marlboro and Camel which were also used by Wang and Finlayson-Pitts (2003) as well as by Ryan and Clark (2010). Zulfiqar et al. (2006) chose a third method of converting the cigarette into ash. Rather than utilizing a pipette bulb or a smoking machine they simply lit the cigarettes and left them to go through the combustion undisturbed. The analytical technique of choice in this study was AAS which has the disadvantage of only being able to analyze one element at a time, yet provided greater sensitivity and precision than previous studies using AES. The results obtained for the amount of Zn and Cr in the Camel and Marlboro ash differ greatly from those obtained in the studies previously discussed which can be due to a variety of factors such as the different analytical techniques used and the different methods of combustion. Interestingly enough, the results obtained by Zulfiqar et al. (2006) for Zn in ash are much closer to Wang and Finlayson-Pitt's (2003) and Ryan and Clark's (2010) results for Zn in tobacco rather than ash. This could be due to the fact that significantly less volatilization took place when the cigarettes were simply left to combust by themselves since temperatures were significantly lower. The comparisons between studies, however, are to be treated with caution since Zulfiqar et al. (2006) reported the concentrations in weight per cigarette which makes it difficult to compare them to other results which were reported in common concentration units since an average weight of cigarettes has to be used for the purpose of conversion. A strength of the study by Zulfiqar et al. (2006) compared to the ones discussed previously, is that triplicate measurements were taken and an inter-laboratory study which produced very similar results was carried out. While Ryan and

Clark's (2010) and Wang and Finlayson-Pitt's (2003) results are relatively limited with regards to cigarette brands and elements analyzed, the results obtained by Zulfiqar et al. (2006) give a first indication that different brands seem to have varying concentrations of certain metals.

Verma et al. (2010) added a different dimension to the question, not only analyzing trace-metal concentrations in Indian cigarette tobacco but also in cigar tobacco and biri, a type of self-rolled cigarette, as well as in several other Indian non-smoking tobacco products. In line with Ryan and Clark (2010) and Wang and Finlayson-Pitts (2003), Verma et al. (2010) used ICP/AES as their instrument of choice and analyzed for Cd, Cr, Cu, Fe, Ni, Pb, and Zn. Their digestion process involved a multi-step procedure using hydrogen fluoride, nitric acid, and perchloric acid. Results indicate that cigarettes show relatively low within-brand variation but high inter-brand variation compared to cigars and other tobacco products thus pointing to the possibility of brand determination based on trace metals. Moreover, the results obtained also show that trace-metal concentrations in cigar tobacco exhibit a much greater degree of variation which, however, for most metals analyzed, includes the range of variation exhibited by cigarette tobacco. Thus, it appears that the tobacco used in cigars is not fundamentally different from that used in cigarettes with regards to trace-metal composition. The same is true for the tobacco used in self-rolled cigarettes, however, this kind of tobacco exhibits a much lower degree of trace-metal-concentration variation compared to cigar and cigarette tobacco for most elements analyzed. This kind of tobacco should thus be relatively easy to distinguish as a result of trace-metal-concentration determinations.

A yet different method of analysis was employed by Çevik et al. (2003) whose study likewise aimed to contribute to knowledge on toxic metals contained in tobacco. The researchers used EDXRF in order to determine the amounts of K, Ca, Ti, Fe, Cu, Br, Sr and Ba present in

tobacco and its ash grown in the Turkish region of Akçaabat. Similar to ICP/AES, EDXRF can analyze multiple elements simultaneously. Another advantage of this method is comparatively fast and easy sample preparation since EDXRF is capable of analyzing solid samples. Thus, the only step necessary is to grind the samples into similarly-sized particles which will result in lower sensitivity and reproducibility. Since this study did not analyze manufactured cigarettes but solely tobacco and the resulting ash, comparisons of the results will not yield fully relevant information.

Swami et al. (2009) studied genuine and counterfeit cigarettes in order to determine whether counterfeit cigarettes had higher concentrations of toxic metals and thus posed a higher risk to human health. Using ICP/MS they measured the concentrations of Be, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Ba, Tl, and Pb. Being a rapid, multi-element analysis, ICP/MS shares the advantages of ICP/AES while at the same time reaching a better sensitivity and selectivity which is crucial when trying to detect less abundant elements. Prior to the actual analysis, Swami et al. (2009) carried out a sample digestion study using certified standards in order to determine how efficient the different closed vessel digestion methods used in conjunction with ICP/MS are. The overall best results for a multi-element standard solution as well as for the two standard reference samples (tomato leaves and Virginia tobacco leaves) were obtained using a digestion method with a solution of nitric acid (2ml) / hydrogen peroxide (4ml). The method only utilizing nitric acid was similarly efficient. Precision and accuracy were also overall best for these two methods. The results obtained for genuine Marlboro Red and Marlboro Gold samples in the final analysis were within the range of values reported in the literature for the same references at the 0.1 to 160 ppm range.

Evaluation of Analytical Approaches

In the following, the most important points from the studies previously reviewed will be summarized and the analytical methods of choice for this study will be described in more detail. Overall, the elements analyzed in cigarette ash include Al, As, B, Ba, Br, Ca, Cd, Co, Cr, Cu, Eu, Fe, Hf, K, La, Li, Mg, Mn, Na, Ni, Pb, Rb, Sb, Sc, Sr, Ti, V, and Zn (Çevik et al., 2003; Iskander, 1992; Pérez-Bernal et al., 2011; Ryan & Clark, 2011; Wang & Finlayson-Pitts, 2003; Zulfaqir et al., 2006) while in cigarette tobacco As, Be, Mo, Se, Sm, and Tl were also quantified (Çevik et al., 2003; Giordani et al., 2005; Ryan & Clark, 2011; Swami et al., 2009; Wang & Finlayson-Pitts, 2003; Zulfaqir et al., 2006). The elements measured in the two studies which provided evidence for the possibility of distinguishing cigarette brands based on trace-metal concentrations include Al, B, Ba, Br, Ca, Co, Cu, Cr, Fe, K, La, Li, Mg, Mn, Na, Rb, Sc, Sr, Ti, and Zn. However, some of these elements were used in the analysis of tobacco prior to smoking.

Analytical techniques. The techniques used in these studies have been similarly diverse, each coming with a different set of advantages and disadvantages which are summarized in Table 1. While INAA and EDXRF have the benefit of being able to analyze solid samples directly without lengthy sample preparation and thus with less sources of contamination their detection limits can be relatively high and typically more sample is necessary compared to methods employed more recently. Moreover, a facility with robust radiological assets is needed to irradiate samples. While AAS methods have lower detection limits and often a higher accuracy, they can only analyze one elements at a time and are thus very time consuming and expensive to run. One method which has commonly and successfully been employed in trace-metal analysis is ICP/AES which has been the method of choice in numerous studies since it can not only analyze multiple elements rapidly and simultaneously but does at the same time not

have the problems of chemical or matrix interferences experienced with AAS methods.

However, this technique has recently been superseded by ICP/MS which, in addition to all the

advantages of ICP/AES achieves both better sensitivity and specificity for the analysis of metals.

ICP/MS is also capable of multi-element analysis over a wide linear dynamic range with high

sample throughput (Swami et al., 2009). Moreover, there is little spectral interference, and a

wide range of samples as well as elements can be analyzed. However, elements such as Ca, V,

Cr, Fe, As, and Se pose challenges due to interferences (Bruker, 2010).

Table 1

Comparison of analytical techniques. Adapted from Bruker, 2010.

Characteristic	ICP/MS	ICP/AES	GFAAS	FAAS
Detection limits	excellent	good	excellent	good
Productivity	excellent	excellent	low	good
Linear dynamic range	10^9	10^5	10^2	10^3
Precision	1-3%	0-3-2%	1-5%	0.1-1%
Spectral Interferences	few	common	very few	almost none
Chemical Interferences	moderate	few	many	many
# Elements	75	73	50	68

Overall, all these features make ICP/MS very well suited for the analysis of trace metals

in cigarette ash. Considering that ICP/MS is the most promising instrument for the proposed

analysis, it will be described in more detail.

Inductively coupled plasma-mass spectrometry. The typical ICP/MS system consists of six components which can be viewed in Figure 1: Sample introduction, plasma generation, interface, ion optics, mass analyzer, and the vacuum system. Samples are generally liquid and homogenous. After a sample has gone through the introduction port, it travels through the nebulizer where it is converted into small droplets. Together with the nebulizer gas it is transferred to the spraychamber where only the smallest droplets proceed further into the plasma. A number of different sample introduction systems and nebulizers are available to suit particular applications. The next step is plasma generation. The ICP plasma is an ionized gas with a temperature of 6000-7000K. Elements introduced into plasma of this temperature experience more than 90% ionization and are largely represented by singly-charged cations. The gas used for plasma generation is typically argon. Radiofrequency (RF) generators supply energy to induction coils thus producing an electromagnetic field to which a high-voltage spark is then applied. This results in the collision-induced ionization of argon which then produces inductively-coupled plasma (ICP). The sample is carried through the plasma with the help of the nebulizer gas (also referred to as carrier gas) and is desolvated, atomized and ionized in the process. This part of the instrument operates under atmospheric pressure. The sample then proceeds towards the interface which consists of a sampler cone and a skimmer cone. They are designed to eliminate the remainder of the gas and thus increase ion sampling efficiency. This part of the instrument is operated at approximately 5 Torr. Using a series of ion optics, the produced ion beam is then focused into a mass analyzer. The challenge at this point is to ensure an efficient transfer of ions from the skimmer cone to the mass analyzer as well as to remove photons and neutral atoms while retaining all charged particles. Ion optics are usually composed of several electrostatic lenses and several different configurations are possible. One particularly

popular option is the ion mirror. This element produces a parabolic electrostatic field which lets photons, neutral as well as solid particles pass through while ions are reflected and focused into the mass analyzer regardless of the energy spread. The ion mirror has become particularly popular since it increases sensitivity, reduces contamination, and improves the stability of the signal in the long run.

The mass analyzer is a very important component in so far as that it is responsible for the high sensitivity of the instrument. It separates the ions coming through based on their mass-to-charge ratio. This part of the instrument operates under high vacuum conditions of approximately 10^{-6} Torr. There are several different types of mass analyzers, including ion traps, time-of-flight, double-focusing magnetic sector, and quadrupole. The latter will be described in more detail here since this kind of mass analyzer is found in the instrument used in this study. The quadrupole mass analyzer consists of four rods to which RF and direct current (DC) voltages are applied in a way that two opposite rods have the same polarity. The specific combinations of RF and DC create a stability field between the rods through which only ions with a specific mass/charge ratio can pass at a time. All other ions will be deflected by the rods and thus not travel to the detector. The ions which reach the detector are converted into electrical pulses with a magnitude proportional to the number of ions. The Discrete Dynode Electron Multiplier (DDEM) is a common ion detector. The impact of the ions causes electrons to be ejected from the surface of the cathode. This effect is amplified at each dynode until it is recorded as a signal. Different DDEMs to suit different applications are available (Bruker, 2010).
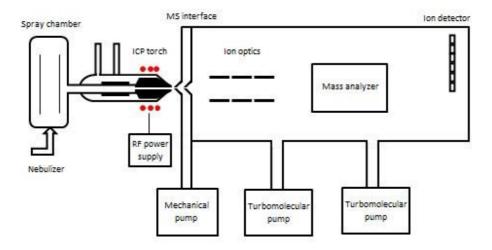
Figure 1. Schematic of an ICP/MS. Based on Bruker (2010).

Sample preparation. Partially due to their use of different analytical techniques, the

reviewed studies also differ with regards to the sample-preparation methods used. One of the

most important differences between the studies concerned with the trace-metal quantitation in

ash is the method of "smoking" the cigarettes. While Ryan and Clark (2011), as well as Wang

and Finlayson-Pitts (2003) utilized a pipette bulb to draw air through the cigarette and thus

facilitate combustion, Zulfaqir et al.(2006) left the cigarette to undergo combustion on its own

after igniting it. Pérez-Bernal et al. (2011) on the other hand used the kind of commercially-

available smoking machine commonly used in research exploring the toxicity of cigarette smoke.

This point deserves special attention since the manner in which a cigarette is smoked has an

influence on the combustion temperature and thus on the concentrations of volatile elements in

the ash (Giordani et al., 2005). Elements such as Br, Cd, and Pb are examples of volatile

elements which have been measured in cigarette ash (Çevik et al., 2003; Swami et al., 2009). At

face value, smoking machines mirror the human smoking process more accurately than pipette

bulbs or the simple undisturbed combustion of a cigarette. However, the degree to which

smoking machines really mimic what happens when a person smokes a cigarette has been controversially discussed for many years. Roemer and Carchmann (2011) argue that the standard smoking regimen which has been adopted by the ISO reflects neither the "average" smoker nor the smoking behavior of a defined population of smokers. They also point out that there is no such thing as an "average" smoker since there is a significant difference between smokers with regards to puff volume, puff frequency and puff duration. While this is of high significance for studies assessing the amounts of toxic components in side- or mainstream smoke, it might not be as critical for the evaluation of metals in ash. Considering the large number of elements which have been measured in ash it seems possible to choose non-volatile elements, the concentrations of which the combustion process will not influence. However, this point will be further examined when looking at forensic applicability.

Another important aspect with regards to the analytical procedure is the processing of the ash after it has been produced. Inorganic samples such as cigarette ash are commonly prepared for analysis using acid digestion, however, there is a range of digestion methods which are most distinctly characterized by their being open- or closed-vessel methods, digestion temperature, and the nature and amount of reagents used. The digestion is necessary to eliminate the solid matrix encasing of the analytes of interest and to ensure the conversion of all trace metals into solution for sample introduction. This digestion can be carried out in open systems at atmospheric pressure or in closed vessels. There are several advantages to closed-vessel digestions. For instance, much higher temperatures can be achieved which leads to a much faster digestion procedure. However, there are also some issues which need to be taken into consideration, such as the pressure increase in the vessel or problems regarding unequal heating. Moreover, vessels have to be manufactured using chemically completely inert materials such as

Teflon® or quartz glass (Bergof, n.d.). The advantages and disadvantages of the two digestion

systems can be viewed in Table 2.

Table 2

Comparison of open and closed acid digestion systems. Based on Berghof (n.d.).

Open acid digestion	Closed acid digestion
Max. temperature limited by solution's bp	Max. temperature 260-300°C
Permits large sample weigh-ins	Large sample weigh-ins not possible
High acid consumption	Reduced acid consumption resulting in reduced blank values
Digestion quality frequently unsatisfactory	High digestion quality
Loss of volatile elements (e.g. Hg, Pb salts)	No loss of volatile elements
Contamination risk	
Digestion duration: 2-15 hours	20-60 min

Another important factor when it comes to acid digestions is the kind of reagent used.

There is a range of mineral acids typically used, however, hydrogen peroxide has also been

successfully employed (Berghof, n.d.). In their study regarding the efficiency of different

reagents in acid digestion methods Swami et al. (2009) have shown that employing nitric acid

and hydrogen peroxide and just nitric acid, respectively have very good overall recovery rates for

trace metals from tobacco. Hydrochloric acid was not included in the recovery study.

Having established that an analytical protocol using ICP/MS and a closed vessel

microwave digestion with either nitric acid and hydrogen peroxide or just nitric acid is likely to

yield the best results, one can now move on to consider the forensic applicability of such a protocol.

Trace-Metal Analysis in the Forensic Context

Environmental and human health experts are not the only ones concerned with determining the trace-metal concentrations in cigarettes and their ash. Two studies of distinctly forensic nature which will be focused on here were identified by the author. Both these studies deal with the distinction of cigarettes based on trace-metal distributions. The study by Giordani et al. (2005) deals with genuine and counterfeit cigarettes whereas the one by Pérez-Bernal et al. (2011) specifically targets the classification of ash by brand for evidential purposes. After the discussion of these two studies, factors which relate to the applicability of this kind of analysis in the context of forensic casework will be summarized. One very critical aspect which will be discussed in detail is the question of "smoking" the samples and in how far the method used has an effect on the trace-metal concentrations in the ash.

Giordani et al. (2005). Giordani et al. (2005) set out to determine whether genuine and counterfeit cigarettes can be distinguished based on trace-metal compositions and if a batch of unlawfully-imported cigarettes originated from the official manufacturer or whether it was also produced illegally. In particular, the study was designed in order to augment the Italian government's knowledge on the origin of smuggled cigarettes. INAA, a non-destructive multi-element technique, was employed in order to determine the concentrations of Sm, Ca, Cr, La, Br, Sc, Rb, Co, Fe, and Zn in smuggled cigarettes of the brands Marlboro Red, Marlboro Light, Benson, and Regal and to compare those to samples purchased in legitimate commerce in different Italian cities. Since the sample preparation for INAA is not applicable to this study, it will not be described here. Preliminary results indicated not only the possibility of

distinguishing between brands based on their distinct trace-metal concentrations but also

between cigarettes of the same brand with different origins. For smuggled cigarettes, a

distinction between different lots seemed to be possible. The authors, however, do not make it

clear whether "lot" refers to a production lot as indicated on the packs or to different seizures of

smuggled cigarettes. The genuine samples exhibited different trace-metal concentrations

between different cities which most likely implies different production lots. Elements such as

Ba, Br, Cr, Rb, and Zn were identified as those elements with the highest degree of variability

and were thus used in the ensuing PLS-DA which was carried out in order to statistically

support the preliminary results.
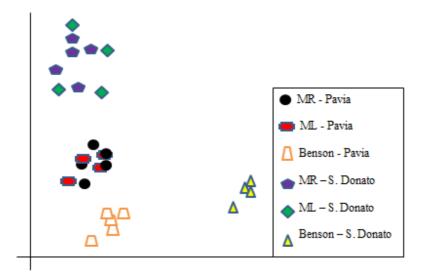
Figure 2. Discrimination of genuine cigarettes. Based on Giordani et al. (2005)

The results demonstrated that based on their trace-metal concentrations cigarettes can be

grouped into different production lots. The location of the purchase seemed to play a greater role

than varieties within the same brands since genuine samples of Marlboro Red and Marlboro

Light purchased in the same cities constituted one group in the discriminant analysis. This is

evident in Figure 2 which shows the approximate relation of the samples to each other based on the discriminant analysis results obtained by Giordani et al.(2005).

Considering the factors which determine the final trace-metal concentrations in cigarettes, it is likely that the same tobacco as well as the same paper is used for the manufacture of Marlboro Red and Marlboro Light. The genuine Benson samples purchased in different cities likewise seemed to belong to different production lots and formed separate groups in the statistical analysis. Assuming that the results are transferrable to cigarette ash, the implication for the proposed study is that while it is possible to distinguish between different cigarette brands and possibly even production lots, it might not be feasible to distinguish between subdivisions within a brand.

Pérez-Bernal et al. (2011). This leads to the discussion of the study which directly relates to the problem at hand. Namely, the study conducted by Pérez-Bernal et al. (2011) with a view to establishing the feasibility of using the trace-metal distribution in cigarette ash as a determinant of the type of tobacco (blond or black) and eventually of the brand. The authors determined the concentrations of Zn, B, Mn, Fe, Mg, Cu, Ti, Al, Sr, Ca, Ba, Na, Li, and K using ICP/AES. The samples used comprised 149 cigarettes bought in different cities and at different points in time, neither of which was further specified. The brands analyzed are some of the most common brands available in Spain where the study was carried out and included Camel (C), Chesterfield (CH), Fortuna (F), Marlboro (M), L&M (LM), Winston (W), Camel Blue (CB), Chesterfield Blue (CHB), Fortuna Blue (FB), Marlboro White (MW), and L&M Blue (LMB) as representatives of blond tobacco while Ducados (D), Reales (R), Kaiser (K), B.N. (BN), Sombra (S) and Habanos (H) were chosen as examples for black tobacco brands. Unlike Swami et al. (2009) Pérez-Bernal et al. (2011) used an open-vessel system to digest the samples prior to

analysis. A 1:3 (v/v) nitric acid/hydrochloric acid mixture was used for the digestion. Due to the fact that concentrations were only reported after auto-scaling, no comparisons with other studies are possible.

An ANOVA comparing the means of the elemental concentrations showed that there were significant differences (significance level not specified) between blond and black tobacco brands with the brand introducing the largest amount of variability thus indicating that inter-brand variability is larger than intra-brand variability. Further evaluation of the results involved pre-processing the data before carrying out principal component analysis (PCA) and PLS-DA. PCA was used in order to detect intrinsic differences between brands whereas PLS-DA was used in order to evaluate the possibility of creating a discriminant model for the brands. PCA reduces the number of variables needed in order to describe a sample. In this case this means that the chemical information of the sample is condensed in a way that allows a characterization of a given sample by using only a limited number of variables, so-called principal components (PCs, typically between two and four), which account for a majority of the variation between the different samples. The formula $\mathbf{X} = \mathbf{TP^T} + \mathbf{E}$ describes how PCA separates the data into two sub-matrices, the scores ($\mathbf{T}$) and the loadings matrix ($\mathbf{P^T}$). The scores matrix contains all the useful information about the samples, especially their relation to each other, while the loadings matrix represents the connections with the initial variables. $\mathbf{E}$ represents the residual matrix which contains all the information not needed in order to explain the variance of the samples or the variables.

Pérez-Bernal et al. (2011) chose two principal components to visualize their results, which makes it easier to understand PCA as an approach. When visualized, the samples were distributed along both axes indicating that the first two components are good at explaining the

variance (see Figure 3). The number of principal components depends on several factors, one

important point being the total variance explained by the factors. However, the type of data also

has to be taken into account. In this case the first two principal components together explained

close to 55% of the variance whereas four principal components explained 75% of the variance.

Some tobacco brands were clearly distinct from the others. For instance, B.N. and Habanos were

clearly distinguishable. The L&M samples, however, were relatively spread out. One

explanation which comes to mind is that more packets from different cities or different

production dates were used; however, this cannot be confirmed without further information on

the sampling process. Overall, the results show that there are indeed intrinsic differences

between different brands of tobacco. The fact that there was no significant difference between

replicates or between different packets of the same brand shows that the measure is robust and

reproducible. It was not determined if cigarettes bought at the same time, or in the same city

showed a within-lot variance bigger than the between-lot variance.
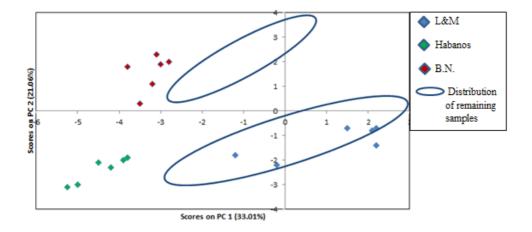
Figure 3. PC1 vs. PC2 scores plot. Tobacco brand label. Based on Peréz-Bernal et al. (2011)

As mentioned previously, the authors proceeded to conduct a PLS-DA, separately for blond and black tobacco, using six latent variables each time. In both cases 75% of the dataset were used to build the classification model while the remaining 25% were used as a "blind set" which was classified using the model. The models were also cross-validated by classifying each one of their data points individually. The two parameters considered when evaluating the ability of a model to classify samples are sensitivity and specificity. While sensitivity refers to the ability to correctly classify samples as belonging to a certain class, specificity refers to the ability to predict that samples of other classes are not part of said class. A sensitivity value of 1.000 thus implies that all samples which belong to a certain class were predicted correctly. A specificity value of 1.000 implies that no samples which belong to other classes were predicted to belong to the class at hand (Peréz-Bernal et al., 2011). Good sensitivity and specificity values were obtained for most of the black tobacco brands in both the prediction and the cross-validation. Particularly good values (1.000) were obtained for Habanos and Sombra while relatively low values were obtained for the brands Ducados and Reales (sensitivity of 0.500 and 0.667, respectively). The PLS-DA classification of the blond tobacco showed good sensitivity and specificity values for both the prediction and the cross-validation (see Table 3). Pérez-Bernal et al. (2011) thus showed that it is generally possible to distinguish common Spanish cigarette brands based on the trace-metal distributions of their ash. However, in order to enhance the strength of the models created, it is necessary to include more brands from different countries as well as more replicates.

Table 3

Sensitivity and specificity values for classification of blond and black tobacco, black tobacco brands and blond tobacco brands. Peréz-Bernal et al. (2011).

	Blond	Black	BL	BN	D	H	K	R	S
Sensitivity (cal)	1.000	1.000	-	0.875	1.000	1.000	1.000	0.833	1.000
Sensitivity (CV)	1.000	1.000	-	0.875	0.833	1.000	0.600	0.677	1.000
Sensitivity (Pred)	1.000	1.000	-	1.000	0.500	1.000	1.000	0.677	1.000
Specificity (cal)	1.000	1.000	-	0.935	0.939	1.000	0.941	0.939	1.000
Specificity (CV)	1.000	1.000	-	0.839	0.818	1.000	0.941	0.909	0.906
Specificity (Pred)	1.000	1.000	-	0.923	0.750	1.000	0.900	0.636	1.000

Blond brands	C	CH	F	M	W	CB	CHB	FB
Sensitivity (cal)	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Sensitivity (CV)	0.800	0.500	0.750	1.000	0.750	0.833	0.750	1.000
Sensitivity (Pred)	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Specificity (cal)	0.932	0.979	0.978	0.933	0.978	1.000	0.978	0.976
Specificity (CV)	0.909	0.957	0.978	0.911	0.956	0.977	0.933	0.952
Specificity (Pred)	0.818	0.909	0.909	0.864	0.905	1.000	1.000	0.955

	LMB	LMR	MW
Sensitivity (cal)	0.833	1.000	1.000
Sensitivity (CV)	0.833	0.750	0.667
Sensitivity (Pred)	1.000	1.000	1.000

Specificity (cal)   0.930   0.956   0.826

Specificity (CV)   0.907   0.911   0.717

Specificity (Pred)   0.909   0.909   0.591

Influence of smoking regime. Generally speaking, trace metals are concentrated in the ash with concentrations of up to 17 times those recorded for the tobacco (Ryan & Clark, 2010; Wang & Finlayson- Pitts, 2003). However, this is not necessarily true for all elements as results to the contrary have been reported for, for instance, Cu, and Cd (Ebisike, Ayejuyo, Sonibare, Ogunkunle, & Ojumu, 2004). The amount of trace metals found in cigarette ash is influenced by the smoking process since volatile metals are partially transferred into the smoke and partially remain in the particulate matter, i.e. the ash. The degree to which this is the case depends on the individual metal, as well as on the temperature and duration of the combustion process. For instance, it has been reported that in certain not further defined "American" cigarettes up to 100% of arsenic present in the tobacco are transferred to the smoke while only 5-10% of potassium are transferred to the smoke (Iskander, 1986). Out of the 14 metals analyzed by Peréz-Bernal et al. (2011) four (K, Na, Zn and Mg) have boiling points within or just outside the range of temperatures cigarettes can reach during the smoking process. Therefore, the concentrations of these metals seem prone to change with varying smoking habits. The important question in this respect is whether different smoking habits influence the concentrations of volatile metals in the ash to such an extent that ash samples from cigarettes of the same brand which are smoked differently have such different trace-metal profiles that they do not fall into the same class in a statistical analysis. Since studies such as that by Pérez-Bernal et al. (2011) used the same parameters on the smoking machine for each sample, this question has not been

addressed previously. In the realm of smoking machine literature there have been no studies

with regards to the influence of smoking parameters on trace-metal concentrations in ash either,

however, there is a wealth of literature which has explored the different ways in which people

smoke cigarettes and the factors which influence these habits (Baker, 2002; ISO, 2005; Kassel et

al., 2007; Purkis et al., 2010; Veilleux et al., 2011). In the following, the topic of smoking

topography will be examined in order to assess just how much smoking behavior differs between

people and thus how many different smoking regimes should be included in the study in order to

cover the range experienced in real life. Based on this it will be possible to determine if cigarette

ash can be classified according to brand despite the differences in smoking habits experienced in

actual practice.

First of all, it is important to establish the parameters which are typically used in order to

describe smoking behavior or topography. The most common variables are puff interval, puff

duration, puff volume, and the total number of puffs taken during the course of smoking one

cigarette which is related to the butt length when smoking ceases (ISO, 2005). As stated

previously, the current consensus in literature is that there is no such thing as an "average"

smoker. No two people smoke in exactly the same way, nor does the same person smoke every

cigarette in the same way (Baker, 2002). For instance, it has been observed that the same person

will smoke cigarettes of different brands in distinct ways depending on the time of the day, the

mood they are in, the level of stress they have recently experienced, environmental conditions,

and even the composition of the cigarette, as well as several other factors. Moreover, smoking

behavior typically even changes over the course of smoking one cigarette, for instance, the puff

volume and puff duration usually decreases towards the end of a cigarette while the puff interval

increases (ISO, 2005). Smokers can generally be grouped into different categories with similar

smoking topographies, such as adolescent and adult smokers. Studies have demonstrated that

adolescent smokers exhibit an even greater variability in their smoking behavior. Though

generally speaking, they take smaller but more frequent puffs than adults. There are, however,

also similarities with regards to the smoking behavior of these two groups. Adults and

adolescents both appear to self-regulate their nicotine intake meaning that they adjust the puff

frequency, volume, and duration depending on the nicotine yield of the cigarette by, for instance,

taking more puffs when smoking denicotinized cigarettes (Kassel et al., 2007).

Variations in butt length have been found to exist between sexes, geographic locations,

occupations, economic situations, and even within the same country over a period of time which

is a good example for just how variable smoking parameters are. An explanation for this

particularly high variation in butt length is that butt length is strongly related to smoke yield

since the smoke in a single puff increases the smaller the butt gets. However, butt length is not

the only parameter which is highly variable. Similar statements can be made regarding other

parameters as evidenced by a study comparing smoke volume, puff number and puff intervals

between Europe and America over several decades (ISO, 2005). Studies regarding ventilation

blocking and the influence of draw resistance have also been carried out, however, these

observations are more detailed than is necessary for the current study (Purkis et al., 2010).

Veilleux et al. (2011) examined the influence of several conditions such as depression,

and anxiety on smoking topography and showed that these also have an influence. While anxiety

increased puff volume and puff duration, depression had the opposite effect. However, all these

studies have to be treated with care since the smoking process was always carried out in a

laboratory environment which means that participants could be stressed or bored or in other ways

prompted to change their smoking behavior. The smoking topography measuring device could also be a distraction.

Summary. Having established that based on the tobacco growing process and the specific formulations used in cigarette manufacture, different cigarette brands should have sufficiently distinct trace-metal concentrations to be distinguished, the theoretical basis of the hypothesis is sound. A thorough review of the relevant literature has shown that ICP/MS in conjunction with closed-vessel microwave digestion is the most promising technique for this analysis. The experimental plan must give special consideration to the exploration of the effects different smoking regimes have since this aspect has not yet been studied. In terms of statistical methods, PCA and PLS-DA have been demonstrated to be useful by both Giordani et al. (2005) and Peréz-Bernal at el. (2011). Based on these results the study design was developed.

Materials and Methods

Sample Procurement

Three groups of cigarette samples were analyzed and include samples of U.S. manufacture, international samples, and samples to test the effect of different smoking regimes on the trace-metal concentrations in cigarette ash. Two packs of each of the American brands were purchased at different points in time so that variations between production lots could be explored (see Table 4). With regards to the manufacturer it is important to note that Philip Morris USA is part of Altria Group Inc., whereas Philip Morris International has been independent from Altria since 2008 (Philip Morris International, *Our History*). A total of 72 samples of international origin were analyzed, three from each of 26 packs of cigarettes summarized in Table 4. International cigarettes were procured during overseas travel by the researcher or colleagues. It was not possible to obtain two sets purchased at different times or in

different locations for all brands from all countries to explore variations between production lots. Dji Sam Soe 234, the Indonesian brand represented in the study, are kreteks, also known as clove cigarettes. This Indonesian type of cigarettes contains a mixture of tobacco, clove and other types of additives. Kreteks are only available in the U.S. through import (CDC, n.d.). More detailed information on the samples, as well as the location and time of purchase can be found at Appendix A.

Table 4

Cigarette samples included in study

Origin	Brand (number of packs)	Manufacturer
USA	Marlboro Reds (2)	Philip Morris USA
	Marlboro Rich Smooth Original Flavor (2)	Philip Morris USA
	Marlboro Smooth Original Flavor (2)	Philip Morris USA
	Marlboro Mellow Flavor (2)	Philip Morris USA
	Marlboro Menthol (2)	Philip Morris USA
	Marlboro 72s (2)	Philip Morris USA
	Newport Non-Menthol (2)	Lorillard Tobacco Co.
	Pall Mall Red (2)	R.J. Reynolds Tob. Co.
	L&M (2)	Philip Morris USA
	Camel Blue (2)	R. J. Reynolds Tobacco Co.
	Winston Red Box (2)	R. J. Reynolds Tobacco Co.
	Kool Super Longs 100s True Menthol (2)	R. J. Reynolds Tobacco Co.
	Natural American Spirit 100% additive-free (2)	Santa Fe Natural Tobacco Co.

	Natural American Spirit Organic Tobacco (2)	Santa Fe Natural Tobacco Co.
Austria	Marlboro Reds (2)	Philip Morris Munich
	Chesterfield (2)	Philip Morris Munich
	Parisienne (2)	BAT Switzerland S.A.
	Pall Mall (2)	BAT Switzerland S.A.
	Gauloises Blondes Bleu (2)	Imperial Tobacco
Germany	Marlboro Reds (2)	Philip Morris Munich
	HB (2)	BAT
UK	Benson & Hedges Gold	BAT
Argentina	Marlboro Reds	Massalin Particulares S.A. (Philip Morris I.)
	43 70	Nobleza Piccardo (BAT)
	Jockey	Nobleza Piccardo (BAT)
	Camel Blue	Nobleza Piccardo (BAT)
India	Marlboro Reds	Godfrey Philips India Limited
Indonesia	Dji Sam Soe 234 Fatsal - 5	Sampoerna (Philip Morris International)
Malaysia	Marlboro Reds	Philip Morris Malaysia
Vietnam	vinataba	BAT
	State Express London 555 Gold	BAT, Ardath Tobacco Co. Ltd. London

The third group of samples consisted of Marlboro Reds of U.S. manufacture and was smoked in several different ways in order to assess the impact of different smoking regimes on the trace-metal concentrations in cigarette ash. The smoking parameters used will be discussed in detail under "Sample Preparation."

Reagents and Solutions

Reagent-grade chemicals were used for all purposes. BDH Aristar Ultra nitric acid 69% and BDH Aristar Ultra hydrochloric acid 37% were procured from VWR International (West Chester, PA). Standard solutions were prepared using 1% nitric acid unless otherwise noted. The nitric acid and any other reagents used which were not designated as ultra-pure were subjected to an elemental analysis and it was determined that the trace-metal concentrations in the reagents are negligibly small.

Sample Preparation

All cigarette samples were smoked using a Gilian Aircon-2 high-volume air sampler pump designed for collecting environmental air samples indoors and outdoors. The pump was connected to a system of Tygon-type tubing, at the end of which the cigarettes were attached. An off/on electric switch was built in in order to allow for "puffing" for pre-determined reproducible intervals. During puffs air was drawn through the cigarette whereas air was drawn from the surroundings during the intervals between puffs.   A BIOS DryCal DC-Lite Primary Flow Meter was used to calibrate the pump prior to the smoking of each cigarette. The flow rate was also measured and recorded after the smoking of each cigarette (see Appendix B). The pump is capable of maintaining a steady air flow over a range of 2-30 L/min.

In accordance with the ISO standard smoking regime as modified following recommendations in 2005, all international and American cigarettes were smoked using a flow

rate of 2L/min, puff duration of 2s, and puff intervals of 30s. The flow rate is slightly higher

than recommended and lies at the upper end of realistic flow rates, however due to restrictions

imposed by the pump, the flow rate could not be lowered (ISO, 2005). The total smoke duration

of each cigarette was also recorded (see Appendix B). In order to measure the potential impact

of smoking parameters, Marlboro Reds were "smoked" using the following parameters which are

still within the range of realistic smoking behavior: 1.5s/2.5s puff duration, 25s/35s puff interval

(ISO, 2005). Moreover, additional Marlboro Reds were "smoked" using a continuous puff in

order to obtain minimum-concentration data for all volatile metals. Due to the limited ash yield

of the cigarettes in this study, more than one cigarette contributed to each sample. Initially, 0.1g

samples were used, however, due to issues during the digestion process which will be discussed

later on the amount of sample used was reduced to 0.05g. All samples were weighed and

weights were recorded and listed in Appendix C. In addition, triplicate Marlboro Reds un-

smoked tobacco samples were analyzed. Three blanks not containing any ash were also prepared

and treated as samples during the remainder of the process. The samples were placed in 10ml

Pyrex digestion vessels for the Discovery system (CEM), which had previously been rinsed with

1% nitric acid and milli-Q water. Initially, each sample was treated with 4ml of concentrated

nitric acid, capped and left to digest several days prior to the microwave digestion procedure.

The pipettes used (Rainin pipette man for nitric acid and Eppendorf pipettor for later use of

hydrochloric acid) were calibrated prior to use in order to record the exact volume of acid

transferred. The microwave digestion was carried out using a CEM Discover SP-D countertop

digestion system with an Explore auto-sampler. A Teflon®-covered magnetic stirring rod was

placed in each vessel prior to the digestion which was carried out using the manually created

method "Cigarette Ash" with the parameters display in Table 5.

Table 5

Initial microwave digestion parameters

	Temperature	Ramp time	Hold time	Pressure	Power	Stirring
Stage 1	100°C	02:00 min	02:00 min	400 PSI	300 V	Medium
Stage 2	180°	02:00 min	02:00 min	400 PSI	300 V	Medium

Under these parameters, samples were not completely digested. At the bottom of the vessels, sediment was still clearly visible and the color of the mixture had only become marginally lighter, changing from a dark reddish brown to a slightly lighter brown. The microwave parameters were thus adjusted as the temperature for stage 2 was increased to 200°C and the hold time was increased to 10:00 and 20:00 min, respectively in two different trials. While the color of the mixture changed to a light orange at 10:00 min and a light yellow at 20:00 min hold time, the amount of sediment was approximately stable (see Figure 4 and Figure 5).
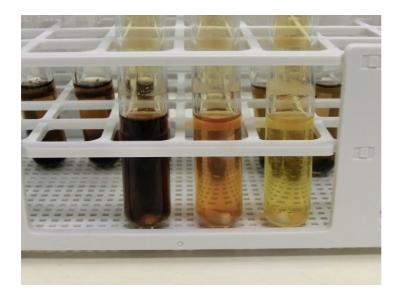
Figure 4. Comparison of digestion results using different parameters
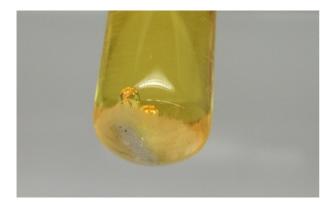
Figure 5. Sediment remaining after digestion

In order to achieve a complete digestion, 1ml of hydrochloric acid was added to the

digestion mixture. This measure decreased the amount of sediment remaining after the digestion

process. The reduction of the amount of sample ash used from 0.1g to 0.05g ensured a complete

digestion. All samples were thus digested using 0.05g of sample, 4ml of nitric acid and 1ml of

hydrochloric acid (or an equivalent ratio for the 0.1g samples to which nitric acid had already

been added). The parameters displayed in Table 6 were used for the microwave digestion of all

remaining samples. The absolute maximum temperature the microwave system operates is

200°C. It was observed that without the stirring rod, the digestion process was not complete.

Therefore, use of the stirring rod is imperative.

Table 6

Final microwave digestion parameters

	Temperature	Ramp time	Hold time	Pressure	Power	Stirring
Stage 1	100°C	02:00 min	02:00 min	400 PSI	300 V	Medium
Stage 2	200°C	02:00 min	10:00 min	400 PSI	300 V	Medium

After the microwave digestion, the samples were transferred to Nalgene polypropylene TC/TD class B trace-metal-free 100ml dilution flasks (VWR# 29615-007) which had previously been washed with 1% nitric acid. The samples were diluted with distilled 18MΩ water and then transferred to VWR HDPE trace-metal-free 125ml plastic bottles (VWR# 414004-156). From these bottles 100µl aliquots were transferred into Fisher 16x125mm polypropylene ICP/MS vessels (Fisher# 14-956-76) and diluted further with 9.9ml 1% nitric acid before injection into the ICP/MS.

Analysis

Samples were analyzed using a Bruker Varian 820 ICP/MS. All standard solutions were prepared in ultra-pure water. Several controls and standards were run in advance of each day's samples in order to ensure that the instrument was operating properly. These control samples included a 5ppb tuning solution, a series of alternating blanks, and 2ppb elemental control standards. In addition, plasma alignment and mass calibration were carried out each day samples were run. A series of multi-elemental standards at increasing concentrations of 2ppb, 5ppb, and 10ppb were analyzed with every sample run. In addition, an internal standard solution containing Li, Sc, Rh and Ho was aspirated simultaneously into the ICP/MS with each standard to calibrate for any changes in the plasma. The calibration curve generated using the data obtained showed a linear response. After every ten samples the 2ppb and blank controls were analyzed in order to ensure the continued correct operation of the instrument. A variation of the Environmental Protection Agency (EPA) method 6020 for the analysis of environmental samples was used. Results were reported for 63 elements highlighted in Table 7. Appendix D highlights the raw data from each measurement.

Table 7

Range of elements analyzed

Element	Abbreviation	Mass number
Beryllium	Be	9
Boron	B	11
Sodium	Na	23
Magnesium	Mg	24
Aluminium	Al	27
Chlorine	Cl	35
Titanium	Ti	49
Vanadium	V	51
Chromium	Cr	52
Manganese	Mn	55
Cobalt	Co	59
Nickel	Ni	60
Copper	Cu	65
Zinc	Zn	66
Gallium	Ga	71
Germanium	Ge	72
Bromine	Br	79
Rubidium	Rb	85
Strontium	Sr	88
Yttrium	Y	89

Zirconium	Zr	90
Niobium	Nb	93
Molybdenum	Mo	98
Ruthenium	Ru	101
Palladium	Pd	105
Silver	Ag	107
Cadmium	Cd	111
Indium	In	115
Tin	Sn	118
Antimony	Sb	121
Tellurium	Te	125
Cesium	Cs	133
Barium	Ba	137
Lanthanum	La	139
Cerium	Ce	140
Praseodymium	Pr	141
Neodymium	Nd	146
Samarium	Sm	147
Europium	Eu	153
Gadolinium	Gd	157
Terbium	Tb	159
Dysprosium	Dy	163
Erbium	Er	166

Thulium	Tm	169
Ytterbium	Yb	172
Lutetium	Lu	175
Hafnium	Hf	178
Tantalum	Ta	181
Tungsten	W	182
Rhenium	Re	185
Iridium	Ir	193
Platinum	Pt	195
Gold	Au	197
Thallium	Tl	205
Lead	Pb	206-208
Bismuth	Bi	209
Thorium	Th	232
Uranium	U	238
Calcium	Ca	44
Iron	Fe	56
Iron	Fe	57
Arsenic	As	75
Selenium	Se	78
Potassium*	K	
Lithium*	Li	
Scandium*	Sc	

Rhodium*   Rh

Holmium*   Ho

---

*Note. Elements marked with an asterisk were not part of the analysis. Their full names are listed since their abbreviations have been mentioned previously.

Data Analysis

Preparation of data. The data reported by the ICP/MS software is already blank corrected since the blank concentrations are taken into account during the creation of the calibration curves. All blank-corrected data was adjusted in order to calculate the original trace-metal concentrations in the ash samples by accounting for the dilutions as well as the mass of each ash sample. This was achieved using the following formula:

$$c_{ash} \, mg/g = c_{reported} \, \mu g/L \, / \, (100 \text{ x } m_{ash}) \tag{1}$$

The factor 100 accounts for the change of concentration due to the dilutions. The fact that the mass was recorded for each individual sample allows for calculation of the concentrations in each specific sample. Concentrations for all samples and all elements can be viewed in Appendix D. While this preliminary step was carried out in Microsoft Excel 2010, the following pre-processing steps as well as the statistical analyses were carried out in SOLO v.7.0 (Eigenvector Research, Inc., WA, USA).

The data was then inspected and results reported for Na, Ca, and Mg were excluded on the grounds that these elements and their salts are so abundant that the environmental contribution to their presence in an ash sample precludes them from being used as markers of

cigarette brands. Cl was excluded since hydrochloric acid was used during the sample

preparation process and Fe56 and Fe57 were excluded due to isobaric interferences with argon

oxide and argon hydroxide, respectively (Bruker, 2010). Due to the fact that neither indium nor

tin were present at detectable levels in any of the samples, these elements were also excluded

from the analysis. The concentrations obtained for these elements are listed in Appendix D.

 The data was pre-processed by means of auto-scaling in order to lower the differences in

magnitude between the various metal concentrations. Auto-scaling combines mean centering

(subtracting the mean value of each variable from each measurement of said variable) and

variance scaling (dividing each measurement by the standard deviation of the corresponding

variable). This method of pre-processing is commonly applied prior to PCA, especially if

different variables have different measurement ranges as was the case in this study (Beebe, Pell,

& Seasholtz, 1998).

Statistical analysis. PCA and subsequent PLS-DA were carried out on different subsets

of the data. For the full model, which served to explore whether it is possible to determine the

brand from which an ash sample could have originated without any prior knowledge as to the

nature of the sample, each three to six samples of one brand/variety were grouped together as

one class. This included samples of U.S. as well as international origin. Class labels are listed in

Table 8. To identify individual samples numbers behind the class label were used to refer to the

pack if two packs were obtained whereas the letters A, B, and C identify the triplicate samples.

Subsequently, a model distinguishing between samples of U.S. and of international origin

(U.S. vs. international model) was created in order to determine whether prior knowledge of the

general geographic origin of the brand and thus a step-wise approach will increase the

confidence of the final brand classification. This step-wise approach would be analogous to

Pérez-Bernal et al.'s (2011) approach to first distinguish between blond and black tobacco before determining brands. This model was created by coding all samples of U.S. manufacture as one class and all samples of international manufacture as another class.

A model just exploring samples of U.S. origin (U.S. model) was then created to complement the U.S. vs. international model as the second stage in the step-wise approach. Two versions of this model were developed: one in which each Marlboro and each Natural American Spirit variety was coded as a separate class and one in which all Marlboro and Natural American Spirit samples were coded as one class, respectively. The reasoning behind the creation of the two models was to explore whether the coding into brands rather than varieties could improve the classification. Another aspect which was explored based on samples of U.S. origin is the distinction between packs purchased at different points in time.

A model exploring the possible distinction of Marlboro varieties was created in order to complete the evaluation of the step-wise approach. Only Marlboro varieties, coded as distinct groups, were included in this model.

An international model was created in order to explore whether it is possible to further narrow the geographic origin of a cigarette ash sample down after it has been determined to be of international rather than U.S. origin.

Another aspect which was explored with regards to the international samples is the discrimination of Marlboro Reds from different countries (Marlboro Reds model) which could be relevant even if the cigarette butt is left at a crime scene. This model was built using Marlboro Reds samples originating from the U.S., Argentina, Austria, Germany, India, and Malaysia.

Lastly, the impact of the different smoking regimes and the continuous puffing of Marlboro Reds were evaluated by creating a model using all samples of U.S. origin and coding

all samples obtained after modified smoking as well as continuous puffing as one group of

unknowns in order to see if they would still be classified as Marlboros.

During PLS-DA the Venetian Blinds method of cross-validation was used for all models.

This method splits the data ten times and each time uses one part of the data to construct the

model while the other part of the data is classified using the previously constructed model.

As will be discussed in more detail, thorium was determined not to contribute to the

discrimination in any of the models and was thus excluded as well. Other elements with no

contribution to the discriminant power of the respective models will be listed in the results

section. During the initial data exploration phase samples MG1A and DEMR2A were found to

be outliers as they consistently fell outside the 95% confidence interval and were thus not

included in any of the models.

Table 8

Sample label codes

Label	Brand
MR	Marlboro Reds
MS	Marlboro Rich Smooth Original Flavor
MG	Marlboro Smooth Original Flavor
MF	Marlboro Mellow Flavor
MM	Marlboro Menthol
M72	Marlboro 72s
NP	Newport Non-Menthol
PM	Pall Mall Red

LM	L&M
CB	Camel Blue
WI	Winston Red Box
KO	Kool Super Longs 100s True Menthol
NF	Natural American Spirit 100% additive-free
NO	Natural American Spirit Organic Tobacco
ATMR	Austria - Marlboro Reds
ATCH	Austria - Chesterfield
ATPA	Austria - Parisienne
ATPM	Austria -Pall Mall
ATGA	Austria - Gauloises Blondes Bleu
DEMR	Germany - Marlboro Reds
DEHB	Germany - HB
GBBH	United Kingdom -Benson & Hedges Gold
ARMR	Argentina - Marlboro Reds
AR4370	Argentina - 43 70
ARJO	Argentina -Jockey
ARCB	Argentina - Camel Blue
INMR	India - Marlboro Reds
IDDS	Indonesia - Dji Sam Soe 234 Fatsal - 5
MYMR	Malaysia - Marlboro Reds
VNVI	Vietnam -vinataba
VNSE	Vietnam - State Express London 555 Gold

Results

Full Model

Principal component analysis. This model was created using all samples of U.S. and

international origin. The number of principal components to be used was decided upon using the

scree plot. For this model five principal components, together accounting for 55.97% of the

variance in the data, were retained in the model. The scores plot (see Figure 6) and loadings plot

(see Figure 7) were then examined.
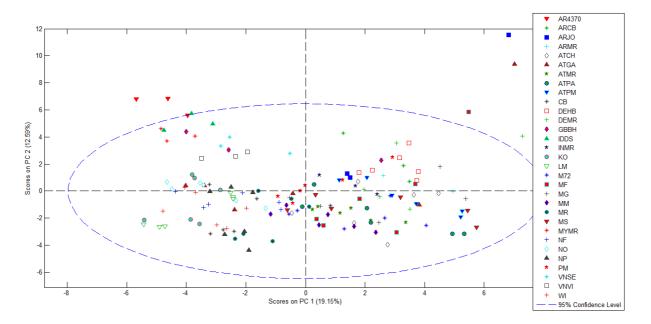
Figure 6. PC1 vs. PC2 scores plot. Full model

The scores plot illustrates the relationship between the samples. Even though at first

glance there are no distinct clusters based on class membership, samples of the same brand do

tend to lie in the same area. For instance, all three samples of each of the brands VNSE, VNVI,

and MYMR as well as the six samples of DEHB clearly cluster in the same area. The six

samples of ATCH and ATPA on the other hand are relatively spread out. However, the plot only

displays two PCs which, together, explain 31.74% of the total variance. Therefore, the plot does

indicate that overall there are inherent differences between the various brands with intra-brand

differences being smaller than inter-brand differences. The plot also shows that both PC1 and

PC2 explain some of the variance within the samples since the samples spread along both axes.
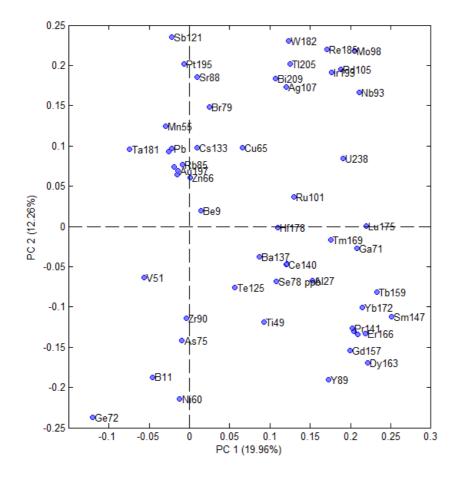
Figure 7. PC1 vs. PC2 loadings plot. Full model

The loadings plot indicates how much each of the variables loads on each principal

component. The distance from the center indicates the discriminative power of the element. For

instance, thorium was excluded from all models since it lay in the center for all PCs. In Figure 7

one can see that, for instance, Be9 does not possess a lot of discriminating power based on PC1

and PC2. However, its loading on all other principal components which are included in the

model needs to be evaluated before it can be excluded. In the case of Be9 it turns out that it loads more strongly on PC5 and is thus retained in the model.

Partial least squares-discriminant analysis. The PLS-DA resulted in a model with five latent variables. Specificity and sensitivity values for both the calibration (cal) and the cross-validation (CV) can be viewed in Table 9. Values range between 0.167 and 1.000 with numerous values being close to 1.000 and thus indicating relatively good sensitivity and specificity. For instance, very good results were obtained for IDDS with both sensitivity values being 1.000 and the specificity values being above 0.900. The same is true for VNSE and MYMR. However, low cross-validation specificity values were obtained for ATGA and GBBH (0.167 and 0.333). Low results were also obtained for CB and ATPA. The results for all other samples fall between these extremes with calibration results generally being better than cross-validation results.

Table 9

Sensitivity and specificity values. Full model

Class	ARMR	AR4370	ARCB	ARJO	ATMR	ATCH	ATGA
Sensitivity (cal)	1.000	1.000	1.000	1.000	1.000	0.833	0.833
Specificity (cal)	0.914	0.960	0.940	0.947	0.696	0.872	0.818
Sensitivity (CV)	0.667	0.667	0.333	0.667	1.000	0.833	0.167
Specificity (CV)	0.921	0.967	0.901	0.934	0.696	0.878	0.838

Class	ATPA	ATPM	CB	DEHB	DEMR	GBBH	IDDS
Sensitivity (cal)	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Specificity (cal)	0.743	0.804	0.791	0.878	0.729	0.960	0.993
Sensitivity (CV)	0.667	0.833	0.500	1.000	0.600	0.333	1.000
Specificity (CV)	0.750	0.824	0.784	0.878	0.832	0.947	0.993

Class	INMR	KO	LM	M72	MF	MG	MM
Sensitivity (cal)	1.000	1.000	1.000	1.000	1.000	1.000	0.833
Specificity (cal)	0.748	0.784	0.831	0.804	0.845	0.832	0.818
Sensitivity (CV)	1.000	1.000	0.833	0.667	0.833	0.800	0.833
Specificity (CV)	0.768	0.764	0.831	0.777	0.831	0.812	0.831

Class	MR	MS	MYMR	NF	NO	NP	PM
Sensitivity (cal)	1.000	1.000	1.000	1.000	0.833	1.000	1.000
Specificity (cal)	0.777	0.770	0.947	0.953	0.878	0.885	0.899
Sensitivity (CV)	0.833	0.833	1.000	0.833	0.833	1.000	0.500
Specificity (CV)	0.770	0.784	0.934	0.966	0.878	0.865	0.878

Class	VNSE	VNVI	WI
Sensitivity (cal)	1.000	1.000	1.000
Specificity (cal)	0.993	0.914	0.838
Sensitivity (CV)	1.000	0.667	0.833
Specificity (CV)	0.993	0.914	0.838

U.S. vs. International Model

      Principal component analysis. This model was created using all samples of U.S. origin and all samples of international origin, however, in this instance all international samples were coded as one class and all U.S. samples were coded as another class. Five principal components, explaining a total variance of 55.97% were retained in the model. The scores plot shows that even though there is some overlap, the two groups are inherently different (see Figure 8).
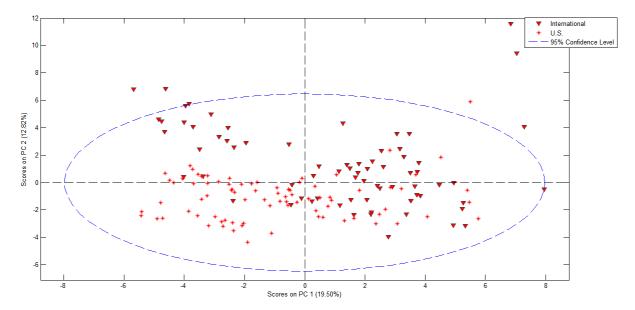
Figure 8. PC1 vs. PC2 scores plot. U.S. vs. international model

      Due to the lower number of classes it is easier to interpret the loadings plot with a view to establishing which class is related to which elements. As the scores plot (see Figure 8) shows, U.S. and international cigarettes are mainly divided by PC2 with most samples of U.S. origin having negative scores for both PCs. When viewing the loadings plot (see Figure 9) one notices that platinum, strontium and antimony load strongly positively on PC2 and are thus related to cigarette ash samples of international origin. Nickel, arsenic, germanium and boron on the other

hand load strongly negatively on PC2 which indicates a relation to cigarette ash samples of U.S. origin.
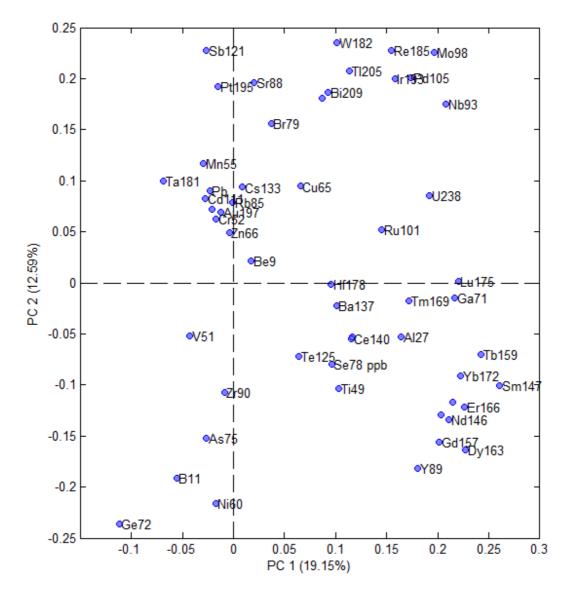
*Figure 9.*PC1 vs. PC2 loadings plot. U.S. vs. international model

Partial least squares-discriminant analysis. A model with four latent variables was created. The model showed relatively good results with only one U.S. sample (out of 83) incorrectly being predicted to be international and only two international samples (out of 71)

being incorrectly predicted to be of U.S. origin in the cross-validation stage. The resulting high

sensitivity and specificity values can be viewed in Table 10.
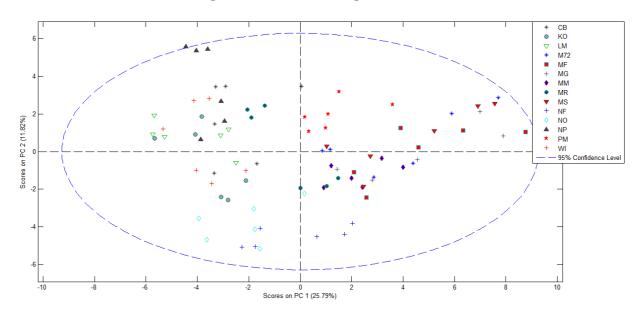
Table 10

Sensitivity and specificity values. U.S. vs. international model

Class	International	U.S.
Sensitivity (cal)	1.000	1.000
Specificity (cal)	1.000	1.000
Sensitivity (CV)	0.972	0.988
Specificity (CV)	0.988	0.972

U.S. Model

      Principal component analysis. This model was created using all samples of U.S. origin.

Six principal components accounting for 68.21% of the variance were retained in the model.

Bismuth was excluded from the model since it did not contribute to the discrimination. The

scores plot shows a clearer clustering pattern than it did for the full model (compare Figures 6

and 10). All six PM samples are clearly distinct from the remainder of the samples. Similarly,

the NO and NF samples cluster together while still exhibiting differences between the two

varieties. The M72 samples on the other hand are very spread out. The visual discrimination

between the samples can be improved when displaying a 3D plot of the data which includes an

additional principal component and thus increases the variance explained from 37.61% to

48.58% (see Figure 11). Both plots indicate that samples of brands of which two packs were

obtained tend to cluster in two groups of three. Whether these two groups reflect the two packs

purchased at different times will be explored under "Time of purchase".

Figure 10. PC1 vs. PC2 scores plot. U.S. model
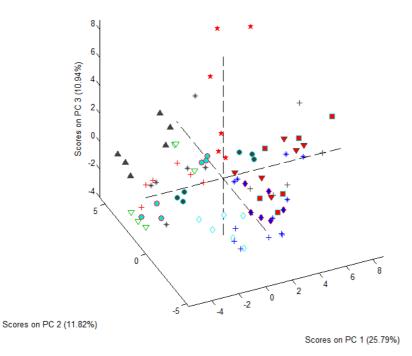
Figure 11. 3D scores plot PC1 vs. PC2 vs. PC3. U.S. model

Partial least squares-discriminant analysis. Three latent variables were retained in the model. Good results were obtained for some of the brands. For instance, five out of six PM samples were classified correctly during the cross-validation. Four out of six NF samples were also classified correctly. The sensitivity and specificity values for both the calibration and the cross-validation can be viewed in Table 11. These reflected the successful classification of PM and NO samples. The lowest results were obtained for MR. Overall, there are only few values above 0.900.

Table 11

Sensitivity and specificity values. U.S. model

Class	CB	KO	LM	M72	MF	MG	MM
Sensitivity (cal)	1.000	1.000	1.000	0.667	0.833	1.000	0.833
Specificity (cal)	0.727	0.688	0.688	0.857	0.740	0.731	0.727
Sensitivity (CV)	0.667	0.833	0.833	0.500	0.667	0.800	0.667
Specificity (CV)	0.701	0.675	0.675	0.844	0.740	0.718	0.688

Class	MR	MS	NF	NO	NP	PM	WI
Sensitivity (cal)	0.500	0.833	1.000	1.000	1.000	1.000	1.000
Specificity (cal)	0.455	0.792	0.961	0.922	0.896	0.922	0.675
Sensitivity (CV)	0.167	0.500	1.000	0.833	1.000	0.833	0.833
Specificity (CV)	0.519	0.792	0.961	0.909	0.896	0.909	0.675

Further Aspects.

Grouping of varieties. Another interesting fact with regards to the discrimination of cigarette brands of U.S. origin is that the clustering in PCA becomes a lot more clear-cut when all Marlboro varieties as well as both Natural American Spirit varieties are grouped as one class each. A 7-PC model which explains 71.94% of the variance shows a relatively good distinction between the brands. However, it has to be noted that packs purchased at the same time regardless of brand still appear to cluster together. The corresponding PLS-DA model with five latent variables showed that the re-coding measure did not have a great impact on the sensitivity values for most brands, however, specificity values increased. Significantly better values were obtained for Marlboros as one class (0.971/0.938/0.914/0.896) as compared to the individual classes (compare Table 11). Moreover, perfect values were obtained for the Natural American Spirit class (1.000 for both sensitivity and specificity for calibration and cross-validation).

Time of purchase. Due to the fact that in the U.S. brand model samples from packs obtained at the same time seemed to cluster together, regardless of the brand (see Figure 11), this aspect was also explored. Samples were coded according to whether they originated from packs purchased with the first or the second sample set. While a PCA model with seven PCs explaining 71.94% of the total variance did not result in strict clustering of the two groups, PLS-DA indicated the possibility to distinguish between the different times of purchase with only three out of 42 "Pack 2" samples being incorrectly classified as belonging to the first purchase and three out of 42 "Pack 1" samples being incorrectly classified as belonging to the second purchase. This results in very good sensitivity and specificity values (see Table 12).

Table 12

Sensitivity and specificity values. Pack 1 vs. pack 2 model

Class	Pack 1	Pack 2
Sensitivity (cal)	1.000	1.000
Specificity (cal)	1.000	1.000
Sensitivity (CV)	0.927	0.929
Specificity (CV)	0.929	0.927

Marlboro Varieties Model

Principal component analysis. Six principal components explaining 67.02% of the total variance were retained in the model. Bismuth was excluded from this model since it was determined not to contribute to its discriminative power (see earlier discussion involving thorium). Only the Marlboro Red samples were clearly distinct from all other samples (see Figure 12). The remainder of the samples does not show a clear clustering pattern according to Marlboro variety.
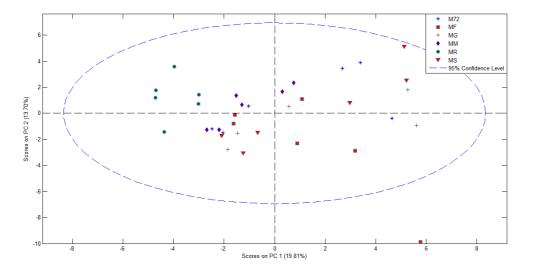
Figure 12. PC1 vs. PC2 scores plot. Marlboro varieties model

Partial least squares-discriminant analysis. The results previously obtained from the PCA are reflected in the four-latent-variable PLS-DA model. The sensitivity and specificity values are not particularly high with the exception of the Marlboro Red values which are at 1.000 for both sensitivity and specificity for the calibration as well as the cross-validation (see Table 13). The cross-validation sensitivity values were overall the lowest.

Table 13

Sensitivity and specificity values. Marlboro varieties model
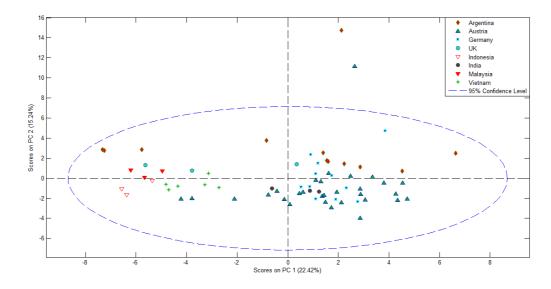
Class	M72	MF	MG	MM	MR	MS
Sensitivity (cal)	0.833	1.000	0.800	1.000	1.000	0.500
Specificity (cal)	0.966	0.966	0.867	0.966	1.000	0.828
Sensitivity (CV)	0.333	0.500	0.400	0.667	1.000	0.500
Specificity (CV)	0.862	0.793	0.767	0.862	1.000	0.724

International Model

Principal component analysis. All samples of international origin were used to create this model. Samples were coded according to their country of origin. Silver was excluded from the sample since it did not contribute to the model's discriminating power. Five principal components explaining 61.21% of the variance were retained in the model. The scores plot shows relatively distinct clustering patterns for most of the countries (see Figure 13). Austrian and German samples clearly cluster together. The British samples on the other hand are relatively spread out. Moreover, Indonesian, Malaysian and Vietnamese samples cluster

together, whereas the Indian samples, the only remaining Asian samples, are not part of the

cluster.

Figure 13. PC1 vs. PC2 scores plot. International model

Partial least squares-discriminant analysis. Five latent variables were retained in this

model. This analysis supports the previously obtained results of the PCA. Perfect sensitivity

and specificity values were obtained for the Indonesian samples (see Table 14). Very good

values were also obtained for German and Argentinian samples. The Indian class had the overall

lowest values with no samples being classified correctly.

Table 14

Sensitivity and specificity values. International model

Class	AT	AR	DE	UK	ID	IN	MY	VI
Sensitivity (cal)	0.967	1.000	1.000	1.000	1.000	0.000	1.000	1.000
Specificity (cal)	0.976	0.966	0.950	0.926	1.000	0.838	0.897	0.969

Sensitivity (CV)	0.900	0.917	1.000	0.333	1.000	0.000	0.667	0.500
Specificity (CV)	0.902	0.966	0.967	0.897	1.000	0.868	0.897	0.908

Marlboro Reds Model

Principal component analysis. All Marlboro Reds samples with the exception of the previously excluded sample DEMR2A were used to construct this model. Five principal components explaining 72.04% of the total variance were retained in the final model. Silver was excluded from the model as it did not contribute to its discriminative power. The scores plot shows a good separation of Marlboro Reds purchased in different countries (see Figure 14). Thus, inherent differences exist between Marlboro Reds with different countries of origin. The Malaysian Marlboro Reds appear to be particularly different from the ones purchased in other countries.
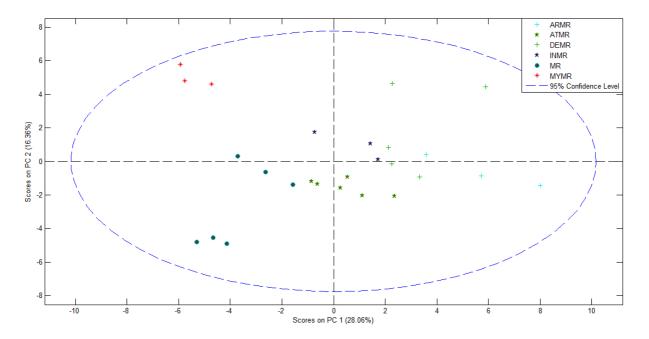
Figure 14. PC1 vs. PC2 scores plot. Marlboro Reds model

Partial least squares-discriminant analysis. Four latent variables were retained in the final model. The model achieved perfect classification for all samples during the calibration stage. However, for the cross-validation only Marlboro Reds of Argentinian, Austrian, Malaysian and U.S. manufacture were classified correctly with no false positives and no false negatives. One Marlboro Reds samples of German origin was incorrectly classified as being of Austrian origin while all three samples of Indian origin were incorrectly classified as being German. This results in the following sensitivity and specificity values (see Table 15).

Table 15

Sensitivity and specificity values. Marlboro Reds model

Class	ARMR	ATMR	DEMR	INMR	MR	MYMR
Sensitivity (cal)	1.000	1.000	1.000	1.000	1.000	1.000
Specificity (cal)	1.000	1.000	0.952	0.739	1.000	1.000
Sensitivity (CV)	0.333	1.000	0.800	0.667	1.000	1.000
Specificity (CV)	1.000	0.950	0.952	0.609	1.000	1.000

Smoking Regimes

Principal component analysis. Five principal components explaining a total variance of 61.52% were retained in the model which was built using all cigarette samples of U.S. origin with all Marlboro samples coded as one group and all Natural American Spirit samples coded as one group. All modified and puffed samples were coded as "unknown". As Figure 15 shows, the "unknown" samples fall within the Marlboro group.
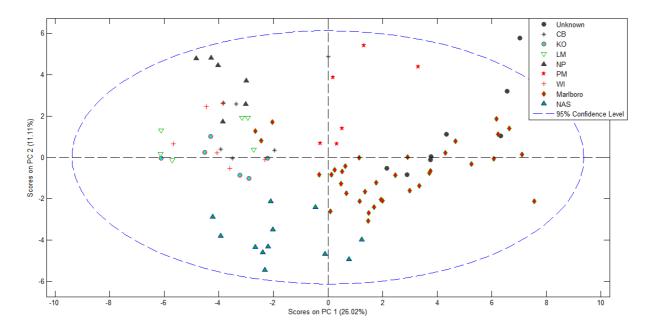
Figure 15. PC1 vs. PC2 scores plot. Smoking regime model

Partial least squares-discriminant analysis. A PLS-DA model with five latent variables confirmed the results previously obtained through PCA. All "unknown" samples were classified as belonging to the Marlboro class (see Figure 16).
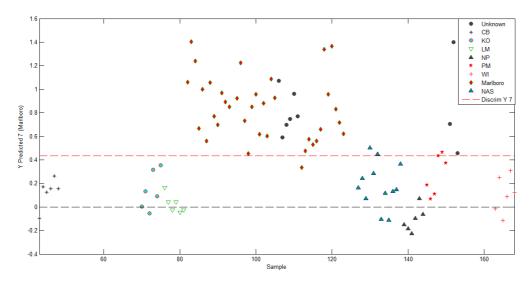
Figure 16. Classification of "unknown" samples as Marlboros

Discussion

As the results show, for the most part the inter-brand variation is larger than the intra-brand variation with regards to trace-metal concentrations in the cigarette ash. Good and sometimes very good discrimination can be achieved with a number of the models while others are not capable of correctly classifying the majority of the samples. What these results imply and how the information obtained can be used in forensic case work will be discussed in the following.

The full model including all samples of U.S. and international origin indicated that there are inherent differences between the cigarette brands with regards to the trace-metal concentrations in their ash. This confirms the results obtained by Pérez-Bernal et al. (2011). The fact that there are several brands which only obtained values in the order of 0.600, especially for cross-validation results, however, suggests that a step-wise classification as was done by Pérez-Bernal et al. (2011) should be explored with a view to increasing sensitivity and specificity values. While Pérez-Bernal et al. (2011) started off by classifying samples according to their originating from blond or black tobacco, the first stage in a step-wise analysis here was the distinction between samples of U.S. or international manufacture. Despite some overlap, the PCA model showed a clear distinction between the two groups (see Figure 8). When regarding the scores plot, one has to bear in mind that only two PCs are displayed. In the case of the U.S. vs. international model these two PCs explain only roughly 30% of the total variance. If the plot were to be displayed in more dimensions the distinction would be significantly clearer. Hence, the fact that it is as clear as it is with only two PCs indicates that samples of U.S. manufacture are distinct from samples of international manufacture. As the PLS-DA shows, only 1.2% of the U.S. samples and 2.8% of the international samples were classified incorrectly. Accordingly,

very high values were achieved for both sensitivity and specificity with 0.972 being the lowest

value. Thus, the distinction between ash samples of U.S and of international origin would be a

potentially successful first step in a step-wise approach to classification.

In line with the step-wise approach the U.S. model was developed. The PCA model

initially exhibited a good distinction of U.S. brands. In particular, the 3D graph including 3 PCs

which explain a total variance of 48.58% showed a distinct clustering of samples belonging to

the same brand. Again, very good PLS-DA results were obtained for some of the brands such as

NF or PM, however, overall results were lower for the U.S. model. In particular, this is true for

cross-validation sensitivity values and for the Marlboro varieties. M72, MR, and MS all had

cross-validation sensitivity values of only 0.500 or lower (compare Tables 9 and 11). Thus, by

coding all Marlboro varieties as one group, and by coding all Natural American Spirit samples as

one group, a measure was taken in order to improve classification. Both groups exhibited

distinct clusters in the PCA scores plot. The sensitivity values for the Marlboro class were

notably higher (0.971/0.938/0.914/0.896) than any of the individual results were on average in

the full model or the U.S. model and the values for the Natural American Spirit class were

perfect with 1.000 for both sensitivity and specificity for calibration and cross-validation. This

points to the possibility of a larger number of samples which capture the range of trace-metal

concentrations possible within one brand more fully resulting in a better classification.

When comparing the sensitivity and specificity values obtained for other brands in the

full model and the model in which all Marlboros were coded as one class, it becomes evident that

no model is strictly better than the other. Due to a lower number of misclassified Marlboro and

Natural American Spirit samples the specificity values increased for most brands, however, a

tendency for sensitivity values to decrease was noted. What can be stated, however, is that a

prior distinction between brands seems to be more successful in terms of sensitivity and specificity values than a direct discrimination of varieties. This result was followed up by the creation of a model meant to distinguish between Marlboro varieties. PCA only showed a distinct clustering of MR samples while all other Marlboro varieties clustered together. Accordingly, MR obtained perfect sensitivity and specificity values for both calibration and cross-validation during PLS-DA. However, the other Marlboro varieties showed mixed results. While cross-validation sensitivity values were clearly lower for all varieties with the exception of MR in the Marlboro varieties model, there was no trend in the other values showing a preference for one model. Values for MS were clearly worse in the Marlboro varieties model (compare Tables 9 and 13). Thus, the step-wise approach to variety classification does not improve sensitivity and specificity values in a way which would commend the use of the step-wise approach.

Overall, the range of sensitivity and specificity results obtained for American samples broadly reflects the range of values obtained by Pérez-Bernal et al. (2011) for their Spanish set of samples. The fact that values seem to be slightly higher in the Spanish study could be explained by the fact that the smoking regime was more homogenous since a smoking machine was employed for this step of the sample preparation.

A model was also developed to explore whether it would be possibly to classify international samples according to their country of origin. PCA indicated that samples from different countries were inherently different from each other with a tendency of Asian samples clustering together being observed. Relatively good sensitivity and specificity values were obtained for all countries with the only low values being cross-validation sensitivity values for samples originating from the UK and Vietnam (0.333 and 0.500, respectively). Another aspect

which was explored with regards to cigarettes of international origin was the distinction of the same brand and variety when produced in different countries. PCA of all Marlboro Reds with different countries of origin showed a clear clustering of samples from each country even when only two PCs explaining 44.42% were used to graphically display the data. PLS-DA resulted in 1.000 sensitivity and specificity values for Malaysian and U.S. Marlboro Reds. German and Indian Marlboro Reds appeared to overlap with regards to their trace-metal concentrations, however, no connection was found with regards to the manufacture of German and Indian Marlboro Reds. Thus, even though one would intuitively assume that it would be desirable to keep the taste of a certain brand and variety of cigarettes and thus the formulation consistent even across borders, there are significant differences between Marlboro Reds manufactured in different countries with regards to trace-metal concentrations. This kind of classification could not only be useful when no cigarette butt is left behind but also when a cigarette butt of a certain brand is left behind and there is reason to assume that the cigarette could have originated from a country outside of that where the cigarette butt is found.

These results demonstrate that a significant amount of information can be obtained from a cigarette sample found at a crime scene. Not only can it be determined with a relatively high certainty whether the ash originated from within the U.S. or from a different country, the brand can also be determined with varying degrees of certainty. In the case of Marlboros or Natural American Spirit the certainty is particularly high. If the ash is determined to originate from a different country, it is possible to name a country that it is most likely from.

The determination of the point in time when a pack of cigarettes was purchased was possible to an extent not anticipated by the researcher. However, this finding confirms the results obtained by Giordani et al. (2005) who concluded that the location of purchase seemed to

play a greater role than varieties within the same brands. In order to use this kind of information

in a criminal case, cigarette ash samples would continuously have to be obtained and analyzed

building a library not only in the brand dimension but also in a temporal dimension. The

possibility that these results are caused by unidentified variations during sample preparation or

due to slightly different calibration curves during ICP/MS analysis cannot be fully excluded and

should be investigated further, for instance, by re-running a set-one sample with set two samples

in order to determine whether the same concentrations are obtained.

The fact that the samples originating from those Marlboro Reds which were smoked

using modified smoking regimes and those which were continuously puffed were classified as

Marlboros strengthens the basis of this kind of analysis. This result implies that the wide range

of smoking habits exhibited by individuals does not affect the concentrations of more volatile

elements to an extent that would cause the trace-metal profiles within a brand to be so diverse

that they do no longer qualify as one class.

Thus, the analysis can be used in order to compare the cigarette brand smoked at a crime

scene to that smoked by a suspect, to determine what brand the perpetrator might smoke in case a

suspect has not yet been identified or to gather information with regards to the number of people

who might have been present at a crime scene. It can also be useful in giving hints as to possible

international travel if the brand smoked originated from a foreign country which can then also be

determined.

Limitations

When evaluating the results one has to bear in mind several limitations of this study. Due

to the fact that individuals outside of the study were involved in procuring samples abroad, it was

not possible to obtain duplicates of all packs purchased outside the U.S. Obtaining those

duplicates could have enhanced the robustness of the models involving international samples and could have potentially improved classification. This assumption is supported by the fact that significantly better sensitivity and specificity values were obtained when Marlboros were coded as one group as discussed above. A generally larger sample size in many respects would have been beneficial to the study as will be discussed in more detail under "Suggestions for Further Research".

Since the researcher did not have access to a commercial smoking machine, it was not possible to use the same parameters used by Pérez-Bernal et al. (2011), however, an alternate reproducible method of "smoking" the cigarettes was explored and developed and its effect on the trace-metal concentrations was taken into account. Thus, even though this might be a limitation, it also increases the closeness of the model to real-world situations which leads to the point that the lack of samples produced by human smoking is a clear limitation of the study.

Suggestions for Further Research

As mentioned previously, a larger range of samples could have increased the robustness of the models and improved classification. Thus, future studies should include more packs of the same brand of cigarettes as well as more cigarettes from an individual pack. Moreover, considering that a possible differentiation between samples purchased in different locations and at different points in time has been implied the geographical range of samples purchased in the same country should be expanded as should the time frame over which samples are purchased. This would yield more information on the intra-brand variability.

Additionally, since it has been indicated that cigar ash contains a comparable range of trace-metal concentrations as does cigarette ash, this aspect should be included in further research as well (Verma et al., 2010). In order to fully explore the topic of tobacco-product ash

self-rolled cigarettes would also have to be included. Moreover, the contribution of the paper and perhaps filter should also be investigated more thoroughly.

Overall, samples originating from different tobacco products purchased in all kinds of locations, at all points in time can be added to the library of trace-metal concentrations which will need to be established and made accessible for criminalists in order to utilize the potential of the kind of examination described in this study.

Conclusion

This study has demonstrated that a significant amount of information can be extracted from ash found at crime scenes. Inter-brand variation has been shown to generally be larger than intra-brand variation. Sensitivity and specificity values for the classification of samples as being of U.S. or international origin are close to 1.000. The classification into brands of cigarettes has been shown to be possible with relatively high sensitivity and specificity values for a number of brands. The distinction of varieties within a brand on the other hand was less successful. The possibility of narrowing down the point in time when the pack of cigarettes that a sample originated from was purchased has been indicated and needs further research. One important aspect which this study has explored is whether different smoking habits have an influence on the trace-metal concentrations of ash to the extent that the samples differ so much from each other that they no longer constitute a class. It has been determined that this is not the case which gives this kind of analysis a solid basis. However, before it can be used in day-to-day casework, an extensive library of trace-metal concentrations needs to be established and made available to analysts.

References

Baker, R.R. (2002). The development and significance of standards for smoking-machine

methodology. *Contributions to Tobacco Research, 20(1),* 23-41.

Baker, R.R., Pereira da Silva, J. R., Smith, G. (2004a). The effect of tobacco ingredients on

smoke chemistry. Part I: Flavourings and additives. *Food and Chemical Toxicology, 42S,* 3-

37. doi:10.1016/S0278-6915(03)00189-3

Baker, R.R., Pereira da Silva, J. R., Smith, G. (2004b). The effect of tobacco ingredients on

smoke chemistry. Part II: Casing ingredients. *Food and Chemical Toxicology, 42S,* 39-52.

doi:10.1016/j.fct.2003.08.009

Beebe, K. R., Pell, R. J., & Seasholtz, M. B. (1998). *Chemometrics: A practical guide.* New

York, NJ: Wiley-Interscience.

Berghof Products and Instruments GmbH. (n.d.). *Theory of sample preparation using acid

digestion, pressure digestion and microwave digestion (microwave decomposition).*

Enningen: Berghof.

British American Tobacco (2011, October). *Cigarettes.* Retrieved from:

*http://www.bat.com/group/sites/uk__3mnfen.nsf/vwPagesWebLive/DO6HHJ9F?opendocume

nt&SKN=1.*

British American Tobacco (2011, October). *Tobacco Blends.* Retrieved from:

*http://www.bat.com/group/sites/uk__3mnfen.nsf/vwPagesWebLive/DO6S8J5Y?opendocumen

t&SKN=1.*

Bruker. (2010). *Bruker 810/820 ICP-MS Customer Training.* Fremont, CA: Bruker Chemical

Analysis.

Centers for Disease Control and Prevention. (2012). Economic facts about U.S. tobacco

   production and use. Retrieved from:

   http://www.cdc.gov/tobacco/data_statistics/fact_sheets/economics/econ_facts/.

Centers for Disease Control and Prevention (n.d.). Smoking & Tobacco Use – Bidis and Kreteks.

   Retrieved from:

   http://www.cdc.gov/tobacco/data_statistics/fact_sheets/tobacco_industry/bidis_kreteks/.

Çevik, U., Ergen, E., Budak, G., Karabulut, A., Tiraşoğlu, E., Apaydin, G., & Kopya, A. I.

   (2003). Elemental analysis of Akçaabat tobacco and its ash by EDXRF spectrometry.

   Journal of Quantitative Spectroscopy & Radiactive Transfer, 78, 409-415. doi:

   10.1016/S0022-4073(02)00263-7.

Durnal, E. W. (2010). Crime scene investigation (as seen on TV). *Forensic Science

   International, 199,* 1-5. doi: 10.1016/j.forsciint.2010.02.015.

Ebisike, K., Ayyejuyo, O.O., Sonibare, J.A., Ogunkunle, O.A., & Ojumu, T.V. (2004). Pollution

   impacts of cigarette consumption on indoor air quality in Nigeria. *Journal of Applied

   Science, 4(4),* 623-629.

Fisher, B. A. J. (2004). *Techniques of crime scene investigation* (7th ed.)*. London, England:

   Taylor & Francis.

Geiss, O., &Kotzias, D. European Commission (2007). *Tobacco, cigarettes and cigarette smoke*

   (EC publication EUR 22783 EN). Luxembourg: Office for Official Publications of the

   European Communities.

Giordani, L., Rizzio, E., & Brandone, A. (2005). Neutron activation analysis in forensic

   investigations: Trace elements characterization of cigarettes. *Journal of Radioanalytical and

   Nuclear Chemistry, 263,* 739-744. doi: 10.1007/s10967-005-0651-7.

Golia, E.E., Dirmikou, A., & Mitsios, I.K. (2007). Accumulation of metals on tobacco leaves

(primings) grown in an agricultural area in relation to soil. *Bulletin of Environmental*

Contamination and Toxicology, 79, 158-162. doi: 10.1007/s00128-007-9111-0

Golia, E.E., Dirmikou, A., & Mitsios, I.K. (2009). Heavy-metal concentration in tobacco leaves

in relation to their available soil fractions. *Communication in Soil Science and Plant*

Analysis, 40, 106-120. doi: 10.1080/00103620802623570

Healton C.G., Cummings, K.M., O'Connor, R.J., & Novotny, T.E. (2011). Butt really? The

environmental impact of cigarettes. *Tobacco Control, 20(1),* i1. doi:10.1136/tc.2011.043729

International Organization for Standardization - Ad Hoc Smoking Behavior Review Team

Working Group 9 of the ISO TC 126 (2005). *A review of human smoking behavior data and*

recommendations for a new ISO standard for the machine smoking of cigarettes. Retrieved

from: http://www.legacy.library.ucsf.edu/documentStore/m/q/t/mqt27a00/Smqt27a00.pdf

Iskander, F.Y. (1986). Cigarette ash as a possible source of environmental contamination.

Environmental Pollution, Series B, 11(4), 291-301.

Iskander, F.Y. (1992). Multielement determination in a Chinese cigarette brand. *Journal of*

Radioanalytical and Nuclear Chemistry, 195(1), 105-110.

Kassel, J.D., Greenstein, J.E., Evatt, D. P., Wardle, M.C., Yates, M.C., Veilleux, J. C., &

Eissenberg, T. (2007). Smoking topography in response to denicotinized and high-yield

nicotine cigarettes in adolescent smokers. *Journal of Adolescent Health, 40*, 54-60.

doi:10.1016/j.jadohealth.2006.08.006

Moermann, J. W., & Potts, G. E. (2011). Analysis of metals leached from smoked cigarette litter.

Tobacco Control, 20, i30-i35. doi: 10.1136/tc.2010.040196.

Peréz-Bernal, J. L., Amigo, J. M., Fernández-Torres, R., Bello, M. A. & Callejón-Mochón, M.

    (2011). Trace-metal distribution of cigarette ashes as marker of tobacco brands. *Forensic*

    Science International, 204, 119-125. doi: 10.1016/j.forsciint.2010.05.014.

Philip Morris International (n.d.). *Our history.* Retrieved from:

    http://www.pmi.com/eng/about_us/pages/our_history.aspx

Philipp Morris USA (n.d.). *Making our cigarettes.* Retrieved from:

    http://www.philipmorrisusa.com/en/cms/Products/Cigarettes/Manufacturing/default.aspx?src

    =top_nav.

Purkis, S.W., Troude, V., Duputié, G., & Tessier, C. (2010). Limitations in the characterization

    of cigarette products using different machine smoking regimes. *Regulatory Toxicology and*

    Pharmacology 58, 501-515. doi:10.1016/j.yrtph.2010.08.022

Ryan, J. & Clark, M. (2010). Trace metal determination in tobacco and cigarette ash by

    inductively coupled plasma-atomic emission spectroscopy. *Concordia College Journal of*

    Analytical Chemistry, 1, 34-41.

Shafey, O., Eriksen, M., Ross, H., & Mackay, J. (2009). *The tobacco atlas* (3rd ed.). Atlanta, GA:

    The American Cancer Society.

Smith, E.A. & Novotny, T.E. (2011). Whose butt is it? Tobacco industry research about smokers

    and cigarette butt waste. *Tobacco Control, 20(1),* i2-i9. doi:10.1136/tc.2010.040105

Swami, K., Judd, C. D., & Orsini, J. (2009). Trace metals analysis of legal and counterfeit

    cigarette tobacco samples using inductively coupled plasma mass spectrometry and cold

    vapor atomic absorption spectrometry. *Spectroscopy Letters, 42,* 479-490. doi:

    10.1080/00387010903267799.

Texas Department of Transportation. (2009). *Visible litter study.* Austin, TX: NuStats

    EnviroMedia, Social Marketing. Retrieved from Don't Mess with Texas:

    http://www.dontmesswithtexas.org/docs/DMWT_2009_Visible_Litter_Exec_Summary.pdf.

U.S. Department of Health and Human Services. (2010). *How tobacco smoke causes disease:*

    The biology and behavioral basis for smoking-attributable disease: A report of the surgeon

    general. Washington, DC: Government Printing Office.

Veilleux, J. C., Kassel, J.D., Heinz, A.J., Braun, A., Wardle, M.C., Greenstein, J., Evatt, D. P., &

    Conrad, M. (2011). Predictors and sequelae of smoking topography over the course of a

    single cigarette in adolescent light smokers. *Journal of Adolescent Health 48,* 176-181. doi:

    10.1016/j.jadohealth.2010.06.015

Verma, S., Yadav, S., & Singh, I. (2010). Trace metal concentration in different Indian tobacco

    products and related health implications. *Food and Chemical Toxicology, 48*, 2291-2297.

    doi:10.1016/j.fct.2010.05.062

Wang, W., & Finlayson-Pitts, B. J. (2003). Measurement of trace metals in tobacco and cigarette

    ash by inductively coupled plasma-atomic emission spectroscopy. *Journal of Chemical*

    Education, 80, 83-85. doi:10.1021/ed080p83.

Zulfiqar, S., Shabbir, S., Ishaq, M., Shaukat, M. S., & Sarwar, M. I. (2006). Metal distribution

    in Pakistani and foreign brands of cigarette ash. *Bulletion of Environmental Contamination*

    and Toxicology, 77, 679-686. doi: 10.1007/s00128-006-1116-6.

Appendix A – Cigarette Sample Information

American cigarettes set 1

Brand	Lot number
Marlboro Reds	V254Y21B1
Marlboro Rich Smooth Original Flavor	V220Z28B2
Marlboro Smooth Original Flavor (Gold Pack)	V285Z24B3
Marlboro Mellow Flavor (Silver Pack)	V262Y22A2
Marlboro Menthol (Silver Pack)	V164Z22B3
Marlboro Seventy-twos	V269Z28B1
Newport Non-menthol	2H217402013
Pall Mall Red	FSCG24CG2PB6
L&M Filter	V285X23D6
Camel Blue	FSCI232I2THO
Winston Red Box	FSCI22FI2KNO
Kool Super Longs 100s True Menthol	FSCH254H21N7
Natural American Spirit (100% Additive-free)	25412416:09
Natural American Spirit (organic tobacco)	29612508:05

* *Note.* All American samples were purchased at Walgreens, 1400 E 2nd Street, Edmond, OK.

All samples of the first set were purchased on 12/11/2012.

American cigarettes set 2

Brand	Lot number
Marlboro Reds	V242Y21B1
Marlboro Rich Smooth Original Flavor	R292Z22A1
Marlboro Smooth Original Flavor (Gold Pack)	V318Z21A3
Marlboro Mellow Flavor (Silver Pack)	V306Z24A3
Marlboro Menthol (Silver Pack)	V333Z22B4
Marlboro Seventy-twos	V214Z28B1
Newport Non-menthol	2W098407:06
Pall Mall Red	FSCL24CL2RT2
L&M Filter	V320X28A1
Camel Blue	FSCL232L2QM7
Winston Red Box	FSCI22FI2TO1
Kool Super Longs 100s True Menthol	FSCK254K2ZM6
Natural American Spirit (100% Additive-free)	31112110:21
Natural American Spirit (organic tobacco)	28912320:04

* *Note.* All American samples were purchased at Walgreens, 1400 E 2nd Street, Edmond, OK.

All samples of the second set were purchased on 02/05/2012.

International cigarettes

Country	Brand	Location	Date	Lot number
Austria	Marlboro Red	Vienna	05/2012	094PC14
	Marlboro Red	Vienna	07/2012	200P024
	Parisienne	Vienna	05/2012	74S32B56
	Parisienne	Vienna	07/2012	74C32F49
	Chesterfield	Vienna	05/2012	illegible
	Chesterfield	Vienna	07/2012	illegible
	Pall Mall	Vienna	05/ 2012	5 x22B35
	Pall Mall	Vienna	07/2012	x5072E22
	Gauloises Blondes bleu	Vienna	05/2012	2A25JR
	Gauloises Blondes bleu	Vienna	07/2012	2007JR
Germany	Marlboro Red	Oer-Erkenschwick	07/2012	3BA W3C RN3 7HW GA41218509
	Marlboro Red	Oer-Erkenschwick	07/2012	2UX R7L 7NN B43 GA41218509
	HB	Oer-Erkenschwick	07/2012	74E22F93
	HB	Oer-Erkenschwick	07/2012	74E22F93
UK	Benson& Hedges Gold	London	12/2011	LJAUDH2
Argentina	Marlboro Red	Córdoba	07/2012	129 B21
	4370	Córdoba	07/2012	T115 22441807
	Jockey	Córdoba	07/2012	T116 22620221
	Camel Blue	Córdoba	07/2012	T118 21921120

India	Marlboro Red	Bombay	08/2012	IA04206313
Indonesia	Dji Sam Soe 234 Fatsal5	Jakarta	04/2012	12762
Malaysia	Marlboro Red	Kuala Lumpur	07/2012	MBC1217118
Vietnam	vinataba	Hanoi	04/2012	020111
	State Express London 555	Hanoi	04/2012	160312 31

Appendix B – Puff Volumes and Smoke Durations

American cigarettes set 1

Brand	AFR* Before L/min	AFR After L/min	Smoke Duration
CB	2.023	1.901	5:20 min
CB	2.046	2.018	5:20 min
CB	2.029	1.925	5:52 min
CB	2.022	2.036	5:20 min
PM	2.066	1.954	5:52 min
PM	2.000	1.868	6:22 min
PM	2.023	1.967	6:22 min
PM	2.026	1.966	6:22 min
PM	2.019	1.880	6:33 min
WI	2.039	1.763	5:20 min
WI	2.024	1.930	4:48 min
WI	2.025	1.792	5:20 min
WI	2.052	1.735	5:52 min
WI	2.032	1.873	5:52 min
LM	2.025	2.010	4:48 min
LM	2.039	1.940	4.48 min
LM	2.008	1.825	4:48 min
LM	2.037	1.979	4:16 min
LM	2.021	1.957	4:16 min

NP	2.029	2.027	4:48 min
NP	2.026	2.047	4:16 min
NP	2.020	1.925	4:16 min
NP	2.033	1.961	4:48 min
KO	2.041	1.857	5:52 min
KO	2.047	1.792	6:24 min
KO	2.028	1.865	5:52 min
MR	2.034	1.858	4:48 min
MR	2.048	1.954	4:16 min
MR	2.026	1.901	3:44 min
MR	2.029	1.925	4:16 min
MF	2.041	2.070	4:48 min
MF	2.044	2.015	4:48 min
MS	2.017	2.060	3:44 min
MS	2.025	2.064	4:48 min
MG	2.008	2.002	4:48 min
MG	2.008	2.020	4:48 min
MM	2.028	1.978	4:48 min
MM	2.018	2.033	4:16 min
M72	2.041	2.021	3:12 min
M72	2.028	2.024	3:44 min
NF	2.028	1.908	8:00 min
NF	2.033	2.030	8:00 min

NF	2.016	1.933	8:00 min
NF	2.038	1.923	8:00 min
NO	2.012	1.885	8:00 min
NO	2.023	2.000	8:00 min
NO	2.025	1.974	8:00 min
NO	2.029	1.069	8:00 min

Note. AFR= Average flow rate

American cigarettes set 2

Brand	AFR Before L/min	AFR After L/min	Smoke Duration
CB	2.002	2.021	6:24 min
CB	2.033	1.907	6:24 min
CB	2.029	1.926	6:24 min
CB	2.034	1.909	5:52 min
PM	2.025	1.783	7:28 min
PM	2.020	1.908	6:56 min
WI	2.028	2.040	5:20 min
WI	2.026	1.960	5:20 min
WI	2.023	2.085	4:48 min
WI	2.051	1.989	5:52 min
LM	2.027	1.958	5:20 min
LM	2.029	1.919	5:20 min
LM	2.034	1.961	4:16 min

LM	2.049	2.018	4:16 min
NP	2.033	1.989	4:48 min
NP	2.025	2.089	4:16 min
NP	2.047	2.097	4:16 min
NP	2.018	1.988	4:16 min
KO	2.027	1.974	6:24 min
KO	2.046	1.955	5:52 min
KO	2.026	1.979	6:56 min
MR	2.030	2.021	5:20 min
MR	2.039	1.964	4:48 min
MR	2.022	1.948	4:16 min
MR	2.028	2.027	4:16 min
MF	2.048	1.980	4:48 min
MF	2.049	2.006	4:48 min
MF	2.016	1.976	4:48 min
MF	2.016	1.912	4:48 min
MS	2.026	1.935	5:20 min
MS	<2.055	1.913	5:20 min
MS	2.018	2.003	4:48 min
MS	2.023	2.007	4:48 min
MG	2.045	2.040	4:48 min
MG	2.052	2.015	4:16 min
MG	2.034	1.931	5:20 min

MG	2.032	1.978	4:48 min
NF	2.026	1.844	8:00 min
NF	2.011	1.935	8:00 min
NO	2.042	2.018	8:00 min
NO	2.022	1.989	8:00 min

Note. AFR= Average flow rate

International cigarettes

Brand	AFR Before L/min	AFR After L/min	Smoke Duration
ATMR1	2.031	2.309	5:20 min
ATMR1	2.041	2.143	4:48 min
ATPA1	2.018	2.142	6:22 min
ATPA1	2.046	2.178	5:20 min
ATGA1	2.025	2.160	3:44 min
ATGA1	2.015	2.136	4:16 min
ATCH1	2.032	2.157	4:16 min
ATCH1	2.040	2.170	4:48 min
ATPM1	2.015	1.942	4:16 min
ATPM1	2.034	2.098	4:16 min
ATMR2	2.028	2.018	4:48 min
ATMR2	2.024	2.044	4:16 min
ATPA2	2.028	2.042	4:16 min
ATPA2	2.023	2.051	4:48 min

ATGA2	2.030	2.030	4:16 min
ATGA2	2.027	2.029	4:16 min
ATCH2	2.043	2.063	4:48 min
ATCH2	2.022	2.032	4:16 min
ATPM2	2.019	1.969	4:48 min
ATPM2	2.021	1.994	5:20 min
ARMR	2.026	2.025	4:16 min
ARMR	2.030	2.031	4:48 min
ARCB	2.026	2.080	4:16 min
ARCB	2.049	2.093	4:16 min
ARJO	2.022	2.102	4:16 min
ARJO	2.024	2.033	3:44 min
AR4370	2.033	2.000	5:52 min
AR4370	2.004	2.013	5:20 min
GBBH	2.007	1.995	4:16 min
GBBH	2.013	1.979	5:20 min
MYMR	2.034	2.016	5:20 min
MYMR	2.021	2.015	4:48 min
INMR	2.008	1.997	4:48 min
INMR	2.005	2.018	4:48 min
IDDS	2.024	1.992	8:00 min
IDDS	2.022	2.059	7:28 min
VNVI	2.028	2.029	4:16 min

Brand	AFR Before L/min	AFR After L/min	Smoke Duration
VNVI	2.029	2.025	4:48 min
VNSE	2.024	2.052	4:16 min
VNSE	2.026	2.024	4:48 min
DEMR1	2.016	2.028	5:20 min
DEMR1	2.024	2.017	4:48 min
DEMR2	2.015	2.025	5:20 min
DEMR2	2.021	2.033	4:48 min
DEHB1	2.034	1.996	4:16 min
DEHB1	2.046	2.094	4:16 min
DEHB2	2.007	2.023	4:48 min
DEHB2	2.033	2.023	4:16 min

Note. AFR= Average flow rate

Additional cigarettes

Brand	AFR Before L/min	AFR After L/min	Smoke Duration
MOD1	2.021	2.024	3:58 min
MOD1	2.025	2.031	4:25 min
MOD2	2.032	1.989	3:10 min
MOD2	2.010	1.990	3:48 min
PUFF	2.021	1.883	≈ 20 s
PUFF	2.021	1.990	≈ 20 s

Note. AFR= Average flow rate

Appendix C – Sample Weights

American samples set 1

Sample	Weight (g)	Sample	Weight (g)	Sample	Weight (g)
CB1A	0.1002	MR1B	0.1000	NF1C	0.0999
CB1B	0.1001	MR1C	0.1003	NO1A	0.1001
CB1C	0.0999	MF1A	0.0502	NO1B	0.1002
PM1A	0.1000	MF1B	0.0503	NO1C	0.1001
PM1B	0.1001	MF1C	0.0501		
PM1C	0.1002	MS1A	0.0503		
WI1A	0.1000	MS1B	0.0500		
WI1B	0.1002	MS1C	0.0502		
WI1C	0.1002	MG1A	0.0500		
LM1A	0.1001	MG1B	0.0502		
LM1B	0.1000	MG1C	0.0502		
LM1C	0.1001	MM1A	0.0502		
NP1A	0.0999	MM1B	0.0502		
NP1B	0.1001	MM1C	0.0500		
NP1C	0.1003	M721A	0.0503		
KO1A	0.1001	M721B	0.0500		
KO1B	0.1003	M721C	0.0499		
KO1C	0.1003	NF1A	0.0998		
MR1A	0.1000	NF1B	0.1003		

American samples set 2

Sample	Weight (g)	Sample	Weight (g)
CB2A	0.0500	MF2A	0.0503
CB2B	0.0497	MF2B	0.0501
CB2C	0.0502	MF2C	0.0500
PM2A	0.0500	MS2A	0.0500
PM2B	0.0503	MS2B	0.0499
PM2C	0.0501	MS2C	0.0500
WI2A	0.0500	MG2A	0.0503
WI2B	0.0502	MG2B	0.0503
WI2C	0.0503	MG2C	0.0502
LM2A	0.0501	NF2A	0.0502
LM2B	0.0501	NF2B	0.0501
LM2C	0.0502	NF2C	0.0501
NP2A	0.0502	NO2A	0.0499
NP2B	0.0503	NO2B	0.0502
NP2C	0.0501	NO2C	0.0502
KO2A	0.0503	MM2A	0.0501
KO2B	0.0501	MM2B	0.0502
KO2C	0.0502	MM2C	0.0503
MR2A	0.0501	M722A	0.0503
MR2B	0.0500	M722B	0.0503
MR2C	0.0500	M722C	0.0502

International samples

Sample	Weight (g)	Sample	Weight (g)	Sample	Weight (g)
ATMR1A	0.0501	ATGA2A	0.0500	GBBHA	0.0504
ATMR1B	0.0502	ATGA2B	0.0504	GBBHB	0.0504
ATMR1C	0.0500	ATGA2C	0.0503	GBBHC	0.0504
ATPA1A	0.0503	ATCH2A	0.0500	MYMRA	0.0501
ATPA1B	0.0501	ATCH2B	0.0504	MYMRB	0.0501
ATPA1C	0.0500	ATCH2C	0.0503	MYMRC	0.0502
ATGA1A	0.0500	ATPM2A	0.0501	INMRA	0.0504
ATGA1B	0.0501	ATPM2B	0.0500	INMRB	0.0501
ATGA1C	0.0503	ATPM2C	0.0501	INMRC	0.0501
ATCH1A	0.0502	ARMRA	0.0500	IDDSA	0.0500
ATCH1B	0.0498	ARMRB	0.0504	IDDSB	0.0501
ATCH1C	0.0498	ARMRC	0.0503	IDDSC	0.0504
ATPM1A	0.0501	ARCBA	0.0500	VNVIA	0.0502
ATPM1B	0.0502	ARCBB	0.0502	VNVIB	0.0503
ATPM1C	0.0501	ARCBC	0.0503	VNVIC	0.0504
ATMR2A	0.0502	ARJOA	0.0501	VNSEA	0.0503
ATMR2B	0.0501	ARJOB	0.0501	VNSEB	0.0504
ATMR2C	0.0502	ARJOC	0.0503	VNSEC	0.0501
ATPA2A	0.0502	AR4370A	0.0503	DEMR1A	0.0504
ATPA2B	0.0500	AR4370B	0.0500	DEMR1B	0.0501
ATPA2C	0.0503	AR4370C	0.0502	DEMR1C	0.0503

Sample	Weight (g)
DEMR2A	0.0500
DEMR2B	0.0502
DEMR2C	0.0504
DEHB1A	0.0504
DEHB1B	0.0503
DEHB1C	0.0502
DEHB2A	0.0503
DEHB2B	0.0503
DEHB2C	0.0501

Additional samples

Sample	Weight (g)	Sample	Weight (g)
TOBA	0.0504	PUFFB	0.0502
TOBB	0.0504	PUFFC	0.0503
TOBC	0.0501		
MOD1A	0.0498		
MOD1B	0.0504		
MOD1C	0.0504		
MOD2A	0.0502		
MOD2B	0.0500		
MOD2C	0.0501		
PUFFA	0.0504		

Appendix D – Sample Concentrations

Samples of U.S. origin: average concentrations in mg/g and standard deviations

Label		Be9	B11	Na23	Mg24	Al27	Cl35	Ti49	V51	Cr52	Mn55	Co59	Ni60
CB	Mean	0.0000	0.3434	2.5737	30.9426	3.9207	125.1351	0.3651	0.0088	0.0211	0.8635	0.0010	0.0303
	Std	0.0000	0.1427	0.4173	2.2572	0.3928	124.8653	0.0448	0.0011	0.0041	0.1188	0.0011	0.0085
KO	Mean	0.0000	0.2312	2.1593	29.9038	3.1837	128.8484	0.3049	0.0081	0.0191	0.9064	0.0010	0.0269
	Std	0.0000	0.0283	0.2819	1.4599	0.2901	123.1026	0.0209	0.0006	0.0007	0.0594	0.0011	0.0067
LM	Mean	0.0000	0.3220	1.8411	27.7700	3.1793	136.6116	0.3052	0.0078	0.0189	0.9166	0.0009	0.0261
	Std	0.0000	0.1435	0.2201	1.3228	0.2852	132.6903	0.0286	0.0008	0.0046	0.0563	0.0010	0.0056
M72	Mean	0.0000	0.2670	1.5724	28.6694	3.5201	2.1078	0.2814	0.0038	0.8313	0.8778	0.2923	0.0390
	Std	0.0000	0.0350	0.1926	1.4553	0.2219	0.8126	0.0083	0.0021	1.9981	0.0833	0.7061	0.0155
MF	Mean	0.0000	0.2732	1.6880	27.1374	3.4894	1.3346	0.3598	0.0031	0.0103	0.8655	0.0035	0.0379
	Std	0.0000	0.0223	0.2482	1.3658	0.2044	0.8451	0.0930	0.0013	0.0041	0.0538	0.0006	0.0034
MG	Mean	0.0000	0.2742	1.2548	29.1917	3.4817	1.6039	0.3472	0.0032	0.0115	0.9249	0.0044	0.0320
	Std	0.0000	0.0177	0.1061	2.1430	0.2761	0.7326	0.0457	0.0012	0.0050	0.1203	0.0009	0.0072
MM	Mean	0.0000	0.2672	1.3199	28.1558	3.1292	1.6477	0.2553	0.0038	0.0148	0.8222	0.0030	0.0372
	Std	0.0000	0.0410	0.1120	1.2083	0.1921	0.5599	0.0175	0.0008	0.0027	0.0960	0.0005	0.0019
MR	Mean	0.0000	0.2425	1.4072	28.4285	3.5618	121.0861	0.3166	0.0086	0.0200	0.8627	0.0012	0.0317
	Std	0.0000	0.0287	0.1878	1.2618	0.3031	114.8800	0.0185	0.0008	0.0014	0.0554	0.0013	0.0064
MS	Mean	0.0000	0.2633	1.2428	28.3602	3.6714	1.7338	0.2894	0.0043	0.0132	0.8656	0.0042	0.0312
	Std	0.0000	0.0318	0.1435	2.4053	0.3659	1.0184	0.0262	0.0010	0.0026	0.0705	0.0006	0.0086
NF	Mean	0.0000	0.3439	2.0368	32.3108	2.3992	96.1552	0.2066	0.0033	0.0091	0.8790	0.0015	0.0201
	Std	0.0000	0.0644	0.2202	1.8094	0.1095	104.2966	0.0211	0.0022	0.0027	0.0774	0.0009	0.0086
NO	Mean	0.0000	0.2174	1.7252	37.3628	2.6584	102.9412	0.2069	0.0038	0.0122	0.7767	0.0018	0.0189
	Std	0.0000	0.0136	0.3076	1.8029	0.1701	111.1498	0.0106	0.0017	0.0013	0.0513	0.0010	0.0082
NP	Mean	0.0000	0.3248	3.2872	27.4614	3.7015	131.9651	0.5189	0.0096	0.0120	0.8503	0.0009	0.0243
	Std	0.0000	0.1454	0.6372	1.4143	0.2064	114.1219	0.1089	0.0018	0.0042	0.1481	0.0033	0.0077
PM	Mean	0.0000	0.2007	2.2998	28.8770	3.9192	105.0212	0.3848	0.0074	0.0188	1.0630	0.0048	0.0353
	Std	0.0000	0.0253	0.4833	1.1050	0.1576	114.2380	0.0452	0.0024	0.0031	0.1140	0.0031	0.0077
WI	Mean	0.0000	0.2052	1.3661	28.9123	3.1186	127.2577	0.3100	0.0083	0.0155	0.9504	0.0009	0.0252
	Std	0.0000	0.0136	0.1781	1.5004	0.3336	122.5164	0.0183	0.0005	0.0012	0.0961	0.0010	0.0075

Label	Cu65	Zn66	Ga71	Ge72	Br79	Rb85	Sr88	Y89	Zr90	Nb93	Mo98	Ru101	Pd105
CB	0.0552	0.1601	0.0010	0.0035	0.0215	0.1039	0.6090	0.0031	0.0057	0.0009	0.0008	0.0000	0.0000
	0.0044	0.0216	0.0001	0.0011	0.0252	0.0093	0.0380	0.0003	0.0016	0.0007	0.0007	0.0000	0.0000
KO	0.0522	0.1669	0.0009	0.0035	0.0252	0.1011	0.4323	0.0029	0.0051	0.0008	0.0004	0.0000	0.0000
	0.0025	0.0217	0.0001	0.0009	0.0276	0.0050	0.0172	0.0002	0.0022	0.0008	0.0005	0.0000	0.0000
LM	0.0577	0.1545	0.0008	0.0039	0.0213	0.1191	0.4930	0.0031	0.0057	0.0007	0.0004	0.0000	0.0000
	0.0064	0.0093	0.0001	0.0008	0.0245	0.0094	0.0338	0.0001	0.0012	0.0007	0.0005	0.0000	0.0000
M 72	0.0632	0.1645	0.0011	0.0031	0.0000	0.0819	0.3704	0.0032	0.0042	0.0015	0.0024	0.0000	0.0002
	0.0122	0.0121	0.0001	0.0001	0.0000	0.0054	0.0222	0.0003	0.0005	0.0004	0.0006	0.0000	0.0002
M F	0.0617	0.1837	0.0011	0.0024	0.0000	0.0773	0.3408	0.0032	0.0044	0.0015	0.0040	0.0000	0.0006
	0.0045	0.0258	0.0001	0.0004	0.0000	0.0025	0.0223	0.0002	0.0010	0.0013	0.0024	0.0000	0.0005
M G	0.0974	0.1975	0.0011	0.0025	0.0000	0.0831	0.3572	0.0034	0.0044	0.0025	0.0038	0.0000	0.0007
	0.0231	0.0082	0.0001	0.0007	0.0000	0.0066	0.0254	0.0003	0.0005	0.0008	0.0022	0.0000	0.0005
M M	0.0581	0.1594	0.0010	0.0028	0.0000	0.0845	0.3583	0.0032	0.0035	0.0009	0.0026	0.0000	0.0001
	0.0051	0.0117	0.0001	0.0006	0.0000	0.0040	0.0086	0.0002	0.0003	0.0003	0.0011	0.0000	0.0001
M R	0.0586	0.1846	0.0009	0.0034	0.0199	0.0857	0.3624	0.0035	0.0050	0.0009	0.0007	0.0000	0.0000
	0.0037	0.0286	0.0001	0.0009	0.0222	0.0065	0.0212	0.0002	0.0025	0.0010	0.0008	0.0000	0.0000
M S	0.0616	0.1680	0.0011	0.0030	0.0000	0.0831	0.3550	0.0033	0.0041	0.0022	0.0028	0.0000	0.0004
	0.0060	0.0214	0.0002	0.0006	0.0000	0.0088	0.0218	0.0003	0.0005	0.0003	0.0004	0.0000	0.0002
N F	0.0618	0.2193	0.0007	0.0026	0.0060	0.0663	0.3885	0.0033	0.0040	0.0007	0.0021	0.0000	0.0001
	0.0064	0.0235	0.0001	0.0002	0.0079	0.0059	0.0171	0.0002	0.0005	0.0001	0.0011	0.0000	0.0001
N O	0.0670	0.1880	0.0007	0.0029	0.0121	0.0895	0.4578	0.0030	0.0036	0.0006	0.0024	0.0000	0.0001
	0.0069	0.0199	0.0001	0.0003	0.0136	0.0095	0.0368	0.0003	0.0001	0.0001	0.0007	0.0000	0.0001
N P	0.0636	0.1460	0.0009	0.0035	0.0168	0.1262	0.5926	0.0033	0.0069	0.0008	0.0009	0.0000	0.0000
	0.0070	0.0207	0.0002	0.0011	0.0199	0.0085	0.0607	0.0002	0.0019	0.0012	0.0011	0.0000	0.0003
PM	0.0588	0.1680	0.0012	0.0027	0.0205	0.1133	0.4777	0.0031	0.0044	0.0022	0.0024	0.0000	0.0005
	0.0047	0.0219	0.0001	0.0009	0.0226	0.0047	0.0160	0.0002	0.0006	0.0009	0.0007	0.0000	0.0003
W I	0.0580	0.1567	0.0008	0.0036	0.0213	0.1147	0.4837	0.0031	0.0051	0.0005	0.0002	0.0000	0.0000
	0.0031	0.0233	0.0001	0.0013	0.0235	0.0142	0.0547	0.0001	0.0013	0.0004	0.0002	0.0000	0.0000

Label	Ag107	Cd111	In115	Sn118	Sb121	Te125	Cs133	Ba137	La139	Ce140	Pr141	Nd146	Sm147
CB	0.0000	0.0004	0.0000	0.0000	0.0002	0.0000	0.0008	0.5054	0.0434	0.0430	0.0015	0.0052	0.0007
	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0001	0.0244	0.0143	0.0132	0.0001	0.0004	0.0001
KO	0.0000	0.0006	0.0000	0.0000	0.0001	0.0000	0.0007	0.4696	0.0287	0.0290	0.0012	0.0043	0.0005
	0.0000	0.0002	0.0000	0.0000	0.0001	0.0000	0.0001	0.0244	0.0132	0.0120	0.0001	0.0004	0.0001
LM	0.0000	0.0006	0.0000	0.0000	0.0001	0.0000	0.0006	0.5665	0.0267	0.0261	0.0013	0.0043	0.0006
	0.0000	0.0002	0.0000	0.0000	0.0001	0.0000	0.0001	0.0417	0.0161	0.0143	0.0001	0.0003	0.0001
M 72	0.0000	0.0007	0.0000	0.0000	0.0001	0.0002	0.0011	0.4477	0.0634	0.0607	0.0019	0.0061	0.0007
	0.0000	0.0004	0.0000	0.0000	0.0001	0.0002	0.0004	0.0280	0.0403	0.0364	0.0004	0.0012	0.0001
M F	0.0003	0.0007	0.0000	0.0000	0.0002	0.0002	0.0009	0.4127	0.0471	0.0451	0.0018	0.0057	0.0007
	0.0006	0.0005	0.0000	0.0000	0.0001	0.0001	0.0001	0.0107	0.0307	0.0269	0.0003	0.0008	0.0001
M G	0.0003	0.0009	0.0000	0.0000	0.0001	0.0001	0.0009	0.4371	0.0602	0.0574	0.0019	0.0060	0.0008
	0.0006	0.0004	0.0000	0.0000	0.0001	0.0001	0.0000	0.0336	0.0364	0.0325	0.0004	0.0011	0.0001
M M	0.0000	0.0008	0.0000	0.0000	0.0002	0.0001	0.0009	0.4541	0.0755	0.0703	0.0020	0.0062	0.0007
	0.0000	0.0002	0.0000	0.0000	0.0001	0.0001	0.0001	0.0217	0.0352	0.0307	0.0004	0.0008	0.0001
M R	0.0000	0.0008	0.0000	0.0000	0.0001	0.0000	0.0007	0.4189	0.0389	0.0387	0.0016	0.0055	0.0006
	0.0000	0.0001	0.0000	0.0000	0.0001	0.0000	0.0001	0.0176	0.0222	0.0202	0.0002	0.0006	0.0000
M S	0.0000	0.0007	0.0000	0.0000	0.0001	0.0001	0.0010	0.4348	0.0540	0.0524	0.0019	0.0060	0.0008
	0.0000	0.0002	0.0000	0.0000	0.0001	0.0001	0.0001	0.0428	0.0427	0.0389	0.0005	0.0014	0.0001
N F	0.0000	0.0011	0.0000	0.0000	0.0001	0.0001	0.0005	0.3360	0.0355	0.0348	0.0017	0.0055	0.0007
	0.0000	0.0005	0.0000	0.0000	0.0001	0.0002	0.0001	0.0324	0.0158	0.0141	0.0002	0.0006	0.0001
N O	0.0000	0.0006	0.0000	0.0000	0.0001	0.0001	0.0004	0.4383	0.0327	0.0319	0.0015	0.0049	0.0006
	0.0000	0.0004	0.0000	0.0000	0.0000	0.0001	0.0001	0.0378	0.0130	0.0123	0.0002	0.0007	0.0000
N P	0.0000	0.0004	0.0000	0.0000	0.0001	0.0000	0.0009	0.6172	0.0284	0.0279	0.0012	0.0044	0.0005
	0.0000	0.0003	0.0000	0.0000	0.0001	0.0000	0.0001	0.0347	0.0118	0.0106	0.0002	0.0005	0.0001
PM	0.0000	0.0008	0.0000	0.0000	0.0002	0.0000	0.0009	0.5465	0.0229	0.0242	0.0013	0.0045	0.0007
	0.0000	0.0001	0.0000	0.0000	0.0001	0.0001	0.0001	0.0490	0.0102	0.0092	0.0001	0.0005	0.0001
W I	0.0000	0.0005	0.0000	0.0000	0.0000	0.0000	0.0006	0.5556	0.0324	0.0318	0.0014	0.0047	0.0006
	0.0000	0.0002	0.0000	0.0000	0.0000	0.0000	0.0001	0.0645	0.0183	0.0160	0.0002	0.0008	0.0000

Label	Eu153	Gd157	Tb159	Dy163	Er166	Tm169	Yb172	Lu175	Hf178	Ta181	W182	Re185	Ir193
CB	0.0002	0.0009	0.0001	0.0004	0.0003	0.0000	0.0002	0.0000	0.0017	0.0004	0.0000	0.0000	0.0000
	0.0000	0.0001	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0010	0.0002	0.0000	0.0000	0.0000
KO	0.0002	0.0008	0.0001	0.0004	0.0002	0.0000	0.0001	0.0000	0.0016	0.0005	0.0000	0.0000	0.0000
	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0013	0.0003	0.0000	0.0000	0.0000
LM	0.0002	0.0008	0.0001	0.0004	0.0002	0.0000	0.0002	0.0000	0.0019	0.0005	0.0000	0.0000	0.0000
	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0008	0.0002	0.0000	0.0000	0.0000
M 72	0.0002	0.0011	0.0001	0.0005	0.0003	0.0000	0.0002	0.0000	0.0020	0.0000	0.0008	0.0000	0.0001
	0.0000	0.0003	0.0000	0.0001	0.0000	0.0000	0.0001	0.0000	0.0002	0.0000	0.0010	0.0000	0.0001
M F	0.0002	0.0011	0.0001	0.0005	0.0003	0.0000	0.0002	0.0000	0.0020	0.0000	0.0017	0.0000	0.0003
	0.0000	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0006	0.0000	0.0029	0.0000	0.0004
M G	0.0002	0.0012	0.0001	0.0005	0.0003	0.0000	0.0002	0.0000	0.0022	0.0000	0.0043	0.0001	0.0004
	0.0000	0.0002	0.0000	0.0001	0.0001	0.0000	0.0001	0.0000	0.0009	0.0001	0.0055	0.0001	0.0005
M M	0.0002	0.0012	0.0001	0.0005	0.0003	0.0000	0.0002	0.0000	0.0018	0.0000	0.0000	0.0000	0.0000
	0.0000	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.0000	0.0000	0.0000	0.0000
M R	0.0002	0.0010	0.0001	0.0005	0.0003	0.0000	0.0002	0.0000	0.0014	0.0004	0.0000	0.0000	0.0000
	0.0000	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0013	0.0003	0.0000	0.0000	0.0000
M S	0.0002	0.0012	0.0001	0.0005	0.0003	0.0000	0.0002	0.0000	0.0018	0.0000	0.0015	0.0000	0.0002
	0.0000	0.0003	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0003	0.0000	0.0018	0.0000	0.0002
NF	0.0002	0.0010	0.0001	0.0004	0.0002	0.0000	0.0002	0.0000	0.0016	0.0001	0.0000	0.0000	0.0000
	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0008	0.0001	0.0000	0.0000	0.0000
NO	0.0002	0.0009	0.0001	0.0004	0.0002	0.0000	0.0001	0.0000	0.0016	0.0001	0.0000	0.0000	0.0000
	0.0000	0.0001	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0006	0.0001	0.0000	0.0000	0.0000
NP	0.0002	0.0008	0.0001	0.0004	0.0003	0.0000	0.0002	0.0000	0.0018	0.0004	0.0000	0.0000	0.0000
	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0012	0.0003	0.0000	0.0000	0.0001
PM	0.0002	0.0008	0.0001	0.0005	0.0003	0.0000	0.0002	0.0000	0.0012	0.0000	0.0000	0.0000	0.0000
	0.0000	0.0001	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0010	0.0000	0.0000	0.0000	0.0001
W I	0.0002	0.0009	0.0001	0.0004	0.0002	0.0000	0.0002	0.0000	0.0016	0.0004	0.0000	0.0000	0.0000
	0.0000	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0009	0.0002	0.0000	0.0000	0.0000

Label	Pt195	Au197	Tl205	Pb	Bi209	Th232	U238	Ca44	Fe57	Fe56	As75	Se78
CB	0.0003	0.0005	0.0000	0.0023	0.0000	0.0000	0.0000	64.8981	3.4844	3.2530	0.0017	0.0000
	0.0004	0.0008	0.0000	0.0005	0.0000	0.0000	0.0001	2.1963	0.2548	0.2707	0.0019	0.0000
KO	0.0004	0.0026	0.0000	0.0023	0.0000	0.0000	0.0001	61.9277	2.9270	2.7349	0.0026	0.0000
	0.0005	0.0034	0.0000	0.0003	0.0000	0.0000	0.0001	1.7100	0.2613	0.2494	0.0016	0.0001
LM	0.0002	0.0005	0.0000	0.0022	0.0000	0.0000	0.0000	58.9022	2.9501	2.7531	0.0023	0.0001
	0.0002	0.0008	0.0000	0.0004	0.0000	0.0000	0.0000	1.6630	0.1751	0.1530	0.0010	0.0001
M 72	0.0002	0.0000	0.0000	0.0023	0.0000	0.0000	0.0004	81.8208	4.3703	4.6047	0.0016	0.0015
	0.0002	0.0000	0.0000	0.0006	0.0000	0.0000	0.0000	22.5185	3.7677	3.8944	0.0005	0.0018
M F	0.0000	0.0000	0.0000	0.0030	0.0000	0.0000	0.0004	62.3185	2.5338	2.9287	0.0025	0.0000
	0.0001	0.0000	0.0001	0.0004	0.0000	0.0000	0.0001	3.8558	0.1094	0.1407	0.0010	0.0000
M G	0.0003	0.0000	0.0000	0.0028	0.0000	0.0000	0.0003	80.3468	2.8032	2.9330	0.0023	0.0006
	0.0004	0.0000	0.0000	0.0008	0.0000	0.0000	0.0000	22.3184	0.5461	0.3111	0.0009	0.0010
M M	0.0000	0.0000	0.0000	0.0025	0.0000	0.0000	0.0002	61.9955	2.2578	2.5400	0.0015	0.0000
	0.0000	0.0000	0.0000	0.0004	0.0000	0.0000	0.0001	2.1831	0.1111	0.1324	0.0015	0.0000
M R	0.0004	0.0039	0.0000	0.0022	0.0000	0.0000	0.0001	63.2342	3.4549	3.2439	0.0021	0.0001
	0.0005	0.0047	0.0000	0.0002	0.0000	0.0000	0.0001	3.4446	0.2467	0.2129	0.0009	0.0003
M S	0.0002	0.0000	0.0000	0.0021	0.0000	0.0000	0.0003	79.0486	2.9137	3.0487	0.0013	0.0004
	0.0002	0.0000	0.0000	0.0004	0.0000	0.0000	0.0001	25.2391	0.5087	0.3361	0.0010	0.0006
N F	0.0003	0.0000	0.0000	0.0030	0.0000	0.0000	0.0002	70.3121	1.7429	1.6706	0.0024	0.0000
	0.0003	0.0000	0.0000	0.0011	0.0000	0.0000	0.0001	2.3625	0.1493	0.0870	0.0021	0.0001
N O	0.0002	0.0000	0.0000	0.0026	0.0000	0.0000	0.0002	65.5811	1.7982	1.7354	0.0012	0.0004
	0.0002	0.0000	0.0000	0.0007	0.0000	0.0000	0.0001	3.9683	0.1345	0.0837	0.0007	0.0007
N P	0.0003	0.0020	0.0000	0.0021	0.0000	0.0000	0.0000	60.3597	3.7089	3.4840	0.0016	0.0001
	0.0004	0.0095	0.0000	0.0006	0.0000	0.0000	0.0001	2.0841	0.3411	0.2398	0.0008	0.0001
PM	0.0004	0.0094	0.0000	0.0033	0.0000	0.0000	0.0003	59.0261	3.3629	3.5270	0.0021	0.0000
	0.0005	0.0115	0.0000	0.0005	0.0000	0.0000	0.0001	1.7946	0.5724	0.2556	0.0007	0.0000
W I	0.0003	0.0001	0.0000	0.0023	0.0000	0.0000	0.0000	58.9147	2.9559	2.7687	0.0013	0.0001
	0.0003	0.0003	0.0000	0.0003	0.0000	0.0000	0.0000	2.1678	0.0596	0.0691	0.0012	0.0002

Ash samples of international origin: average concentrations in mg/g and standard deviations

Label		Be9	B11	Na23	Mg24	Al27	Cl35	Ti49	V51	Cr52	Mn55	Co59	Ni60
AR4370	Mean	0.0000	0.1887	1.0703	24.3676	2.2700	52.6501	0.2382	0.0040	2.2295	0.8179	1.1612	0.0221
	Std	0.0000	0.0079	0.1346	1.6225	0.1080	20.2528	0.0466	0.0013	3.8402	0.0635	2.0064	0.0338
ARCB	Mean	0.0000	0.2501	0.8529	31.1992	3.9907	2.2269	0.3907	0.0101	0.0129	0.7925	0.0053	0.0096
	Std	0.0000	0.0212	0.1479	2.6840	0.3708	0.3175	0.0667	0.0024	0.0022	0.0979	0.0005	0.0030
ARJO	Mean	0.0000	0.1904	0.3278	25.4247	4.6153	3.7021	0.3653	0.0078	0.0073	0.6879	0.0031	0.0038
	Std	0.0000	0.0157	0.5613	0.9725	0.6749	1.8957	0.0231	0.0011	0.0039	0.0454	0.0004	0.0016
ARMR	Mean	0.0000	0.2047	1.3852	26.5996	4.3932	3.5565	0.4077	0.0084	0.0114	0.8951	0.0045	0.0136
	Std	0.0000	0.0057	0.4630	1.4002	0.1827	0.2590	0.0302	0.0007	0.0020	0.1065	0.0002	0.0021
ATCH	Mean	0.0000	0.2740	1.1120	26.0130	3.2793	2.8542	0.3231	0.0066	0.0148	0.9833	0.0051	0.0219
	Std	0.0000	0.1389	0.6341	1.8597	0.2977	1.7600	0.0211	0.0013	0.0024	0.0780	0.0011	0.0132
ATGA	Mean	0.0000	0.2649	1.2268	28.6786	2.6470	2.2212	0.1933	0.0017	0.0079	1.1709	0.0041	0.0259
	Std	0.0000	0.1219	0.5648	4.0922	0.4372	0.6864	0.0317	0.0010	0.0032	0.1511	0.0015	0.0090
ATMR	Mean	0.0000	0.2119	1.0080	26.4546	3.7228	2.2658	0.3475	0.0046	0.0113	0.8346	0.0040	0.0311
	Std	0.0000	0.0142	0.0454	1.3706	0.2280	0.9916	0.0141	0.0015	0.0047	0.0472	0.0006	0.0104
ATPA	Mean	0.0000	0.1980	2.4206	29.8780	3.5524	2.5595	0.3057	0.0047	0.0090	1.0765	0.0050	0.0278
	Std	0.0000	0.0173	0.4281	0.9675	0.3747	1.3268	0.0256	0.0010	0.0022	0.0982	0.0010	0.0075
ATPM	Mean	0.0000	0.2064	1.5419	32.9286	4.2148	3.7831	0.3424	0.0073	0.0114	0.9579	0.0054	0.0156
	Std	0.0000	0.0440	0.4005	1.4387	0.3821	0.7349	0.0336	0.0014	0.0042	0.1269	0.0006	0.0078
DEHB	Mean	0.0000	0.1534	2.0101	30.1175	3.9359	82.8781	0.3556	0.0061	0.0077	0.9237	0.0050	0.0069
	Std	0.0000	0.0083	0.4014	1.5088	0.1775	8.4734	0.0172	0.0005	0.0022	0.0785	0.0002	0.0014
DEMR	Mean	0.0000	0.1782	0.9449	27.9870	3.9827	87.9980	0.3893	0.0066	0.0132	0.9704	0.0043	0.0074
	Std	0.0000	0.0125	0.2732	0.5894	0.4009	8.8930	0.0354	0.0025	0.0077	0.0998	0.0002	0.0012
GBBH	Mean	0.0000	0.1647	2.6195	29.3454	2.1886	57.0192	0.1580	0.0023	0.0091	0.9782	0.0033	0.0006
	Std	0.0000	0.0102	0.1680	1.0424	0.0207	17.4662	0.0030	0.0006	0.0013	0.0780	0.0001	0.0011
IDDS	Mean	0.0000	0.1630	4.6356	32.4059	4.1817	80.5532	0.2394	0.0090	0.0148	2.3079	0.0033	0.0055
	Std	0.0000	0.0165	1.0413	1.5829	0.2421	9.8714	0.0196	0.0001	0.0021	0.5972	0.0001	0.0018
INMR	Mean	0.0000	0.1732	0.9282	28.1628	3.9944	69.5029	0.3813	0.0075	0.0155	0.8848	0.0044	0.0109
	Std	0.0000	0.0233	0.0694	3.2955	0.1619	4.8722	0.0416	0.0006	0.0018	0.1159	0.0005	0.0020
MYMR	Mean	0.0000	0.1860	1.1641	32.3679	3.2332	70.0706	0.2488	0.0060	0.0175	1.0066	0.0036	0.0056
	Std	0.0000	0.0035	0.0759	0.8864	0.1849	2.2188	0.0233	0.0003	0.0068	0.0356	0.0002	0.0001
VNSE	Mean	0.0000	0.1865	1.4897	34.3039	2.6055	86.7839	0.1590	0.0046	0.0153	1.6681	0.0047	0.0037
	Std	0.0000	0.0152	0.1968	3.0091	0.2244	2.5579	0.0151	0.0004	0.0017	0.1257	0.0006	0.0014
VNVI	Mean	0.0000	0.1956	2.4524	35.0820	3.4154	83.4498	0.2295	0.0047	0.0146	1.0311	0.0049	0.0109
	Std	0.0000	0.0259	0.2641	4.7814	0.2636	11.4391	0.0182	0.0013	0.0022	0.0599	0.0006	0.0019

Label	Cu65	Zn66	Ga71	Ge72	Br79	Rb85	Sr88	Y89	Zr90	Nb93	Mo98	Ru101	Pd105
AR4370	0.0639	0.1054	0.0009	0.0024	0.0308	0.0948	0.9241	0.0016	0.0029	0.0018	0.0033	0.0000	0.0007
	0.0265	0.0045	0.0005	0.0004	0.0056	0.0102	0.0584	0.0000	0.0003	0.0001	0.0002	0.0000	0.0001
ARCB	0.0906	0.1591	0.0012	0.0023	0.0085	0.0745	0.8500	0.0035	0.0051	0.0027	0.0031	0.0000	0.0005
	0.0115	0.0264	0.0002	0.0004	0.0146	0.0088	0.0371	0.0004	0.0005	0.0002	0.0009	0.0000	0.0001
ARJO	0.0467	0.0807	0.0014	0.0019	0.0755	0.0568	0.9269	0.0023	0.0066	0.0022	0.0064	0.0002	0.0005
	0.0037	0.0100	0.0000	0.0010	0.0625	0.0060	0.0512	0.0004	0.0009	0.0010	0.0053	0.0002	0.0007
ARMR	0.0714	0.1613	0.0013	0.0018	0.0642	0.1114	0.8817	0.0038	0.0051	0.0030	0.0047	0.0003	0.0003
	0.0024	0.0139	0.0001	0.0003	0.0071	0.0085	0.0654	0.0001	0.0003	0.0002	0.0004	0.0001	0.0002
ATCH	0.0711	0.1607	0.0009	0.0027	0.0436	0.1594	0.6699	0.0043	0.0040	0.0014	0.0034	0.0001	0.0001
	0.0022	0.0287	0.0001	0.0010	0.0480	0.0110	0.0405	0.0005	0.0005	0.0005	0.0008	0.0001	0.0001
ATGA	0.0602	0.1441	0.0008	0.0027	0.0114	0.1283	0.5984	0.0032	0.0041	0.0012	0.0042	0.0001	0.0004
	0.0116	0.0317	0.0001	0.0011	0.0278	0.0146	0.0760	0.0005	0.0014	0.0012	0.0041	0.0001	0.0004
ATMR	0.0586	0.1236	0.0010	0.0028	0.0057	0.1194	0.5212	0.0034	0.0044	0.0012	0.0027	0.0000	0.0002
	0.0059	0.0212	0.0001	0.0005	0.0065	0.0055	0.0205	0.0003	0.0003	0.0003	0.0004	0.0000	0.0001
ATPA	0.0777	0.1180	0.0011	0.0028	0.0037	0.1439	0.5686	0.0040	0.0043	0.0010	0.0026	0.0000	0.0003
	0.0150	0.0135	0.0001	0.0002	0.0083	0.0079	0.0259	0.0004	0.0003	0.0003	0.0004	0.0000	0.0001
ATPM	0.0807	0.1533	0.0012	0.0025	0.0493	0.1442	0.6885	0.0035	0.0048	0.0019	0.0032	0.0001	0.0002
	0.0073	0.0160	0.0002	0.0005	0.0464	0.0183	0.0217	0.0003	0.0005	0.0003	0.0006	0.0001	0.0002
DEHB	0.0942	0.1912	0.0012	0.0028	0.0441	0.1646	0.6482	0.0037	0.0033	0.0020	0.0032	0.0002	0.0005
	0.0079	0.0114	0.0001	0.0006	0.0150	0.0093	0.0350	0.0002	0.0003	0.0003	0.0003	0.0001	0.0002
DEMR	0.0646	0.1957	0.0011	0.0022	0.0471	0.1270	0.5406	0.0038	0.0038	0.0020	0.0050	0.0000	0.0008
	0.0046	0.0068	0.0001	0.0007	0.0087	0.0070	0.0314	0.0003	0.0010	0.0011	0.0038	0.0000	0.0010
GBBH	0.0488	0.1267	0.0006	0.0016	0.0392	0.1470	0.6019	0.0029	0.0029	0.0014	0.0022	0.0000	0.0004
	0.0020	0.0021	0.0001	0.0000	0.0154	0.0207	0.0595	0.0009	0.0008	0.0002	0.0006	0.0000	0.0002
IDDS	0.1142	0.2262	0.0009	0.0028	0.0324	0.2858	0.9232	0.0021	0.0038	0.0006	0.0029	0.0000	0.0001
	0.0169	0.0432	0.0001	0.0002	0.0097	0.0328	0.0602	0.0001	0.0004	0.0000	0.0020	0.0000	0.0001
INMR	0.0912	0.2063	0.0010	0.0025	0.0253	0.1080	0.5696	0.0036	0.0029	0.0013	0.0027	0.0000	0.0001
	0.0381	0.0133	0.0001	0.0003	0.0089	0.0115	0.0622	0.0005	0.0003	0.0000	0.0003	0.0000	0.0000
MYMR	0.0994	0.1968	0.0008	0.0022	0.0128	0.1157	0.6283	0.0021	0.0034	0.0010	0.0025	0.0000	0.0002
	0.0052	0.0110	0.0001	0.0003	0.0042	0.0048	0.0159	0.0001	0.0002	0.0001	0.0005	0.0000	0.0001
VNSE	0.0792	0.2281	0.0007	0.0027	0.0530	0.1028	0.6202	0.0034	0.0029	0.0006	0.0019	0.0000	0.0000
	0.0064	0.0237	0.0001	0.0006	0.0056	0.0063	0.0693	0.0001	0.0002	0.0001	0.0002	0.0000	0.0000
VNVI	0.0758	0.1959	0.0009	0.0024	0.0495	0.1311	0.7480	0.0027	0.0036	0.0007	0.0025	0.0000	0.0001
	0.0075	0.0179	0.0001	0.0000	0.0121	0.0230	0.0924	0.0003	0.0003	0.0000	0.0007	0.0000	0.0002

Label	Ag107	Cd111	In115	Sn118	Sb121	Te125	Cs133	Ba137	La139	Ce140	Pr141	Nd146	Sm147
AR4370	0.0000	0.0002	0.0000	0.0000	0.0006	0.0000	0.0009	0.5586	0.0138	0.0162	0.0010	0.0031	0.0003
	0.0000	0.0001	0.0000	0.0000	0.0001	0.0000	0.0001	0.0541	0.0048	0.0069	0.0004	0.0009	0.0000
ARCB	0.0000	0.0002	0.0000	0.0000	0.0005	0.0000	0.0010	0.5305	0.0312	0.0286	0.0015	0.0052	0.0008
	0.0000	0.0001	0.0000	0.0000	0.0003	0.0001	0.0001	0.0643	0.0244	0.0214	0.0003	0.0010	0.0002
ARJO	0.0005	0.0002	0.0000	0.0000	0.0002	0.0000	0.0009	0.4577	0.0770	0.0717	0.0017	0.0052	0.0006
	0.0008	0.0001	0.0000	0.0000	0.0002	0.0000	0.0001	0.0206	0.0339	0.0292	0.0003	0.0007	0.0001
ARMR	0.0000	0.0003	0.0000	0.0000	0.0001	0.0000	0.0009	0.6471	0.0594	0.0568	0.0018	0.0062	0.0009
	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0001	0.0376	0.0382	0.0336	0.0005	0.0016	0.0001
ATCH	0.0000	0.0003	0.0000	0.0000	0.0001	0.0001	0.0007	0.6613	0.0294	0.0267	0.0016	0.0054	0.0008
	0.0000	0.0003	0.0000	0.0000	0.0001	0.0001	0.0001	0.0363	0.0232	0.0205	0.0003	0.0009	0.0001
ATGA	0.0002	0.0010	0.0000	0.0000	0.0002	0.0001	0.0007	0.5319	0.0424	0.0388	0.0016	0.0051	0.0007
	0.0005	0.0003	0.0000	0.0000	0.0001	0.0001	0.0001	0.0688	0.0190	0.0164	0.0003	0.0009	0.0002
ATMR	0.0000	0.0005	0.0000	0.0000	0.0001	0.0001	0.0008	0.5410	0.0317	0.0320	0.0016	0.0051	0.0008
	0.0000	0.0001	0.0000	0.0000	0.0001	0.0002	0.0001	0.0264	0.0264	0.0245	0.0002	0.0007	0.0001
ATPA	0.0000	0.0008	0.0000	0.0000	0.0001	0.0001	0.0008	0.5730	0.0504	0.0475	0.0018	0.0058	0.0008
	0.0000	0.0003	0.0000	0.0000	0.0001	0.0001	0.0000	0.0274	0.0328	0.0295	0.0004	0.0011	0.0002
ATPM	0.0000	0.0003	0.0000	0.0000	0.0001	0.0002	0.0008	0.6517	0.0378	0.0368	0.0017	0.0055	0.0008
	0.0000	0.0001	0.0000	0.0000	0.0001	0.0002	0.0001	0.0594	0.0347	0.0318	0.0003	0.0008	0.0002
DEHB	0.0000	0.0007	0.0000	0.0000	0.0002	0.0000	0.0008	0.6634	0.0325	0.0307	0.0016	0.0052	0.0008
	0.0000	0.0002	0.0000	0.0000	0.0001	0.0000	0.0000	0.0365	0.0158	0.0142	0.0001	0.0004	0.0000
DEMR	0.0003	0.0006	0.0000	0.0000	0.0003	0.0001	0.0008	0.5575	0.0319	0.0322	0.0017	0.0059	0.0008
	0.0008	0.0002	0.0000	0.0000	0.0001	0.0001	0.0001	0.0361	0.0205	0.0187	0.0003	0.0008	0.0001
GBBH	0.0000	0.0007	0.0000	0.0000	0.0003	0.0000	0.0006	0.5601	0.0476	0.0438	0.0015	0.0051	0.0006
	0.0000	0.0004	0.0000	0.0000	0.0000	0.0001	0.0000	0.0369	0.0340	0.0309	0.0004	0.0012	0.0002
IDDS	0.0000	0.0013	0.0000	0.0000	0.0003	0.0000	0.0040	0.3644	0.0575	0.0545	0.0011	0.0039	0.0004
	0.0000	0.0002	0.0000	0.0000	0.0001	0.0001	0.0011	0.0145	0.0326	0.0299	0.0003	0.0008	0.0000
INMR	0.0000	0.0004	0.0000	0.0000	0.0003	0.0000	0.0008	0.5333	0.0430	0.0424	0.0017	0.0057	0.0007
	0.0000	0.0002	0.0000	0.0000	0.0001	0.0000	0.0001	0.0482	0.0247	0.0219	0.0002	0.0008	0.0001
MYMR	0.0000	0.0007	0.0000	0.0000	0.0003	0.0000	0.0007	0.3736	0.0169	0.0181	0.0009	0.0032	0.0004
	0.0000	0.0002	0.0000	0.0000	0.0001	0.0001	0.0001	0.0142	0.0090	0.0085	0.0001	0.0003	0.0000
VNSE	0.0000	0.0036	0.0000	0.0000	0.0007	0.0001	0.0007	0.4513	0.0666	0.0620	0.0018	0.0058	0.0006
	0.0000	0.0004	0.0000	0.0000	0.0001	0.0002	0.0001	0.0600	0.0329	0.0304	0.0004	0.0009	0.0001
VNVI	0.0000	0.0012	0.0000	0.0000	0.0003	0.0001	0.0007	0.4803	0.0270	0.0272	0.0013	0.0043	0.0005
	0.0000	0.0001	0.0000	0.0000	0.0001	0.0001	0.0001	0.0446	0.0026	0.0024	0.0001	0.0001	0.0001

Label	Eu153	Gd157	Tb159	Dy163	Er166	Tm169	Yb172	Lu175	Hf178	Ta181	W182	Re185	Ir193
AR4370	0.0002	0.0005	0.0001	0.0003	0.0002	0.0000	0.0001	0.0000	0.0017	0.0004	0.0049	0.0000	0.0003
	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0002	0.0009	0.0000	0.0001
ARCB	0.0002	0.0010	0.0001	0.0005	0.0003	0.0000	0.0002	0.0000	0.0025	0.0004	0.0094	0.0001	0.0005
	0.0000	0.0002	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0003	0.0000	0.0031	0.0000	0.0001
ARJO	0.0002	0.0010	0.0001	0.0004	0.0003	0.0000	0.0002	0.0000	0.0032	0.0010	0.0063	0.0001	0.0003
	0.0000	0.0003	0.0000	0.0001	0.0000	0.0000	0.0001	0.0000	0.0008	0.0003	0.0110	0.0000	0.0005
ARMR	0.0003	0.0011	0.0001	0.0006	0.0003	0.0000	0.0002	0.0000	0.0025	0.0005	0.0000	0.0000	0.0002
	0.0001	0.0003	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0004	0.0002	0.0000	0.0000	0.0002
ATCH	0.0003	0.0010	0.0001	0.0006	0.0003	0.0000	0.0002	0.0000	0.0022	0.0004	0.0000	0.0000	0.0000
	0.0000	0.0002	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0004	0.0004	0.0000	0.0000	0.0000
ATGA	0.0002	0.0009	0.0001	0.0004	0.0003	0.0000	0.0002	0.0000	0.0025	0.0002	0.0003	0.0000	0.0001
	0.0000	0.0001	0.0000	0.0001	0.0000	0.0000	0.0001	0.0000	0.0012	0.0002	0.0006	0.0000	0.0003
ATMR	0.0002	0.0010	0.0001	0.0005	0.0003	0.0000	0.0002	0.0000	0.0022	0.0001	0.0000	0.0000	0.0000
	0.0000	0.0002	0.0000	0.0001	0.0001	0.0000	0.0000	0.0000	0.0003	0.0001	0.0000	0.0000	0.0000
ATPA	0.0003	0.0012	0.0001	0.0005	0.0003	0.0000	0.0002	0.0000	0.0022	0.0001	0.0000	0.0000	0.0000
	0.0000	0.0002	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0001	0.0001	0.0000	0.0000	0.0000
ATPM	0.0003	0.0010	0.0001	0.0005	0.0003	0.0000	0.0002	0.0000	0.0024	0.0004	0.0005	0.0000	0.0001
	0.0000	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0003	0.0008	0.0000	0.0001
DEHB	0.0003	0.0010	0.0001	0.0005	0.0003	0.0000	0.0002	0.0000	0.0016	0.0002	0.0045	0.0000	0.0001
	0.0000	0.0001	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0002	0.0001	0.0016	0.0000	0.0001
DEMR	0.0003	0.0010	0.0001	0.0005	0.0003	0.0000	0.0003	0.0000	0.0019	0.0004	0.0070	0.0000	0.0003
	0.0000	0.0002	0.0000	0.0000	0.0001	0.0000	0.0001	0.0000	0.0012	0.0003	0.0081	0.0001	0.0004
GBBH	0.0002	0.0009	0.0001	0.0003	0.0002	0.0000	0.0002	0.0000	0.0019	0.0004	0.0033	0.0000	0.0002
	0.0000	0.0002	0.0000	0.0001	0.0001	0.0000	0.0001	0.0000	0.0007	0.0001	0.0011	0.0000	0.0001
IDDS	0.0001	0.0008	0.0001	0.0003	0.0002	0.0000	0.0001	0.0000	0.0013	0.0007	0.0008	0.0000	0.0000
	0.0000	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.0001	0.0004	0.0000	0.0000
INMR	0.0002	0.0010	0.0001	0.0005	0.0003	0.0000	0.0002	0.0000	0.0015	0.0007	0.0023	0.0000	0.0000
	0.0000	0.0001	0.0000	0.0001	0.0001	0.0000	0.0000	0.0000	0.0001	0.0001	0.0004	0.0000	0.0000
MYMR	0.0001	0.0006	0.0001	0.0003	0.0002	0.0000	0.0001	0.0000	0.0020	0.0006	0.0044	0.0000	0.0001
	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0006	0.0000	0.0000
VNSE	0.0002	0.0011	0.0001	0.0004	0.0002	0.0000	0.0001	0.0000	0.0013	0.0008	0.0001	0.0001	0.0000
	0.0000	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0003	0.0001	0.0001	0.0000	0.0000
VNVI	0.0002	0.0008	0.0001	0.0004	0.0002	0.0000	0.0002	0.0000	0.0018	0.0008	0.0018	0.0000	0.0000
	0.0000	0.0001	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0004	0.0001	0.0010	0.0000	0.0001

Label	Pt195	Au197	Tl205	Pb	Bi209	Th232	U238	Ca44	Fe57	Fe56	As75	Se78
AR4370	0.0008	0.0041	0.0000	0.0041	0.0000	0.0000	0.0002	90.6576	8.9763	8.8612	0.0000	0.0000
	0.0001	0.0030	0.0000	0.0048	0.0000	0.0000	0.0000	4.4535	11.5437	11.7543	0.0000	0.0000
ARCB	0.0000	0.0000	0.0000	0.0055	0.0000	0.0000	0.0002	100.5487	4.1049	4.0551	0.0009	0.0000
	0.0000	0.0000	0.0000	0.0037	0.0000	0.0000	0.0000	6.6750	0.4315	0.5084	0.0009	0.0000
ARJO	0.0000	0.0000	0.0001	0.0026	0.0001	0.0000	0.0003	95.7094	4.3027	4.2804	0.0005	0.0000
	0.0001	0.0000	0.0001	0.0009	0.0001	0.0000	0.0000	6.7096	0.5865	0.5404	0.0008	0.0000
ARMR	0.0000	0.0000	0.0000	0.0026	0.0000	0.0000	0.0003	102.8830	4.5582	4.4774	0.0021	0.0000
	0.0000	0.0000	0.0000	0.0007	0.0000	0.0000	0.0000	4.9758	0.2081	0.2056	0.0013	0.0000
ATCH	0.0000	0.0000	0.0000	0.0019	0.0000	0.0000	0.0002	80.2510	2.9337	2.9973	0.0008	0.0000
	0.0000	0.0000	0.0000	0.0005	0.0000	0.0000	0.0001	24.7015	0.6976	0.4521	0.0007	0.0000
ATGA	0.0001	0.0000	0.0000	0.0042	0.0000	0.0000	0.0002	81.2959	2.2222	2.1809	0.0024	0.0009
	0.0001	0.0000	0.0001	0.0009	0.0001	0.0000	0.0000	24.8110	0.6071	0.4614	0.0010	0.0014
ATMR	0.0001	0.0000	0.0000	0.0020	0.0000	0.0000	0.0002	81.1397	2.9899	3.1868	0.0009	0.0009
	0.0001	0.0000	0.0000	0.0010	0.0000	0.0000	0.0000	23.6763	0.2951	0.1525	0.0007	0.0010
ATPA	0.0001	0.0000	0.0000	0.0057	0.0000	0.0000	0.0002	81.8903	3.0405	3.1905	0.0016	0.0008
	0.0001	0.0000	0.0000	0.0043	0.0000	0.0000	0.0000	22.7771	0.5745	0.3365	0.0015	0.0009
ATPM	0.0001	0.0000	0.0000	0.0014	0.0000	0.0000	0.0002	94.9560	3.9107	3.8571	0.0007	0.0015
	0.0002	0.0000	0.0000	0.0003	0.0000	0.0000	0.0000	3.3664	0.1770	0.2061	0.0007	0.0016
DEHB	0.0010	0.0004	0.0000	0.0025	0.0000	0.0000	0.0002	100.3594	3.4956	3.3244	0.0006	0.0000
	0.0001	0.0009	0.0000	0.0005	0.0000	0.0000	0.0000	4.1357	0.1445	0.1517	0.0008	0.0000
DEMR	0.0009	0.0026	0.0001	0.0029	0.0001	0.0001	0.0003	107.3867	3.7579	3.5981	0.0005	0.0000
	0.0003	0.0049	0.0003	0.0016	0.0002	0.0001	0.0000	9.4559	0.2608	0.2476	0.0008	0.0000
GBBH	0.0007	0.0036	0.0000	0.0021	0.0000	0.0000	0.0003	100.0833	1.8924	1.6035	0.0000	0.0000
	0.0001	0.0035	0.0000	0.0006	0.0000	0.0000	0.0000	2.3127	0.0648	0.0603	0.0000	0.0000
IDDS	0.0008	0.0000	0.0000	0.0049	0.0000	0.0000	0.0002	116.3628	3.6888	3.5384	0.0000	0.0000
	0.0001	0.0000	0.0000	0.0041	0.0000	0.0000	0.0000	7.1758	0.2061	0.2321	0.0000	0.0000
INMR	0.0006	0.0000	0.0000	0.0023	0.0000	0.0000	0.0002	107.1027	3.7843	3.6562	0.0004	0.0000
	0.0001	0.0000	0.0000	0.0018	0.0000	0.0000	0.0000	1.7653	0.0170	0.0347	0.0006	0.0000
MYMR	0.0007	0.0005	0.0000	0.0016	0.0000	0.0000	0.0002	111.2839	3.0994	2.9163	0.0000	0.0000
	0.0001	0.0009	0.0000	0.0003	0.0000	0.0000	0.0000	4.0472	0.1812	0.2002	0.0000	0.0000
VNSE	0.0006	0.0000	0.0000	0.0102	0.0000	0.0000	0.0002	129.3861	2.4288	2.0924	0.0005	0.0000
	0.0001	0.0000	0.0000	0.0006	0.0000	0.0000	0.0001	7.4230	0.2390	0.2375	0.0008	0.0000
VNVI	0.0006	0.0000	0.0000	0.0032	0.0000	0.0000	0.0002	122.7190	2.9650	2.7656	0.0000	0.0000
	0.0001	0.0000	0.0000	0.0008	0.0000	0.0000	0.0000	17.0878	0.2982	0.3008	0.0000	0.0000

Additional samples: average concentrations in mg/g and standard deviations

Label		Be9	B11	Na23	Mg24	Al27	Cl35	Ti49	V51	Cr52	Mn55	Co59	Ni60
MOD1	Mean	0.0000	0.2214	1.5576	31.4156	3.7052	86.2717	0.3202	0.0043	0.0123	0.9429	0.0042	0.0132
	Std	0.0000	0.0215	0.0426	2.5981	0.6023	9.4456	0.0536	0.0031	0.0053	0.0694	0.0004	0.0030
MOD2	Mean	0.0000	0.2099	1.4225	31.0393	4.0412	95.4009	0.3478	0.0068	0.0160	0.9525	0.0044	0.0161
	Std	0.0000	0.0094	0.1475	2.0996	0.5007	7.3697	0.0319	0.0008	0.0012	0.0741	0.0008	0.0049
PUFF	Mean	0.0000	0.2231	1.4401	29.3660	3.6275	88.5322	0.3095	0.0048	0.0138	0.9018	0.0042	0.0134
	Std	0.0000	0.0012	0.2665	0.7263	0.1467	2.4831	0.0076	0.0009	0.0005	0.1103	0.0005	0.0010
TOB	Mean	0.0000	0.0307	0.1943	4.6116	0.6559	62.2251	0.0360	0.0000	0.0008	0.1429	0.0012	0.0012
	Std	0.0000	0.0068	0.0200	0.4587	0.0307	17.2506	0.0034	0.0000	0.0012	0.0200	0.0001	0.0013

Label	Cu65	Zn66	Ga71	Ge72	Br79	Rb85	Sr88	Y89	Zr90	Nb93	Mo98	Ru101	Pd105
MOD1	0.0689	0.2594	0.0010	0.0028	0.0222	0.0892	0.3852	0.0037	0.0032	0.0012	0.0022	0.0001	0.0002
	0.0082	0.0210	0.0002	0.0004	0.0014	0.0066	0.0161	0.0005	0.0003	0.0002	0.0003	0.0001	0.0001
MOD2	0.0647	0.2480	0.0011	0.0030	0.0209	0.0915	0.3981	0.0038	0.0037	0.0012	0.0026	0.0001	0.0000
	0.0074	0.0144	0.0001	0.0003	0.0134	0.0116	0.0399	0.0007	0.0008	0.0001	0.0005	0.0000	0.0000
PUFF	0.0680	0.2681	0.0010	0.0032	0.0094	0.0905	0.3909	0.0034	0.0037	0.0010	0.0026	0.0001	0.0002
	0.0065	0.0152	0.0001	0.0003	0.0126	0.0047	0.0149	0.0004	0.0008	0.0001	0.0007	0.0001	0.0003
TOB	0.0090	0.0476	0.0002	0.0027	0.0136	0.0130	0.0591	0.0005	0.0020	0.0006	0.0008	0.0002	0.0002
	0.0008	0.0151	0.0000	0.0004	0.0089	0.0021	0.0011	0.0000	0.0006	0.0001	0.0004	0.0001	0.0001

Label	Ag107	Cd111	In115	Sn118	Sb121	Te125	Cs133	Ba137	La139	Ce140	Pr141	Nd146	Sm147
MOD1	0.0000	0.0009	0.0000	0.0000	0.0003	0.0000	0.0009	0.5067	0.0614	0.0580	0.0021	0.0068	0.0009
	0.0000	0.0001	0.0000	0.0000	0.0000	0.0001	0.0002	0.0172	0.0348	0.0292	0.0004	0.0011	0.0000
MOD2	0.0000	0.0011	0.0000	0.0000	0.0003	0.0000	0.0009	0.5391	0.0632	0.0605	0.0022	0.0068	0.0009
	0.0000	0.0004	0.0000	0.0000	0.0001	0.0000	0.0003	0.0439	0.0421	0.0367	0.0001	0.0006	0.0001
PUFF	0.0000	0.0009	0.0000	0.0000	0.0003	0.0001	0.0008	0.5142	0.0784	0.0732	0.0022	0.0070	0.0009
	0.0000	0.0007	0.0000	0.0000	0.0001	0.0002	0.0000	0.0247	0.0764	0.0674	0.0008	0.0024	0.0000
TOB	0.0000	0.0010	0.0000	0.0000	0.0002	0.0001	0.0003	0.0640	0.0021	0.0025	0.0002	0.0007	0.0001
	0.0000	0.0001	0.0000	0.0000	0.0001	0.0001	0.0000	0.0047	0.0007	0.0006	0.0000	0.0001	0.0000

Label	Eu153	Gd157	Tb159	Dy163	Er166	Tm169	Yb172	Lu175	Hf178	Ta181	W182	Re185	Ir193
MOD1	0.0003	0.0012	0.0001	0.0006	0.0003	0.0000	0.0002	0.0000	0.0015	0.0001	0.0026	0.0000	0.0000
	0.0000	0.0003	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0004	0.0000	0.0000
MOD2	0.0002	0.0013	0.0001	0.0006	0.0003	0.0000	0.0002	0.0000	0.0013	0.0002	0.0018	0.0000	0.0000
	0.0000	0.0001	0.0000	0.0002	0.0001	0.0000	0.0001	0.0000	0.0000	0.0001	0.0001	0.0000	0.0000
PUFF	0.0002	0.0013	0.0001	0.0005	0.0003	0.0000	0.0002	0.0000	0.0019	0.0002	0.0027	0.0000	0.0000
	0.0000	0.0006	0.0000	0.0001	0.0000	0.0000	0.0001	0.0000	0.0008	0.0002	0.0015	0.0000	0.0000
TOB	0.0000	0.0002	0.0000	0.0001	0.0001	0.0000	0.0000	0.0000	0.0021	0.0001	0.0029	0.0000	0.0000
	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0004	0.0002	0.0011	0.0000	0.0000

Label	Pt195	Au197	Tl205	Pb	Bi209	Th232	U238	Ca44	Fe57	Fe56	As75	Se78
MOD1	0.0009	0.0000	0.0000	0.0032	0.0000	0.0000	0.0004	106.7322	3.2381	3.0420	0.0022	0.0000
	0.0002	0.0000	0.0000	0.0023	0.0000	0.0000	0.0000	0.2247	0.4528	0.4634	0.0010	0.0000
MOD2	0.0009	0.0000	0.0000	0.0030	0.0000	0.0003	0.0004	106.1184	3.6718	3.5030	0.0015	0.0000
	0.0001	0.0000	0.0000	0.0007	0.0000	0.0005	0.0001	9.3628	0.4384	0.4780	0.0005	0.0000
PUFF	0.0008	0.0000	0.0001	0.0022	0.0000	0.0001	0.0004	100.0626	3.2962	3.1189	0.0012	0.0000
	0.0000	0.0000	0.0001	0.0007	0.0000	0.0001	0.0000	3.6726	0.1344	0.1652	0.0002	0.0000
TOB	0.0008	0.0000	0.0000	0.0005	0.0000	0.0000	0.0001	18.9394	0.7906	0.5493	0.0007	0.0000
	0.0001	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	1.3333	0.0381	0.0283	0.0007	0.0000