COMPARISON OF DIGESTION METHODS APPLIED FOR LEAD QUANTIFICATION IN DRINKING WATER SAMPLES

by

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ABSTRACT

This study evaluated the digestion efficiency of a new rigorous digestion technique: focused shortwave infrared radiation digestion (SWIR) by examining the factors influencing digestion efficiency. Digestion time and nitric acid (HNO_3) concentration were significant determinants of lead recovery for the SWIR method, but the power intensity of radiation was not. The increases of acid concentrations and extended digestion time could increase lead recovery of PbO_2 digestion; however, the increase of the power intensity accompanied a decrease of lead recovery.

In this thesis, the SWIR method was also compared against standard preservation (direct analysis) and hot block digestion (conventional rigorous digestion method), on different lead and iron compounds digestion, including lead (IV) oxides (PbO_2), lead (II) phosphate ($PbSO_4$), hematite (Fe_2O_3), magnetite (Fe_3O_4), and chloropyromorphite ($Pb_5(PO_4)_3Cl$.

For PbO_2 digestion, the recovery by the SWIR method was 69.4%, exceeding the lead recovery by standard preservation and hot block digestion by factors of approximately 28 and 6, respectively. With the addition of hydrochloric acid (HCl), lead recovery of PbO_2 digestion by hot block digestion and the SWIR method were both increased (102.6% and 98.1%, respectively). In terms of lead (II) sulfate digestion, lead scale digestion, and chloropyromorphite digestion, standard preservation was able to recover the highest concentrations of lead. For hematite digestion (with HNO_3 only), the iron recovery by standard preservation was the lowest (1.5%), while the iron recovery by hot block digestion and the SWIR method were 17.1% and 15.2%, respectively. The iron recovery of magnetite digestion (with HNO_3 only) by standard preservation remained the lowest (1.7%) among three methods, while hot block digestion recovered 45.2% of iron and the SWIR method recovered 42.3%. With addition of the reducing agent (H_2O_2), the iron recovery of both hematite and magnetite digestion by the SWIR method were all increased and slightly higher than the iron recovery by hot block digestion.

LIST OF ABBREVIATIONS AND SYMBOLS USED

BLLs	blood lead levels
CDC	Centers for Disease Control and Prevention
EBL	elevated blood level
Fe_2O_3	hematite
Fe_3O_4	magnetite
HCl	hydrochloride acid
HDPE	high-density polyethylene
HNO_3	nitric acid
H_2O_2	hydrogen peroxide
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
LSLR	lead service line replacement
mm	millimeters
mL	milliliters
LSLs	lead service lines
NOM	natural organic matter
NTU	nephelometric turbidity unit
Pb	lead
$Pb_5(PO_4)_3Cl$	chloropyromorphite
PbO_2	lead (IV) oxide
$PbSO_4$	lead (II) sulfate
ppb	parts per billion
SWIR	shortwave infrared radiation
µg/L	micrograms per liter
µm	micrometers
WHO	Word Health Organization

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Chapter 1 INTRODUCTION

1.1 Project rationale

Lead (Pb) has been recognized as a possible carcinogen and a neurotoxin, and the exposure to lead is strongly associated with many serious adverse health effects, such as intellectual deficits, irreversible cognitive problems and organ damage (Flora et al., 2012; Testud et al., 2001; Triantafyllidou & Edwards, 2012). The toxicity of lead is based on blood lead levels (BLLs) and significant reduction of BLLs was observed (McFarlane et al., 2013; Lanphear et al., 2002). However, intellectual deficits along with behavioural problems were associated with a BLL lower than 10 µg/L which was once considered to be safe (Triantafyllidou & Edwards, 2012; Jusko et al., 2008; Bellinger et al., 1987). Among these lead-associated problems, central nervous system problems caused by lead exposure even at low level in early childhood, could be prolonged and persist into adulthood (Reuben et al., 2017). Clearly, accurately assessing the extent of lead exposure requires accurate quantification of the total lead that is actually present in drinking water.

Drinking water was overlooked as a significant contributor to lead exposure until a serious lead-contaminated drinking water crisis occurred in Washington D.C. in 2003 (Triantafyllidou & Edwards, 2012; Butler et al., 2016). Treated drinking water leaving treatment plants or flowing through water mains normally is lead free. As it enters into distribution systems, treated water gets contaminated by contact with lead leached from lead-containing materials, such as lead service lines (LSLs), brass, solder, faucets and other household plumbing elements (Sandvig et al., 2009; Cartier et al., 2013; Elfland et al., 2010). Among these sources, LSLs represent the major source of lead occurring in drinking water, contributing up to 50-75% of the total lead in drinking water (Schock & Neff, 1988; Sandvig et al., 2009).

In drinking water, total lead concentrations consists of three fractions, which are dissolved lead, colloidal lead, and particulate lead. Particulate lead is operationally defined as the fraction of lead retained by a 0.45µm water filter, whereas the lead particles, which are able to pass through the filter, were considered as dissolved lead (USEPA. Method 200.8) . It has been confirmed that up to 94% of total lead in the water samples are in colloidal and particulate form (Hulsmann, 1990, McNeil & Edwards, 2004). However, due to the occurrence of particulate and colloidal lead, accurate quantification of lead can be challenging.

For the quantification of lead in drinking water (and wastewater), USEPA Method 200.8 is one of the most commonly employed analysis methods , by using inductively coupled plasma combined by a mass spectrometry (ICP-MS). This method consists of sample preparation and detection by ICP-MS. In terms of sample preparation, standard preservation is normally applied for direct quantification of lead in drinking water samples with low turbidity (lower than 1 NTU). And rigorous digestion methods, such as hot block digestion, are chosen to digest samples with turbidity greater than 1 NTU. However, the lead recovery by standard preservation may not be adequate, especially with the occurrence of PbO_2 in drinking water (Zhang et al., 2009). Moreover, a significant fraction of particulate lead can be present in drinking water even with turbidity lower than 1 NTU (Edwards et al., 2004). In these cases, lead concentration can be dramatically underestimated. Moreover, tetravalent lead particulates can remain highly insoluble in diluted nitric acid solution, even samples are subjected to the hot block digestion which typically digests samples with 5% *v/v* nitric acid at around 100ºC (Lytle et al., 1993, Edwards et al., 2004)

1.2 Research objectives

First, this study evaluated the digestion efficiency of a new rigorous digestion technique: focused shortwave infrared radiation digestion (SWIR). Factors influencing digestion efficiency including power intensity, acid concentrations, and digestion time, were also investigated, and the SWIR method was optimized accordingly in order to obtain an optimal lead recovery.

Second, in this study, the optimized SWIR method was compared against standard preservation (direct analysis) and hot block digestion (conventional rigorous digestion method), on different lead and iron compounds digestion. These compounds, including lead (IV) oxides, lead (II) phosphate, hematite, magnetite, and chloropyromorphite, were selected because they are prevalent in distribution systems, having different levels of solubility in water and dilute nitric acid.

1.3 Organization of thesis

This thesis investigated the digestion ability of the new digestion method, SWIR digestion, and compared this new alternative against standard preservation and hot block digestion. Five chapters present the findings from the investigation, and are briefly introduced below.

Chapter 1 briefly introduces the adverse health impact of lead exposure via drinking water and the challenges in accurate measurement of total lead content when particulate lead is present in drinking water. This chapter also summarizes the overall objectives of this thesis and provides the outline of this document.

Chapter 2 provides a background of common sources of lead occurring in water, pretreatment methods applied in total lead measurement in drinking water samples, and the limits of these pretreatment methods.

Chapter 3 outlines the procedures of the three pretreatment methods investigated in this study – standard preservation, hot block digestion, and the SWIR method and also introduces the materials used in each phase of experiment. The experimental design is also explained in detail in this chapter.

Chapter 4 presents the results of the evaluation of the SWIR method, the results of optimization of the SWIR method, and the comparison of lead recovery of PbO_2 digested by the optimized SWIR method against standard preservation and hot block digestion. And also compares the lead recovery by three methods on digestion of different lead compounds including lead (II) sulfate $PbSO_4$, hematite (Fe_2O_3), magnetite (Fe_3O_4), and chloropyromorphite ($Pb_5(PO_4)_3Cl$).

Chapter 5 summarizes the conclusion obtained from this study and provides the recommendations for future research in this field.

Chapter 2 LITERATURE REVIEW

2.1 Lead exposure from drinking water

Lead is found naturally in the environment and as a result of human activities. It has been recognized as one of the most ubiquitous environmental threats due to the wide application in many industrial areas, such as gasoline, painting, and premise plumbing materials. (Triantafyllidou et al., 2009; Flora et al., 2012; Testud et al., 2001). As a soft metal that naturally occurs on earth and is easy to extract, lead is often used in combination with other elements for making alloys (Triantafyllidou et al., 2012). It was also considered as a popular ingredient in early centuries because of its properties like softness, low melting point, high density, poor electricity conduction, and resistance to corrosion. Therefore, lead and its alloy was widely applied in many industrial areas, but also in commercial products, such as gasoline, paint, household plumbing elements, batteries and underwater pipelines which still currently exist (Brown et al., 2012).

Lead exposure occurs mainly through the ingestion of lead-containing products which can come from various sources, such as gasoline, paintings, drinking water and dust (Lanphear et al., 2002). Among these potential sources of lead, drinking water has been considered to only contribute 10-20% of total lead exposure (Triantafyllidou et al., 2009; Triantafyllidou et al., 2013), and it has been underestimated for decades until serious problems associated with lead contamination of drinking water occurred in Washington D.C. in 2003 (Triantafyllidou et al., 2012). That incident due to lead-contaminated drinking water compelled governments to reconsider drinking water as a possible and occasionally the major pathway of lead exposure (Zhang et al., 2012; Butler et al., 2016).

2.2 Adverse health effects of lead exposure

A variety of health impacts are strongly associated with lead exposure. Lead has been considered as one of the most serious hazards to human health and even the greatest environmental hazard to young children. It is a neurotoxin which can cause irreversible cognitive problems, severe central nerve system problems, and organ damage (Brown et al., 2011)Moreover, the damage could be more severe at the blood lead level (BLL) of 40 – 60 µg/dL without in-time treatment (Flora et al., 2012). Although lead poisoning was defined as a whole blood lead level exceeding 10µg/dL (Belligner et al., 1987; CDC 1991; WHO 1995), intellectual deficits were still observed from children with a blood lead level lower than 10µg/dL (Jusko et al., 2008; Mazumdar et al., 2011). These findings demonstrated that lead exposure even at low level can cause adverse impacts on humans. Compared with adults, children are more sensitive and vulnerable to the exposure by absorbing up to 5 times more lead (Elfland et al., 2010; Clark et al., 2015; Clark et al., 2014; Triantafyllidou et al., 2009). These lead-associated intellectual deficits and even soft tissue damage in early childhood could be prolonged and persist into adulthood (Reuben et al., 2017). Moreover, identifiable adverse health impacts could be found even at blood lead levels considered safe (Jusko et al., 2008).

In the past few decades, efforts have been made to reduce the use of lead in order to control lead exposure of the public from paint, gasoline, food, and drinking water. Clinical evidence has showed that the BLL has decreased, but concerns about exposure to a low lead level has increased (Triantafyllidou et al., 2012). In North America, 10-20% of total lead exposure is considered to occur via drinking water consumption (Health Canada, 2016). Although drinking water consumption accounts for only a small portion of lead poisoning, it is more likely to be extremely underestimated due to the insufficiency of standard analytical methods and it is difficult early recognition of lead poisoning (Triantafyllidou et al., 2009; Belligner et al., 1987). Significant reduction of lead application in paints and gasoline, drinking water along with food is belatedly considered to be the principal contributor to lead exposure (Testud et al., 2001). According to what CDC's investigation, at least 30% of elevated blood level (EBL) cases were attributed to lead from drinking water (Triantafyllidou et al., 2012). Under some circumstances, lead-contaminated water can be the dominant contributor to total lead exposure (Triantafyllidou et al., 2009; Testud et al., 2001). For example, in Greenville, N.C., lead poisoning was strongly related with elevated particulate lead in water, since no other sources of lead could be identified during the one-year investigation (Triantafyllidou et al., 2007; Bachelor et al., 2005). Investigation of childhood lead exposure in North Carolina and Maine demonstrated the strong association between lead in water and EBL (Triantafyllidou et al., 2012; Testud et al., 2001).

Due to a dramatically high lead concentration in drinking water, the water crisis that happened in 2014 in Flint, Michigan, in the United States. This incidents caused increased the sensitivity and concern of the public about drinking water safety (Butler et al., 2016). In all these examples listed above, blood lead levels continued to increase. However, in the meantime, sources like lead paint, dust or other potential sources (toys) were being monitored. Thus, drinking water containing lead is prevalent and presumed to be the major contributor to the lead exposure (Triantafyllidou et al., 2007; Bachelor et al., 2005).

2.3 Occurrence of lead in drinking water

Treated drinking water leaving treatment plants or flowing through water mains normally is lead free. As enters into distribution systems, treated water gets contaminated by contact with lead leached from lead-containing materials (Figure 2.1), such as lead service lines (LSLs), brass, solder, faucets and other household plumbing elements. These lead-containing components are considered to be the cause of the presence of lead occurring in drinking water, which is generated from corrosion of lead-containing scale materials and physical degradation.

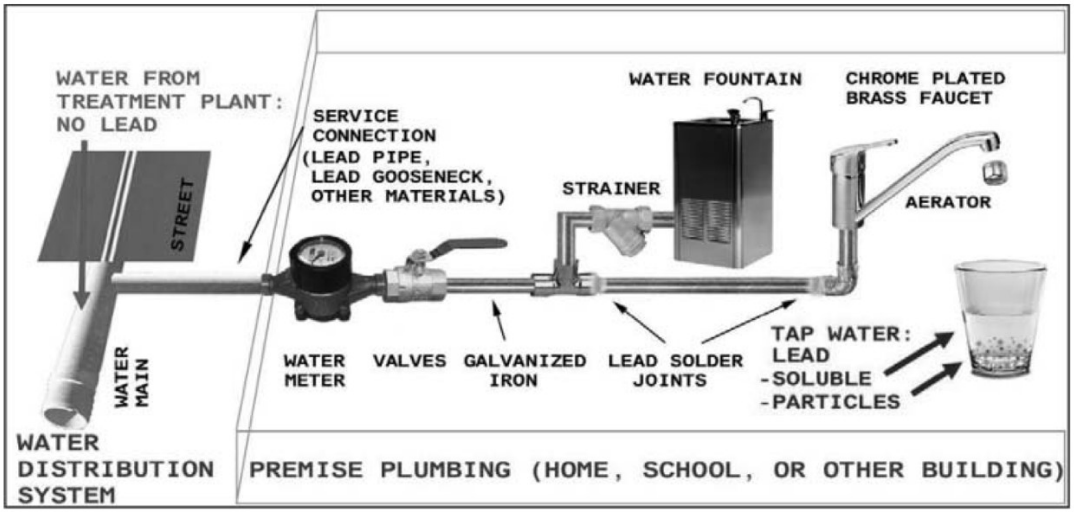

Figure 2. 1 Potential sources of lead in tap water of homes, schools, and other buildings (Source: Triantafyllidou et al., 2012)

In drinking water, lead could exist in various physicochemical forms, such as free aqueous ions, inorganic/organic complexes, in association with highly dispersed colloidal materials, suspended insoluble salts, or adsorption onto inorganic particulates (Hulsmann, 1990; USEPA. Method 200.8, 1994). Total lead content consists of three fractions which are dissolved lead, colloidal lead and particulate lead. Particulate lead is operationally defined as the fraction of lead retained by a filter with 0.45µm pore size, whereas the lead particles, which were able to pass through the filter were considered as dissolved lead (USEPA. Method 200.8) .

The colloidal lead was the fraction defined as the lead with particle size ranging from 0.08 to 12 µm, typically correlated with the presence of iron oxides in drinking water (Hulsmann, A.D. 1990).

However, a pipe rig examination study noted that colloidal lead can also be released from copper pipes with lead-containing joints even without the presence of iron in drinking water (Bisogni et al., 2000). Particulate lead along with colloidal lead might be significantly missed by conventional filtration (using 0.45µm filter paper). It has been confirmed that up to 94% of total lead in the water samples are in colloidal and particulate form (Hulsmann, 1990, McNeill et al., 2004).

According to Hulsmann (1990), there are at least two types of particulate lead in water, and both types can concurrently exist. The first type mainly consists of lead particles with size fraction ranging from 0.08 µm to 12 µm, which are not clearly observed by consumers. This type is commonly associated with iron or manganese and mostly described as “dirt”. It can also originate from the adsorption of dissolved lead on to other metals. The other type of particulate lead is species-related particles with various size fractions. For instance, one special form is commonly referred to as flaking lead, large particles with more than 12µm. Due to the large particle size, flaking lead particles often visible if they are present in drinking water, otherwise these particles are trapped by aerator screens. However, those large lead particles larger than 12 µm not being passed by the aerator still can continue leaching lead into drinking water (Hulsmann, 1990). Apart from flaking lead, there are many other lead particles from different sources (Figure 2.2), that are small enough to pass through the aerator screen (dimension of 1.0 × 1.0mm)(presented in the bottom center of Figure 2.2) (Triantafyllidou et al., 2007).

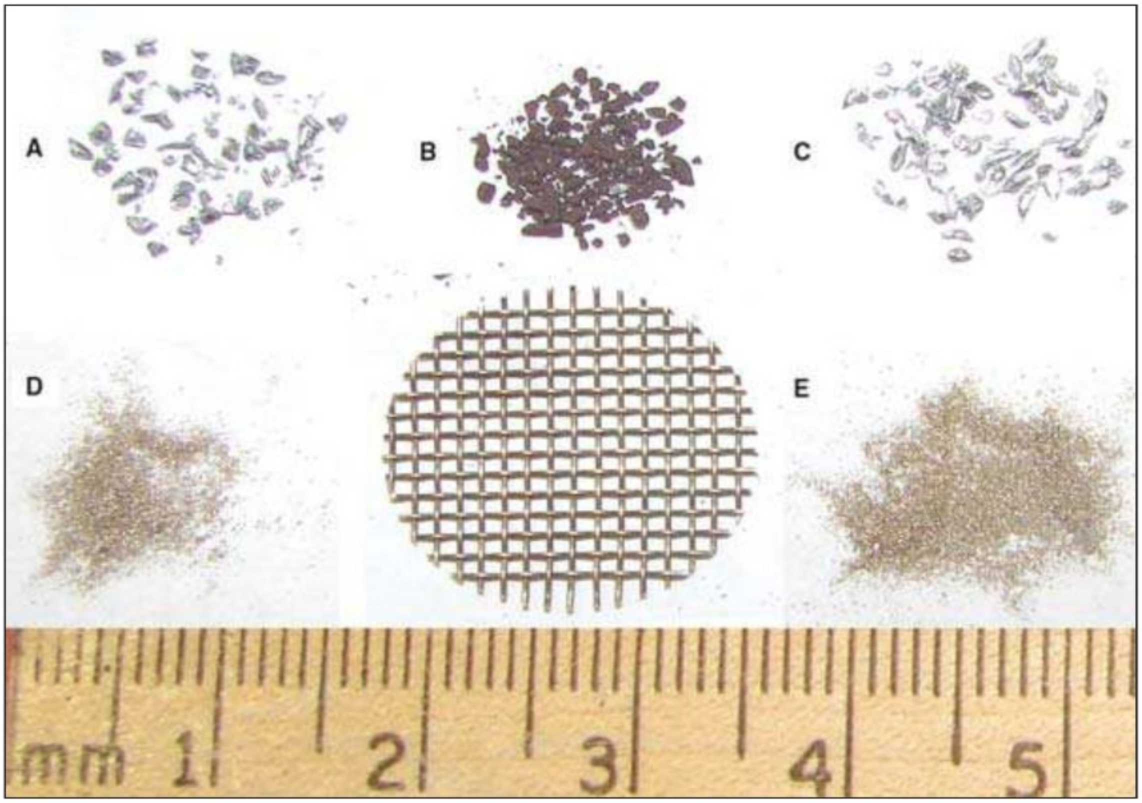

Figure 2. 2 Different lead particles types in drinking water samples includes (A) pure lead, (B) lead(IV), (C) 50:50 lead: tin solder, (D) red brass, (E) yellow brass (Source: Triantafyllidou et al., 2007).

Once particulate lead occurring in the potable water, accurately assessing the extent of lead contamination in drinking water becomes more difficult (Triantafyllidou et al., 2009). Due to this fact, drinking water was not strongly associated with lead exposure when analyzing the correlation between infants in Boston and possible sources of lead exposure in 1985 (Rabinowitz et al., 1985). In that study, the method used to quantify lead in water samples was only for measuring the lead in dissolved form, but not particulate lead, thus the measured lead concentration was significantly underestimated. Under this circumstance, particulate lead was problematic in accurately assessing the correlation of public health risk related to lead contamination (Triantafyllidou et al., 2009). Another example is that, Galke (2006) demonstrated that lead in water is a significant pathway of lead exposure in the experiment area, and concluded the increase of lead in blood was associated with the increased consumption of lead-containing tap water. However, the concentration of lead in the water samples did not strongly associate with the risk of elevated blood lead level.

These contradictory findings happened in two studies and both were attributed to the presence of lead particulates in the water samples. First of all, failure may occur during the sampling process, causing some lead particulates missed by the flow rates chosen to fill the sampling bottle (Triantafyllidou et al., 2009). Only cold water was collected, but warm water was considered as a significant contributor to the particulate lead, occasionally contributing even greater lead into drinking water (Triantafyllidou et al., 2009; Triantafyllidou et al., 2013). Secondly, even if particulate lead was collected, sample pre-treatment and conventional digestion methods may not be able to solubilize lead into matrix; therefore, lead was still in the forms which cannot be detected by analyzer (Triantafyllidou et al., 2007 & 2009; Zhang et al., 2010). The deficiencies of conventional sample pre-treatment methods will be introduced in detail in the following section (section 2.6).

Particulate lead along with colloidal lead can cause the actual lead concentration in water samples not precisely quantified by the analytical methods and significant underestimation of the risk of lead exposure through drinking water (Triantafyllidou et al., 2013).

2.4 Sources of lead in drinking water

In this section, different sources of lead from lead containing materials are introduced. Unlike dissolved lead of which the source could be predicted based on measurement of lead service lines length, it is challenging to establish the source of particulate lead. The mobilization of particulate lead is highly variable and intermittent, and can be easily affected by factors like water flow, water chemistry, the species of disinfectant, natural organic matter and temperature of source water (Masters et al., 2016). The various sources of lead particulates made predicting its occurrence in drinking water even more difficult.

2.4.1 Lead service lines (LSLs)

Lead service lines (LSLs) refer to the lead- containing pipes connecting the water main and premise plumbing which have been widely applied in North America until 1986 when lead-free pipe materials were required. In consequence, numerous LSLs are still existing in North American distribution systems, providing a long-term lead leaching source (Deshommes et al., 2012; Sandvig et al., 2009). Lead service lines are considered as the major contributor to total lead in drinking water (Trueman et al., 2016). At sites with LSLs, 50 – 75% of lead occurring in tap water might be attributed to LSLs (Sandivig et al., 2009). Moreover, in Washington, D.C., by replacing LSLs at homes has demonstrated to significantly increase the possibility of having EBL (Reuben et al., 2017).

Deshommes et al. (2010), observed a low to moderate concentration of particulate lead from residential cites with LSLs. Unlike dissolved lead, its occurrence and source can be predicted based on the length measurement of LSLs, but, it is challenging to estimate the occurrence of particulate lead (Deshommes et al. 2010). The occurrence of particulate lead may be influenced by the construction of lead service line replacement (Trueman et al., 2016), by the physical conditions of LSLs, the usage of water by consumers, and the water flow rate (Deshommes et al. 2010).

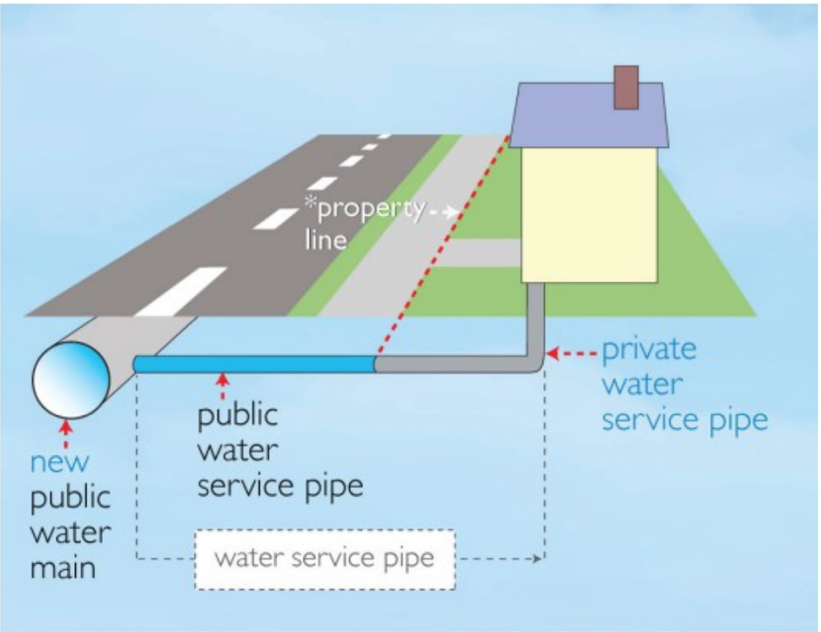

Figure 2. 3 Schematic diagram of public and private service lines (Source: Halifax water 2014)

In order to control lead exposure caused by LSLs, a practice was conducted — lead service line replacement (LSLR). However, this practice might cause more lead released into drinking water, making the risk of lead exposure even greater (Trueman et al., 2016).

As shown in Figure 2.3, LSLs consist of a public service section and a private service section. The property service section is not the responsibility of utilities. Under this circumstance, a large percentage of partial LSLR was performed by only replacing public service pipes with copper but retaining the private lead service pipes (Triantafyllidou et al., 2012). However, partial LSLR may not be an effective strategy for lead release control. In the short term (2-3 months), partial LSLR can only provide limited help with lead control, and in some cases partial LSLR makes lead concentration greater than that detected from a full lead pipe (Sandvig et al., 2009; Cartier et al., 2013). For the long-term aspect, partial LSLR after 6 months may even increase lead concentration in drinking water due to galvanic corrosion, which results in exceeding the U.S. EPA action level (15µg/L) (Trueman et al., 2016). This result might confirm the higher rate of EBL cases found from children living in homes with partially replaced LSLs than that found in homes with full LSLs (Triantafyllidou et al., 2012).

The existence of LSLs can increase the possibility of lead occurring in drinking water, thus, LSLs are considered to be the most significant contributor (Deshommes et al., 2010).

2.4.2 Brass and bronze plumbing elements

Contamination from brass fittings has been demonstrated to be a significant contributor to lead at the tap (Schock et al., 1988), due to the corrosion and dissolution of brass elements. In some cases, lead from brass was the main cause of childhood lead poisoning (Triantafyllidou et al., 2012). Without the presence of other lead parts but only brass compression, lead release was detected in a copper pipe loop system (Sandvig et al., 2009).

Brass and bronze are copper alloys containing other materials like zinc, lead and a small portion of iron. Up to 8% of lead by weight (normally is 1.5-8% by weight) can be legally introduced to improve the metallic performance of alloys and for leak control. These lead-included copper alloys are popular in manufacturing in-line components (Figure 2.4) of distribution systems, which include meters, valves, pressure regulators, pump components and connection devices, such as fittings, and couplings (Sandvig et al., 2009). Even the new type of brass component, which is called “lead- free”, developed to reduce the lead leaching problem is demonstrated to contain up to 0.25% lead by weight (Triantafyllidou et al., 2012).

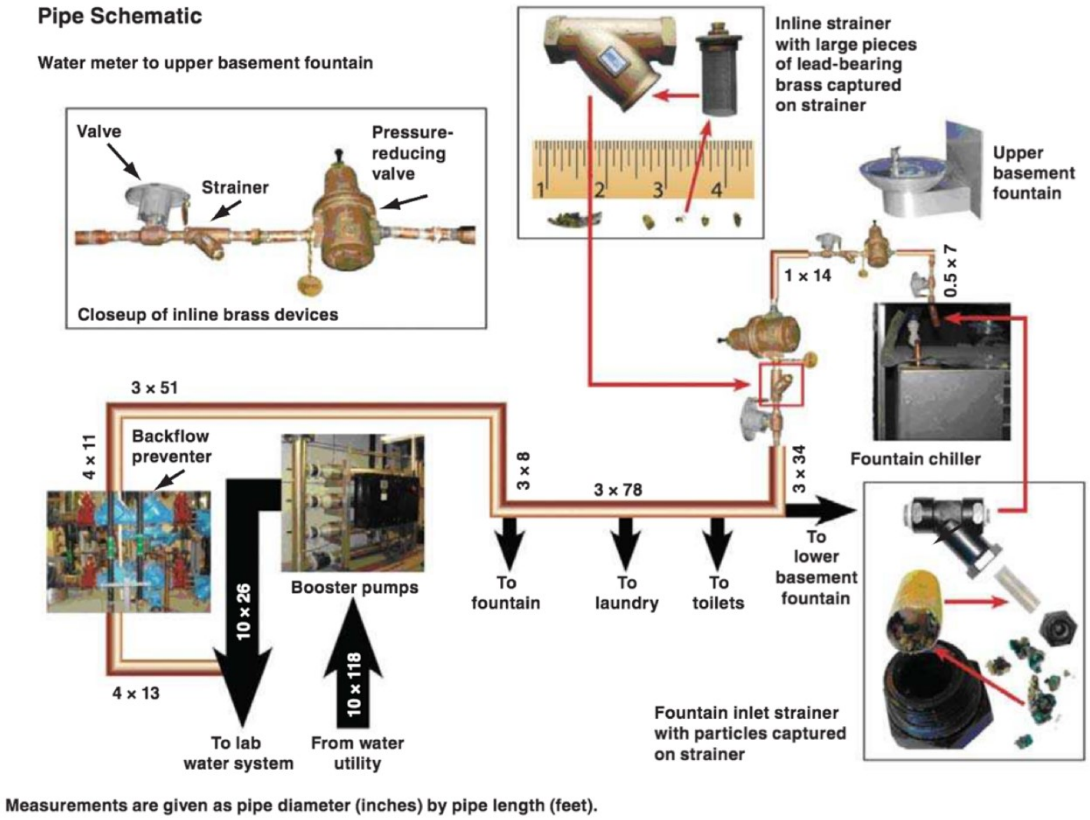

Figure 2. 4 Schematic diagram of the brass devices serving the water fountains (Source: Elfland et al, 2010)

Elfland et al, (2010) found that the corrosion of in-line brass devices was identified to be the cause of lead contamination in drinking water at the University of North Carolina. High lead concentration (almost 300µg/L) was measured in the new constructions at Chapel Hill campus. This significant lead release was confirmed to be from brass ball valves including more than 8% lead by weight (Elfland et al., 2010). Lead released from various in-line devices will finally be measured at the tap. Moreover, due to the variabilities in manufacture procedures, installation processes, lead content of the brass, and water demand, it might be difficult to accurately predict the source of the contamination (Sandvig et al., 2009; Triantafyllidou et al., 2012).

2.4.3 Solder

Solder is a low-melting alloy that is widely applied to join less fusible premise piping materials in order to seal them. The concentrations of lead released from solder can be variable based on the lead content, water demand and how many joints it is applied to (Sandvig et al., 2009). After 1986 when high lead content solder (40-50% lead by weight) was banned, only no leaded solder is required in new construction, and this includes lead content less than 0.2% by weight (Triantafyllidou et al., 2012). In North Carolina and Maine, childhood lead poisoning through drinking water was caused by the presence of solder particles (Elfland et al., 2010).

In addition, lead can also be released through galvanized pipes, which have been considered as a potential long-term source of contamination (Clark et al., 2015). Galvanized steel pipes are pipes with zinc coatings which contain 0.5% - 1.4% lead by weight. With the presence of lead, galvanized steel pipes could continue releasing lead into potable water.

2.5 Speciation of lead in drinking water

The corrosion of lead containing plumbing materials installed in drinking water distribution systems, was the main pathway for lead getting into drinking water (McNeill et al., 2004; Kim et al., 2010). As primary lead corrosion by-products, divalent lead (Pb (II)) and tetravalent lead (Pb (IV)) are the major contributors to particulate lead that is present in drinking water. Pb (IV) corrosion by-products are less soluble and less studied than Pb (II) lead solids. Thus, the minerals released in waters were presumed to exist in the form of divalent lead species such as cerussite ($PbCO_3$) and hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) (Renner, 2004). However, a crucial amount of tetravalent lead compounds, mainly in the form of PbO_2, was found in lead service line specimens from seventeen water distribution systems in the U.S and four in Canada (Triantafyllidou et al., 2015). More than one third of water distribution systems investigated have PbO_2 solids inside the pipe samples, thus, showing that widespread presence of PbO_2 in pipe scales is reasonably common in North America (Triantafyllidou et al., 2015; Lytle et al., 2005).

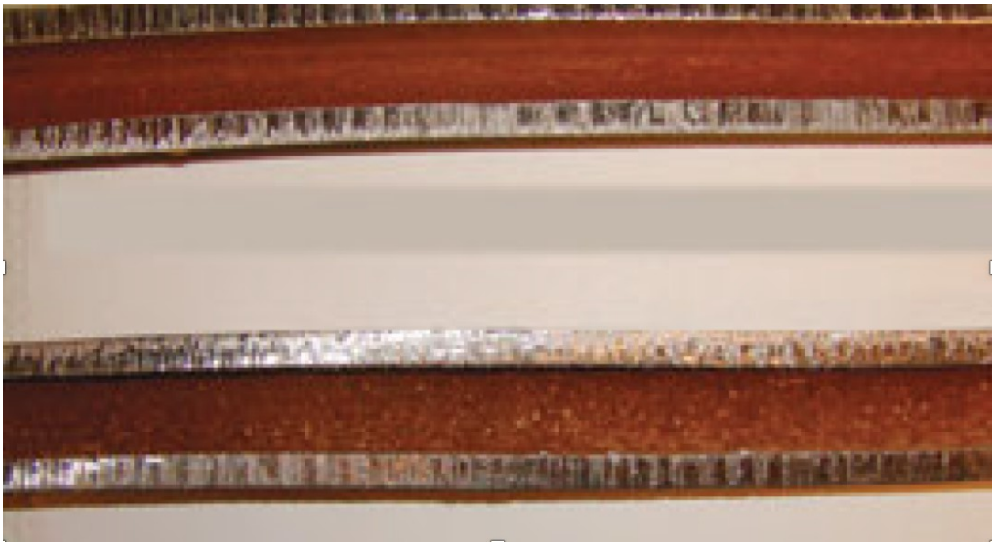

Figure 2. 5 The red-brown coating inside service lines was confirmed to consist of PbO2 (Source: Renner, 2004)

The occurrence of PbO_2 is associated with chlorination of lead containing plumbing materials, and conversion from Pb (II) carbonates or hydrocarbonates to PbO_2 corrosion solids. In Figure

2.5, PbO_2 was even found to dominate on the inner walls of the pipe scales examined by Triantafyllidou (2015) (Renner, 2004; Triantafyllidou et al., 2015; Schock et al., 2005).

The solubility of PbO_2 solids is low and relatively stable in treated water. For instance, in a high oxidizing environment, pipe scales with the formation of PbO_2 coating have much lower lead concentration measured than the concentration with the occurrence of Pb (II) coating, effectively controlling lead leaching into drinking water (Renner, 2004; Triantafyllidou et al., 2015; Lytle et al., 2005). However, the stability of PbO_2 solids can be altered by the drop of high oxidizing potentials in drinking water. The drop of oxidizing potentials can be attributed to the change in pH, increase of natural organic matter, the occurrence of lower oxidizing potential metal ions, such as Mn^{2+}/ Fe^{2+} (Shi et al., 2009), and the shift of disinfectant from free chlorine to monochloramine (Zhang et al., 2010; Lytle et al., 2005). The dissolution of PbO_2 can cause a significant amount of lead released, becoming one of the major contributors to lead contamination in drinking water.

When PbO_2 corrosion solids were present, except potential increase of lead concentration, issues associated with accurate measurement of lead have been confirmed to be challenging. This is due to the incomplete dissolution of PbO_2 before the detection step. As a result, the actual lead concentration that is present in water can be inaccurately quantified and potentially significantly underestimated. This can be true because the standard pre-treatment method under USEPA protocol is insufficient in rendering PbO_2 completely solubilized. For instance, according Edwards and Dudi (2004), the red-brown PbO_2 solids were preserved in the solution of 0.15% *v/v* concentrated nitric acid for three months, still undissolved and attached to the inside wall of sample bottles. A more rigorous digestion method was applied by adding 5% *v/v* nitric acid and digesting sample aliquots at 100°C for 24h, detecting that lead concentration was about five times higher than the concentration pretreated under USEPA protocol. Even more rigorous digestion procedures were performed, but even these methods are not capable to completely solubilize PbO_2 particles. For example, the conclusion noted by Zhang et al., (2009), was that only 1-4% of PbO_2 (spiked concentration: 0.5-10 mg/L) was dissolved after digestion in 5% *v/v* nitric acid solution at 85°C for 2h.

Apart from PbO_2, $PbSO_4$, another lead compound often used in batteries, is a white microcrystalline powder. $PbSO_4$ is insoluble in water, but soluble in concentrated nitric acid solution. The solubility of $PbSO_4$ decreases in diluted nitric acid solution, but is still higher than the solubility of PbO_2 particles. Digestion of samples containing $PbSO_4$ should be easier than digestion of samples containing PbO_2. Thus, $PbSO_4$, a less insoluble lead powder, was selected.

High levels of iron in public water distribution systems were detected and widespread accumulation of iron deposits in the lead service lines (LSLs) corrosion scale has been observed. As explained previously, LSLs corrosion is a major route of lead occurrence in water; prevalent existence of iron-rich particles is strongly associated with elevated concentrations of lead in drinking water. Moreover, due to the adsorption effect, lead can be also mobilized by iron particulates from sources to the tap. Magnetite (Fe_3O_4) and hematite (Fe_2O_3) are recognized as main compositions of iron main corrosion scale, and magnetite is often found in drinking water collected downstream from corroded iron mains (Sarin et al., 2004; Sarin et al., 2001; Peng et al., 2010; Gerke, 2008). Therefore, Fe_3O_4 along with Fe_2O_3 was selected to evaluate the digestion efficiency of the three digestion methods, especially the SWIR method.

LSLs have been recognized as the most significant contributor to the lead in drinking water. According to Hulsmann (1990), the particulate lead corrosion products are formed on the inner surface of LSLs; therefore, the mechanical disturbance of the inner corrosion layer can cause a long-lasting effect on the occurrence of lead in water. In addition, large lead particles with size greater than 12 μm mainly consisting of the corrosion layer, have been confirmed to be associated with physical disturbance such as cleaning, scraping, or maintenance work (Hulsmann, 1990). Therefore, lead scale was selected to be digested by standard preservation, hot block digestion and the SWIR method, in order to further compare the digestion efficiency of the three methods.

Formation of least soluble inorganic coating on the inner walls of lead pipes has become one effective way to reduce ionic lead entering into drinking water, by suppressing the oxidative corrosion of lead pipes and removing soluble lead from waters to form insoluble mineral scale. With sources of phosphate and chloride, chloropyromorphite ($Pb_5(PO_4)_3Cl$), a mixed phosphate and chloride mineral of lead, one of the least soluble commonly-occurring lead forms, is more likely to form by simultaneous oxidation and precipitation (Hopwood et al., 2002). Due to its solubility, coatings with formation of chloropyromorphite are supposed to be effective on reduction of lead levels in waters. Therefore, chloropyromorphite has been chosen to be digested by the three methods in order to evaluate the digestion efficiency of the three digestion methods and further investigate the stability of chloropyromorphite in different digestion environments.

In this study, the lead and iron particulates introduced above were selected to be digested and compared.

2.6 Total lead detection in drinking water samples

In order to evaluate the effect of lead on public health, it is necessary to accurately quantify the total lead that is present in water. USEPA Method 200.8 is one of the most commonly employed methods for the quantification of lead in drinking water (and wastewater) samples, by using inductively coupled plasma (ICP) combined by a mass spectrometry (MS) (Geana et al., 2011; Jenner et al., 1990). The measurement of total lead under Method 200.8 is a combination of a sample preparation procedure for dissolution of lead from corrosion solid by-products and a subsequent measurement of the solubilized lead (Geana et al., 2011). Sample preparation is required to ensure both dissolved and particulate forms of lead can be detected by Inductively coupled plasma mass spectrometry (ICP-MS). The entire determination procedure is listed in Figure 2.6 in detail, including sampling protocol, turbidity measurement, acid digestion and lead levels measurement (Triantafyllidou et al., 2007).

ICP-MS is a powerful technique with great ability in accurately quantifying trace metals and outstanding instrumental sensitivity, applied in the analysis of diverse environmental samples. High accuracy and precision in determination of total lead in samples are also demonstrated by G.A. Jenner (Jenner et al., 1990). For the measurement of total lead, ICP-MS typically has a method detection limit value ranging from 0.02 to 0.6 μg/L and requires preliminary treatment steps including acid preservation or digestion prior to analysis (Health Canada 2016). Preliminary treatment is crucial because this step could prevent metal precipitation and adsorption by liberating target analytes from particulates or solids. Thus, metals could become soluble and measurable by ICP-MS (Jenner et al., 1990; Haas et al., 2013).

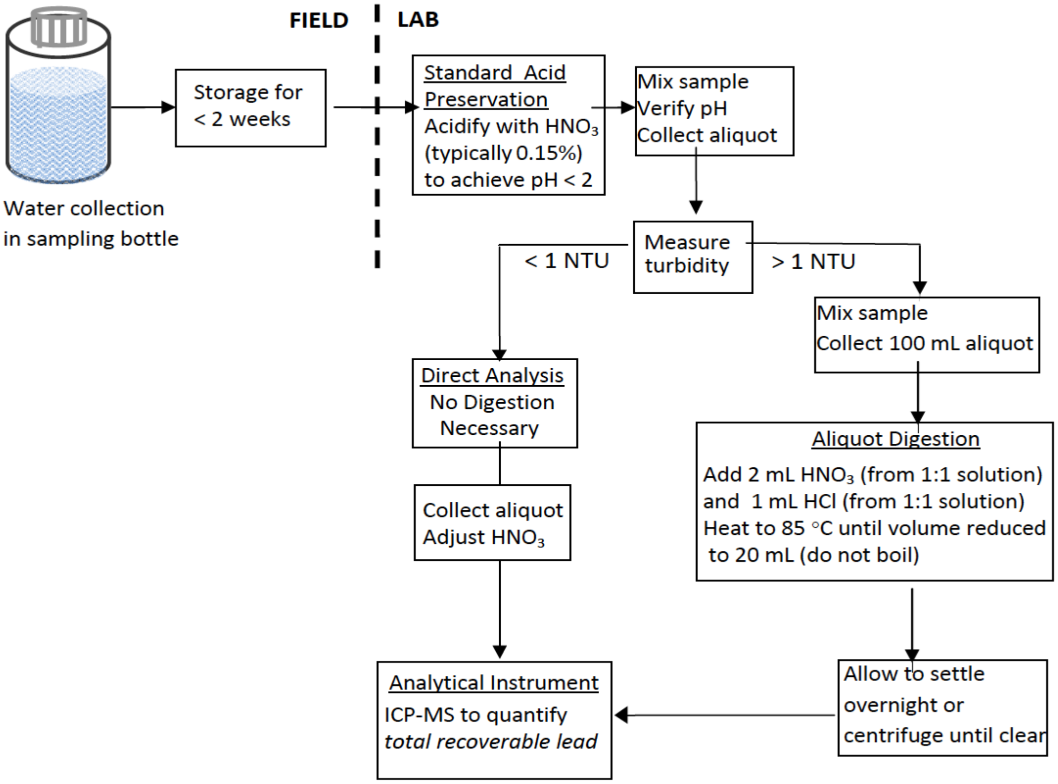

Figure 2. 6 Procedures of USEPA Method 200.8 for total lead and other trace elements measurement in drinking water and waste water samples (Source: Haas et al., 2013)

According to the instructions of Method 200.8, the maximum storage period of samples for up to 2 weeks without immediate acid preservation is allowed after collection on site. Plastic bottles are used as containers to collect water samples along the distribution systems. Two weeks are considered as a reasonable time frame without affecting lead recovery greatly, which is supported by Miller et al., (1985). A “loss” of lead could happen during the unpreserved period because of the adsorption onto container walls and perception. The type of sample container can also affect lead quantification (Haas et al., 2013). However, acid preservation is indicated to be able to resolubilize lead, therefore preventing the “loss” of lead and alleviating the effect of sample containers on lead quantification. After shipment to the laboratory, acidification proceeds as soon as practical by adding concentrated nitric acid to pH less than 2. 0.15% *v/v* concentrated nitric acid is commonly recommended under the standard acid preservation method to achieve a pH lower than 2. Samples are typically held for at least 16h (16~24h) at room temperature following acid preservation. After 16hr holding time, pH is adjusted if it exceeds the value of 2.

An aliquot is taken from samples with required pH value (2 or less) to measure turbidity. The following procedures are based on the result of turbidity measurement. If the turbidity is less than 1 nephelometric turbidity unit (NTU), lead is considered to be fine powder or mostly present in dissolved form and therefore the sample aliquot can be directly analyzed by ICP-MS without additional digestion required. Full digestion is required for the samples with turbidity more than 1 NTU before measurement by ICP-MS. This is because samples with high turbidity (greater than 1 NTU) typically contain a large fraction of lead particles with large size which are difficult to be introduced to the sample matrix by the standard acid preservation. The standard acid preservation was considered to be insufficient and ineffective in dissolving some lead particulates, especially with the presence of lead(IV) particles (Triantafyllidou et al., 2007). In this case, undissolved lead cannot be captured and measured by following the analytical method. In addition, high turbidity water samples are more likely to contain potential interference factor like organic matter, which can gravely affect lead measurement (Xie et al., 2010; Dryer et al., 2007; Xie et al., 2010). Therefore, to ensure lead particles can be quantified following digestion, a rigorous digestion method is needed for high turbidity samples. Rigorous digestion is commonly performed by addition of certain amount of concentrated nitric acid or mixtures of acid and heating the aliquots to a certain temperature. The options, procedures, limits of different digestion methods will be introduced in detail in the following section. Because filtration is not required for total recoverable element analysis, and aliquots were not filtrated before the full digestion step.

2.6.1 Standard acid preservation

Standard acid preservation is a conventional sample preservation and analytical method which was approved by the U.S. Environmental Protection Agency (USEPA) for the analysis of trace heavy metal in drinking water (USEPA. Method 200.8). For quantification of total lead in drinking water samples , standard preservation is also applicable. This method is routinely used as the first step to pre-treat water samples after shipment to the laboratory instead of acidification at the collection site for safety reasons. It is also the only treatment step for low turbidity samples, which can be analyzed directly.

Standard acid preservation is performed as soon as practical by adding 0.15% *v/v* concentrated nitric acid into samples in order to reduce pH value to lower than 2; afterwards the acidified samples are held for at least 16hr before measuring turbidity. If turbidity is lower than 1 NTU, aliquots are not subjected to the rigorous digestion step before quantification by ICP-MS. Low turbidity samples are considered to contain fine lead powder which can be easily liberated into the sample matrix, and as less likely to contain large amount of particulate lead. In this case, a low pH condition renders dissolved lead soluble and prevents perception as well as adsorption, ensuring obtaining reproducible results. Therefore, standard acid preservation is commonly performed for low turbidity water samples for total lead quantification.

The adequacy of standard preservation was examined by Lytle et al., (1993). In that study, 60:40 tin:lead solder powder was preserved under the standard acid preservation procedures, and completely recovered. Lytle et al., (1993) concluded that 0.15% *v/v* nitric acid and 16h holding time are adequate for recovering 100% of the lead in the solder powder. That study also demonstrated that the particle size and the time of acid preservation are the key factors controlling the degree of lead dissolution. Lead or solder particles might be present in the sample collection field before acidification and the size of particles was within the capacity of acidification. In other words, in the study conducted by Lytle et al., (1993), adequate acid preservation time was given to recover the lead or solder powder with appropriate size. That study could explain why addition of 0.15% *v/v* nitric acid and 16hr holding time was demonstrated to be adequate for detecting lead in low turbidity water samples where lead contamination is predominantly in dissolved form. However, recovery problems may happen with the existence of particulate lead in water. For instance, water samples collected in Washington D.C in 2003 actually containing 508 ppb, but only 102 ppb of lead were measured by the standard preservation method (Triantafyllidou et al., 2009).

Moreover, in the study of lead in school drinking water, only 3ppb of lead were measured by using the standard preservation method but it actually contained lead concentration over 1500 ppb lead (Triantafyllidou et al., 2009). It was showed that the standard preservation method caused 99.8% of lead missed in the detection step. The inconsistency between actual and measured lead content is mainly caused by the prevalent presence of particulate lead, and also reveals the need of reconsideration of standard preservation's adequacy (Triantafyllidou et al., 2009).

Particulate lead, as the majority form of lead that is present in public water distribution systems, is presumed to be responsible for much of the lead in samples containing over 100µg/L lead (Triantafyllidou et al., 2009). Whether lead is in dissolved or particulate form is critical, because the standard preservation method is based on the assumption that the majority of lead in drinking water is dissolved. When particulate lead exists in water samples, the particulates can adhere to the inside of plasticware or settle down quickly to the bottom of bottles due to large particle size. These phenomena can cause samples actually containing high turbidity to be measured lower than 1NTU. Therefore, full digestion was not applied for these samples with underestimated turbidity which are more likely to have a high concentration of lead (Triantafyllidou et al., 2007). But particulates do not dissolve in 0.15% *v/v* nitric acid solution after 16hr under the instruction of standard preservation method, and not detected by ICP-MS when aliquots are taken for detection.

Edwards and Dudi (2004) reported the significant underestimation of lead quantification by the standard analytical method when analyzed drinking water samples collected in Washington, D.C. were analyzed. Reddish-colored particles remained undissolved in 0.15% *v/v* HNO_3 even after three-month holding time. These reddish-colored particles were composed of lead oxides, which still could be observed on the bottom of the sampling bottles (showed in figure 2.7)(Triantafyllidou et al., 2007).

Figure 2. 7 Reddish-colored particles were undissolved in 0.15% *v/v* nitric acid solution after three-month exposure (Source: Triantafyllidou et al., 2007)

Lead oxides particles collected in their study performed the same as tetravalent lead (IV) oxides of which the nature is acid-resistant and less soluble in solution. This is the reason why those reddish-colored particles can last three months in nitric acid solution. In order to render the reddish-colored particles completely dissolved, a more rigorous digestion procedure was applied, including adding 5% *v/v* HNO_3 and heating the entire acidified water sample to 100°C for 24h. After digestion by much more aggressive procedures, lead oxides particles were dissolved, and the concentration of lead increased to 500% higher than the concentration quantified by the standard acid preservation procedure. This finding was consistent with the conclusion noted by Lytle (1993) that the recovery of lead possibly was affected by the particle size and the time of acid preservation prior to analysis. In addition, the dramatic increased lead concentration indicated that standard preservation as the pre-treatment step is sometimes inadequate.

According to previous research by Edwards (2004), lead (IV) particles can come from detaching from the pipe, and solder lead-tin joints in pipe rigs as well (Bisogni et al., 2000). These particles are recalcitrant even in an acidified solution and more likely to adhere to the sampling bottles. In this case, much of lead (IV) particles would have been missed by routine analytical procedures. As a result, the drinking water with lead particles were labeled as "safe", resulting in greater possibility of lead exposure due to the misclassification. For instance, the incidents that happened in Greenville, N.C. and Washington, D.C were both due to the consumption of water with higher lead concentration than those reported, which was much greater than the guideline of 20 ppb. The incidents and research clearly demonstrated that standard preservation procedures could miss up to 71% - 98% of the total lead that is in drinking water, because of inadequate capability in recovering the particulate lead (Triantafyllidou et al., 2007&2013)

2.6.2 Hot block digestion

This section focuses on introducing hot block digestion from aspects including the mechanism briefly, the digestion procedure for total lead measurement, the efficiency and limitations of the method.

Under the USEPA Method 200.8, hot block digestion is required to pre-treat high turbidity drinking water samples (>1 NTU), which are commonly considered to contain more particulate and colloidal lead than low turbidity samples. Due to the fact that the majority of lead corrosion solids are present in particulate and colloidal form which are not detectable by ICP-MS (McNeill et al., 2004), and standard acid preservation is insufficient in completely releasing lead from those forms, rigorous digestion plays a significant role in accurate quantification of total lead in drinking water.

Rigorous digestion is employed to completely transfer the analyte metals from particulate or solid forms into a form that can be detectable by ICP-MS (usually in the form of free metal ions), and also to minimize the interference caused by organic matter. For drinking water sample preparation, hot block digestion, a conventional digestion technique, is commonly applied by adding concentrated acid and heating samples on a heating block. In terms of the selection of acid, as an oxidizing agent, some characteristics have to be considered, such as the oxidizing ability of the selected acid, the boiling point, the solubility of generating salts. Concentrated inorganic acids are generally selected, such as nitric acid (HNO_3), hydrochloric acid (HCl), because of the low cost and low resulting salts after digestion (Idera et al., 2014). Therefore, sulphuric acid (H_2SO_4) is not considered for digesting water samples containing lead, due to the coprecipitation reaction between sulphuric acid and lead (Oliva et al., 2003). Acids can be used either alone or in mixtures (Standard method 3030).

Concentrated nitric acid is commonly used by hot block digestion. This is because nitric acid has been confirmed to be capable of adequately digesting most water samples; besides, nitrate is a preferred as a matrix by ICP-MS. According to the Method 200.8, 5% *v/v* of concentrated nitric acid is added into the aliquots which were already preserved by the standard preservation method. Then, aliquots are placed in the sample preparation block in fume hood and digested at the target temperature of 105°C for a minimum 2h. During the digestion process, samples are continuously heated by the sample preparation block (the heating source), but sample boiling should be avoided. After digestion, aliquots are cooled outside of the hot block. Following that, the volume adjustment is performed to top up the digestion aliquot to the original volume by adding ultrapure water.

Although hot block digestion has been believed to be efficient and is used as a conventional sample preparation method (Yahaya et al., 2013), it does have limitations in further increasing digestion efficiency (Huang et al., 2004; Mohammed et al., 2017). The digestion efficiency of hot block digestion is determined by three factors, which are the acid applied and its concentration of it, digestion time, and digestion temperature (Mohammed et al., 2017). First, acids introduced previously in this work could be used individually or in mixtures. In some cases, in order to optimize lead recovery, reducing agents like hydroperoxide (H_2O_2) are considered (Hseu et al., 2004). Nevertheless, the hot block digestion method digests samples by continuously conducting heat to the acidified samples for a relatively long timeframe. The more the consumption of acid, the aliquots are more likely to boil during the process. In addition, the amount of acid fume can be great and the potential loss of target analytes can occur due to sample boiling. Second, it is difficult to achieve and maintain a higher digestion temperature, although a higher temperature can increase the reaction kinetics (Mohammed et al., 2017).This is because the digestion temperature is partially controlled by the boiling points of the selected acid in order to avoid sample boiling. In addition, with the open-vessel design of the digestion block, it is challenging to maintain high temperature and it takes time to reach the recommended digestion temperature (105 °C) (ISO et al., 1972). Third, another drawback of the open-vessel design is that there is potential sample contamination in the process, since fume hoods can contribute an excessive amount of contamination (Standard method 3030; Geana et al., 2011). Fourth, hot block digestion requires constant supervision, including placing aliquots at the right temperature, removing aliquots from the digestion block to cool down aliquots, and adjusting the aliquot volumes to the original volumes.

Most importantly, some research showed that the recovery of lead by hot block digestion occasionally is low, especially with the presence of PbO_2. Only 63% of lead was recovered in blood samples digestion (Yahaya et al., 2013). Edwards and Dudi (2004) reported that it took 24h to completely digest from lead pipe the red-brown coating of lead pipe which mainly consists of PbO_2. Moreover, within the standard digestion time -- 2h, only 1- 4% of PbO_2 were recovered by hot block digestion (Zhang et al., 2010; Geana et al., 2011).

Therefore, in this study, direct analysis (standard preservation) along with hot block digestion were examined on digesting PbO_2, and were compared with a new alternative digestion method (focused short wavelength infrared (SWIR) digestion).

Chapter 3 METHODS AND MATERIALS

3.1 Chemicals and reagents

3.1.1 Preparation of residential water samples

The residential drinking water samples were collected at collection site where was considered to be exposed to LSLs. The samples were collected by following the 6h stagnation sampling procedures and then stored in a high-density polyethylene (HDPE) bottle. These samples were not preserved at the collection, but after shipment to the lab these samples were preserved by 0.2% *v/v* HNO_3 (trace metal grade, Fisher Scientific) and held overnight at room temperature (standard preservation procedures). For preparing the aliquots digested by hot block digestion, an extra 5% *v/v* HNO_3 was added into these aliquots prior to digestion. As for the aliquots digested by the SWIR method, aliquots were directly digested without extra acid added.

3.1.2 Preparation of suspensions

Lead (IV) oxide suspension was also prepared in a HDPE bottle by dispersing 45 mg lead (IV) oxide in 1 liter ultrapure water with 0.25% *v/v* HNO_3. This elevated concentration of lead is comparable with extreme levels observed during the Washington, D.C , 2003 lead-in-water crisis. The concentrations of other suspensions investigated in this study, including chloropyromorphite mineral (Mineralogical Research Co.), lead scale, and $PbSO_4$, were all kept at 45 mg/L, the same as the concentration of lead (IV) oxide suspension.

45 mg PbO_2 (bought from Alfa Aesar) particles were measured by an analytical scale, and the weighting process was performed in a fume hood due to the high toxicity of PbO_2. The suspension was prepared by dispersing 45 mg of lead (IV) oxide in 1 L solution of ultrapure water (18.2 $M\Omega\ cm^{-1}$, 5 ppb or less total organic carbon) and 0.2% *v/v* concentrated nitric acid (HNO_3; trace metal grade, Fisher Scientific). The suspension-making processes of chloropyromorphite mineral, lead scale, and $PbSO_4$ all followed the same procedure.

Suspensions were stored in HDPE bottles (1L size). In this study, the HDPE bottles were not acid washed or washed by ultrapure water prior to use. The effect of HDPE bottles on lead recovery has been examined, suggesting that HDPE bottles are less likely to adsorb lead onto container walls in low-pH environment ($pH < 2$) (Triantafyllidou et al., 2012).

The suspensions were swirled well by shaking HDPE bottles and held at room temperature for exactly 24 hours.

For "Initial SWIR optimization", 1L PbO_2 suspension in ultrapure water was prepared and preserved by following the procedures of standard preservation, which acidified suspension with 0.2% *v/v* HNO_3 and held the suspension for 24 hours at room temperature. In order to optimize the digestion ability of the SWIR method, this phase of experiments was conducted based on the two-level design. Certain amount of acid along with digestion time was added in accordance with two-level design.

For "Recovery comparison of PbO_2 digestion", (A) Digestion of PbO_2 with HNO_3 only: 1L PbO_2 suspension in ultrapure water was made and preserved by following the standard preservation. For digestion by hot block digestion, an extra 5% *v/v* HNO_3 was added into the aliquots taken from the 1L suspension. For digestion by the SWIR method, aliquots were also added with an extra 5% *v/v* HNO_3, and digested under the optimized operational settings;

(B) Digestion of PbO_2 in different water matrices: 1L PbO_2 suspension in municipal tap water was prepared and preserved by standard preservation. For digestion by hot block digestion, an extra 5% *v/v* HNO_3 was added into the aliquots taken from the 1L suspension. For digestion by the SWIR method, aliquots were also added with an extra 5% *v/v* HNO_3;

(C) Digestion of PbO_2 with mixtures of HNO_3 and HCl: 1L PbO_2 suspension in ultrapure water was made and preserved by standard preservation (0.2% *v/v* HNO_3). For digestion by hot block digestion, 0.5% *v/v* HCl was added into the aliquots taken from the 1L suspension. For digestion by the SWIR method, aliquots were also added with 0.5% *v/v* HCl, and digested under the optimized operational settings. Filtration was performed after centrifugation by using 0.45µm filter paper. The filtration components used were all acid washed.

For “Comparison of $PbSO_4$ digestion”, 1L $PbSO_4$ suspension in ultrapure water was made and preserved by standard preservation for 24h. For the aliquots preserved by standard preservation, three aliquots were taken from the 1L suspension and analyzed by ICP-MS. For the aliquots digested by hot block digestion and the SWIR method, extra 5% *v/v* HNO_3 was dosed prior to digestion.

For “Comparison of hematite (Fe_2O_3) and magnetite (Fe_3O_4) digestion”, 1L Fe_2O_3 and Fe_3O_4 suspension in ultrapure water were prepared by standard preservation with 0.2% *v/v* HNO_3 and held for 24h. For aliquots digested by hot block digestion and the SWIR method, extra 5% *v/v* HNO_3 or 2% *v/v* H_2O_2 was dosed into the aliquots based on the experimental design.

For “Comparison of lead scale digestion”, 45 mg lead scale pieces were dispersed in 1L solution containing 0.2% *v/v* HNO_3. After 24-hour holding period, three aliquots were taken from the 1L suspension and analyzed by ICP-MS. For digestion by hot block digestion and the SWIR method, extra 5% *v/v* HNO_3 was dosed into the aliquots prior to digestion.

For “Comparison of chloropyromorphite ($Pb_5(PO_4)_3Cl$) digestion”, 1L $Pb_5(PO_4)_3Cl$ suspension was prepared in ultrapure water by standard preservation method. For digestion by hot block digestion and the SWIR method, 0.5% *v/v* HCl was dosed into the aliquots and no extra HNO_3 was required.

3.1.3 Preparation of filtration

After digestion or standard preservation, if undissolved particles were observed, syringe filtration of the supernatant was applied after centrifugation. The syringe filtration components consisted of 0.45 µm cellulose nitrate membrane filter paper (Whatman), a syringe and filter assembly. These filtration components were soaked in acid mixtures of 10% *v/v* HNO_3 and 0.2% *v/v* H_2O_2 for at least 16 hours, in order to minimize the background and leftover contamination.

The acid-washed filtration components were rinsed with ultrapure water three times before assembly, and after filtration for one aliquot, the components were rinsed with fresh-made solution of 5% *v/v* HNO_3 and 0.2% *v/v* H_2O_2 for getting rid of leftover contamination.

3.2. Experimental Design

3.2.1 Standard preservation for direct analysis

Standard acid preservation generally employs USEPA Method 200.8 to pre-treat water samples before analysis. Normally, samples with turbidity > 1 NTU require further rigorous digestion via heat along with addition of stronger acid, while samples under thresholds (turbidity < 1 NTU) are recommended to be preserved with 0.15% *v/v* concentrated HNO_3 to achieve pH < 2 and then held at room temperature for a minimum of 16hr before analysis. However, as explained in the previous chapter, 0.15% *v/v* concentrated HNO_3 and a 16-hour holding time may occasionally be inadequate.

In this study, in order to evaluate and compare the efficiency of the standard preservation method, some adjustments such as the increase of acid concentration from 0.15% *v/v* to 0.2% *v/v*, and the increase of holding time from 16 hours to 24 hours, were made. The experimental design for the standard preservation method was kept the same in all phases of each experiment. In addition, turbidity of suspensions was not measured in all phases of each experiment. The particle sizes of the target compounds were larger than 0.45μm which were more likely to settle quickly down to the bottom of the sampling bottle and then not be measured in turbidity measurement. Moreover, the concentration of suspensions was around 45mg/L which was relatively high and then the turbidity was more likely to exceed 1 NTU. In this case, turbidity measurement might not be necessary and not performed in this study. In order to minimize the interference of the suspension holding time for the next experiment, suspension was freshly made for each run.

All residential water samples and suspensions were preserved by the standard preservation method before direct analysis or digestion by the other two digestion methods, by adding 0.2% *v/v* concentrated trace-grade nitric acid, and held for 24h at room temperature prior to analysis. After 24-hour holding, triplicate aliquots were transferred into 15 ml falcon tubes for centrifugation. In order to make sure the same amount of the lead compound was drawn for each aliquot, 10sec shaking was performed between each dosing (3 x 10sec for each aliquot). The same sample-taking manner was also performed in drawing aliquots for hot block digestion and

SWIR digestion. Then, aliquots were centrifuged at 3000rpm for 10 minutes and then diluted by appropriate fold which was calculated according to the method detection limit of ICP-MS. Three drops of HNO_3 were added into the diluted aliquots before analysis by ICP-MS.

3.2.2 Conventional hot block digestion

For each experiment with hot block digestion, triplicate aliquots were taken from the suspension, which was preserved by the standard preservation method. After transfer into the digestion containers, aliquots were prepared with the acid or acid mixtures or reducing agents, which were selected based on the experimental design.

Triplicate-prepared aliquots (15 ml for each) for hot block digestion were pipetted into digestion vials by following the same procedures as samples drawn for standard preservation. The vials used for hot block digestion are one-time use only. Therefore, no acid-washing steps were performed prior to digestion. Since the digestion was performed in the fume hood for safety reasons, contamination prevention was conducted by using watch glasses as the covers of the vials. Watch glasses were employed to prevent contamination from the fume hood falling into the aliquots, as well as the loss of volatile compositions. In addition, the gap between watch glass and vial allows the acid vapor to escape during the digestion process (Deshommes et al., 2017). The watch glasses were acid washed by soaking in an acid bath (10% HNO_3) for several days and rinsed three times with reverse osmosis water and three times with ultrapure water as well.

Extra 5% *v/v* concentrated trace-grade nitric acid (HNO_3) were dosed into triplicate aliquots. Then the aliquots were placed in the sample preparation block (SPB 50-24, PerkinElmer; see its feature in Figure 3.1) for 2h at 105 ºC, covered by acid-washed watch glasses. The digestion mode was pre-programmed and could be adjusted based on need.

After 2h digestion, samples were cooled in the fume hood to room temperature and then fresh ultrapure water was applied to correct the volumes of the aliquots back to the original volume(15ml). Volume-corrected samples were centrifuged at 3000rpm for 10 minutes and diluted by an appropriate fold. Three drops of concentrated HNO_3 were added to the diluted samples prior to analysis by ICP-MS.

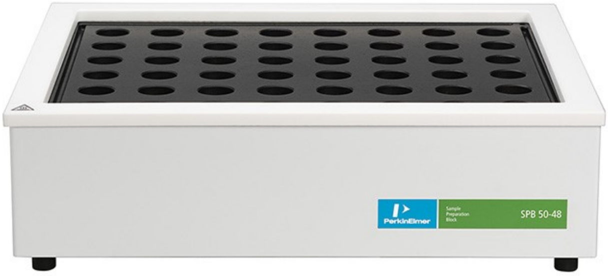

Figure 3. 1 Hot block digestion system (Source: http://www.perkinelmer.ca)

Apart from different aliquot preparation procedures in different phases of experiments, the digestion procedures under hot block digestion were kept consistent during the whole study period.

3.3 Design of short-wavelength infrared (SWIR) digestion apparatus

Microwave-assisted digestion or conventional methods like hot block digestion have been widely used for decades as rigorous pre-treatment methods (Hseu et al., 2004; Oliva et al., 2003; Yahaya et al., 2013). Digestion efficiency can be significantly improved by covering weaknesses in these methods. Microwave-assisted digestion has been considered to be an effective method which can decompose target compounds by significantly raising temperature, whereas infrared irradiation (IR) digestion is able to provide more intense energy by 2-4 orders of magnitude.

(Helmeczi et al., 2016; Wang et al., 2016). IR digestion shows its potential to increase digestion efficacy by transmitting more intense energy, compared with conventional digestion methods.

In this study, the IR digester (ColdBlock Technologies, St. Catherine's, ON) is the first digester applying focused short-wavelength IR irradiation (SWIR), which can conduct the digestion process more effectively. The SWIR digester consists of seven main components (in Figure 3.2): (1) AC power supply (adjustable to maximum power output 1800W); (2) Infrared emitter (adjustable height); (3) Quartz digestion flask (125 ml each); (4) ribbed watch glass; (5) mini fan; (6) Peltier cooling block; (7) Aluminum reflective dish. A digestion flask containing a sample is vertically inserted into the digester chamber and encircled by up to two IR lamps that are able to directly energize target compounds in the sample zone. The digestion flask is made of high-purity quartz, which enables maximum IR beams to be transmitted directly to target particles in samples. In addition, the specially-made quartz can prevent particles sticking on the surface of the flask minimizing potential background contamination. IR radiation is focused towards the sample through the ceramic coating on the outside surface of the IR lamps. Instead of horizontally delivering IR beams (Figure 3.2), the coating area design on the upper IR lamp is adjusted to radiate downwards to the loaded samples with higher IR irradiation intensity (Figure 3.3).

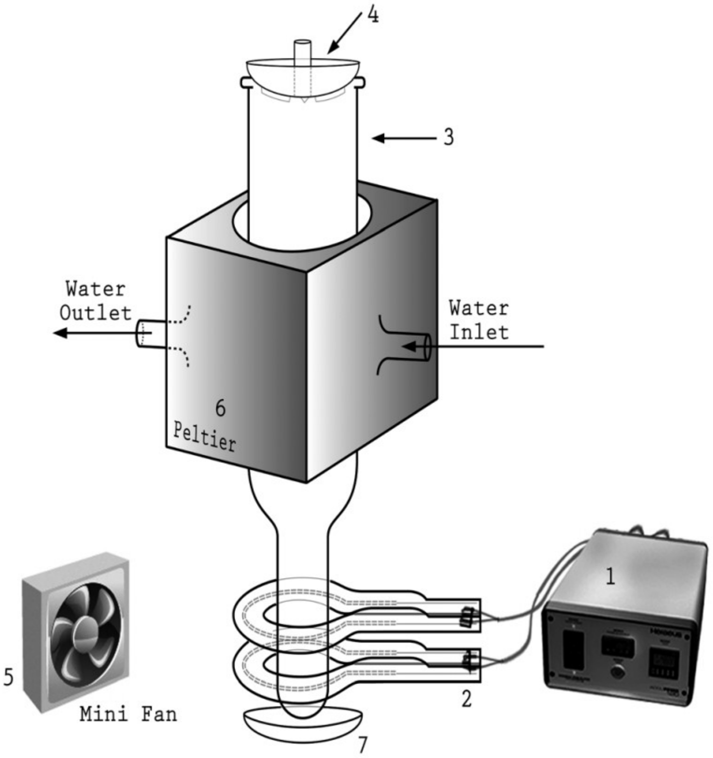

Figure 3. 2 The schematic design of SWIR digester (Source: Wang, et al., 2016)

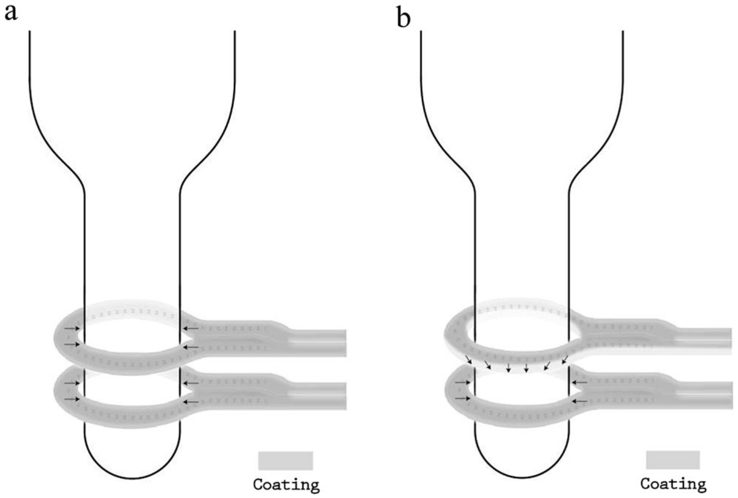

Figure 3. 3 Comparison of original coating design (left) and modified coating design (right) (Source: Wang et al., 2016)

For further optimizing the efficiency of SWIR digestion, there is an aluminum disk situated 1 cm under the digestion flask, with a polished surface which is able to reflect IR radiation which misses back to the sample matrices maximizing IR beams transmitted to the target area. In addition, a semi-cooling system is implemented, including a Peltier cooling block, a mini fan and a ribbed watch glass, enabling in-situ cooling after digestion by rapidly moderating the heat generated during the process. The Peltier cooling block operated at 4 ºC holds the upper part of the digestion flask. Therefore, handling is facilitated without a long cooling time because the temperature of the upper part of the digestion tube remains moderate. A mini fan is situated near the bottom part of the quartz flask, automatically blowing cool air onto the sample zone right after the digestion process finishes, removing the exceptionally high heat generated by IR rings. Another component of the cooling system is the ribbed watch glass; in this study a foam-free glove was substituted for the ribbed watch glass (Figure 3.4) to prevent acid fumes and target particles from samples being released into the working environment.

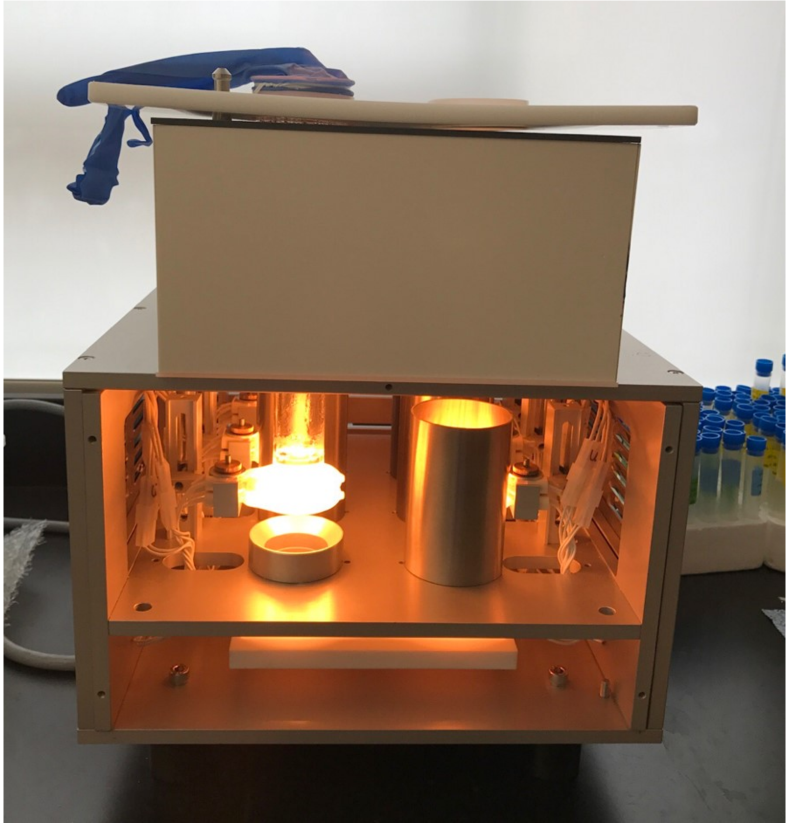

Figure 3. 4 SWIR digester operational in Clean Water Technologies Laboratory, Dalhousie University

3.3.1 Optimization of SWIR digestion parameters

For SWIR optimization, a full factorial design was performed to examine the effect of factors on method performance. Full factorial design has been widely adapted for preliminary studies or initial steps of method optimization, because it allows to investigate the effect of factors in possible combinations instead of investigating the factors individually (Clark et al., 2015). Thus, optimization by using full factorial design is a simple way to identify the experimental factors affecting the method performance (Clark et al., 2014&2015). According to Novozamsky (1993), the full factorial design has also been used to optimize simultaneous determination of multielement and metals like cadmium and lead (Clark et al., 2015).

For this experiment, three factors were investigated by two-level full factorial design (4): (1) nitric acid concentration: 0.2% vs 5% (*v/v*); (2) digestion time: 0.5h vs 2h; (3) IR intensity: 25% vs 100% of maximum 400W/ quartz flask. The design is outlined in Table 3.1.

Table 3. 1 Two-level experimental design for SWIR digestion optimization

Run	IR intensity (%)	Nitric acid (%)	Run time (h)
1	25	0.2	0.5
2	25	0.2	2
3	25	5	0.5
4	25	5	2
5	100	0.2	0.5
6	100	0.2	2
7	100	5	0.5
8	100	5	2

A digestion time of 0.5-h has been confirmed to be a sufficient timeframe for soil and sludge to be digested by SWIR method, whereas it normally takes hot block digestion 2-h (Wang et al., 2016; Helmeczi et al., 2016). Another goal for SWIR method in this study was to achieve higher recovery of lead using less acid. Thus, effectiveness of 0.2% and 5% (*v/v*) acid was evaluated. In addition, the influence of IR lamp intensity on lead recovery was also investigated via 24 runs in total (3 replicates x 8 factorial combinations). Aliquots were irradiated at 100W (25% power intensity) or 400W (100% power intensity) for 0.5h or 2h based on the particular operating cycle. Mean temperatures of 0.5h experiment set were 81.2 ± 3.5 ºC (SD) at 100W and 79.2 ± 2.5 ºC (SD) at 400W respectively.

For the 2h experiment set, mean temperatures were 84.6 ± 1.5 ºC (SD) at 100W and 86. ± 0.9 ºC (SD) at 400W respectively. Mean temperatures of aliquots from different sets were comparable. For the two methods at different power intensities, samples were all irradiated at 400W for 80sec in order to bring the temperature up rapidly, and cooled for 3min. Then, samples of the 100W digestion set were repeatedly irradiated for 25min with 1.5min cooling, and samples of the 400W digestion set were repeatedly irradiated for 20sec with 3min cooling. Sample loss was more likely to happen during the continuously energizing process. Under this circumstance, samples were corrected to original volume (15ml) by freshly-made ultrapure water. After volume correction, aliquots were centrifuged at 3000rpm for 10min and then diluted by appropriate fold.

3.3.2 Experimental preparation of SWIR digestion

Aliquots digested by SWIR method and hot block digestion were taken from the suspension which was preserved by the standard preservation method. The aliquots were further acidified with 5% HNO_3 *v/v* (15 ml for each) and irradiated based on the operating cycle created in the optimization step. 5 ml pipette was used to transfer samples into digestion tubes. According to a previous study (Hass et al., 2013), shaking well can significantly influence results in the presence of particulate analyte because large particles can settle quickly to the bottom and might not be transferred properly. In this regard, HDPE sample bottle was shaken for 10s before each time of pipette transfer (3 x 10s for each). Twenty glass beads (3mm diameter, acid washed) were employed in each quartz tube to prevent particles flash boiling. Glass beads were acid washed by holding them in acid bath (10% HNO_3) overnight and washing with ultrapure water three times, then over dried in oven. Nitrile gloves were utilized to cover the wide opening of glass flask in order to reduce the release of acid fume but also maintain temperature. Quartz tubes were emerged in acid bath over 16h with 10% HNO_3 for minimizing background contamination. Before use, each tube was washed by ultrapure water five times.

3.3.3 Experimental procedures

For different phases of the experiments, the parameters of SWIR digester were adjusted on the control computer, based on the operating conditions in each experiment.

First, the control computer was connected with the SWIR digester by turning on the main power switch on the controller. Then, parameters including power intensity, running time, and the cooling time could be adjusted on the ColdBlock control panel under the Favorites tab named "ColdBlock". The control panel was refreshed before running each experiment, to make sure the parameters are able to be adjusted. If the characters on display are grey, it means the parameter are under default mode, otherwise, parameters can be adjusted if they are black. After digestion, in-situ cooling down is allowed before transfer aliquots into falcon tubes.

For experiments of SWIR digestion optimization, SWIR digester was operated based on the experimental design, which is introduced in the previous section. For experiments of recovery comparison between SWIR digestion, hot block digestion and standard preservation, SWIR digestion method was conducted at 300W (75% of power intensity) for 2h in order to compare with conventional digestion methods. First, aliquots preserved with 5% HNO_3 *v/v* were irradiated at 400W for 80sec followed with 3min cooling time. Then, aliquots were irradiated at 300W with 40sec radiation and 2min cooling in a repeated cycle. The samples' mean temperature was 95.3 ± 0.6 ºC (SD). After digestion, samples were treated with the same procedures described above.

3.4 Analytical method using ICP-MS

The concentration of total lead in samples was analyzed using an X-series 2 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; Thermo Fisher Scientific, MA, USA). The method detection limit was 0.025µg/L (for both lead and iron). Caps used for ICP-MS sample were soaked in an acid bath (10% HNO_3) for several days and rinsed with ultrapure water three times. In addition, three drops of concentrated trace-grade nitric acid were added into samples.

3.5 Data analysis

A paired t-test in Excel 2016 was performed to determine a p value in order to compare the data. A p value greater than 0.05 was considered not significant, whereas a p value less than 0.05 was considered significant. A confidence interval of 95% was used.

Chapter 4 RESULTS AND DISCUSSION

4.1 Introduction

This chapter focuses on method development of the SWIR digestion and comparison of digestion efficiency of three digestion methods.

In Section 4.2.1 “The evaluation of SWIR digestion”, digestion of residential drinking water samples with lead by SWIR is compared with digestion by standard preservation and hot block digestion, in order to evaluate the performance of the SWIR method.

In Section 4.2.2 “Initial SWIR optimization”, the significant determinants affecting recovery of lead by SWIR digestion were investigated. And appropriate operational settings are determined based on the results, in order to obtain optimized digestion capacity of SWIR digestion.

In Section 4.2.3 “Recovery comparison of PbO_2 digestion”, the comparison of PbO_2 suspension digestion by three methods is discussed from the following aspects. (A) Digestion of PbO_2 with HNO_3 only; (B) Digestion of PbO_2 in different water matrices; (C) Digestion of PbO_2 with mixtures of HNO_3 and HCl; (D) Digestion PbO_2 with reducing agent.

In Section 4.3 “Recovery comparison of different compounds digestion”, digestion of $PbSO_4$, Fe_2O_3, Fe_3O_4, lead scale, and $Pb_5(PO_4)_3Cl$ digestion by the three digestion methods are compared.

4.2 Results and Discussion

4.2.1 Evaluation of SWIR digestion

The goal of the first phase of the experiment was to evaluate the digestion ability of the SWIR method in recovering lead in drinking water samples, by comparing the concentration of lead recovered by the SWIR method with the concentration recovered by hot block digestion and standard preservation methods on point-of-use drinking water samples, which were collected at residential sites with sources of lead contamination. The SWIR digestion was initially operated at 200W (50% power intensity) for 5 minutes without pulse period performed, according to the successful application of the SWIR method in digesting mineral ore samples within 10 minutes (Helmeczi et al., 2016; Wang et al., 2016). Aliquots taken from samples preserved by standard preservation were directly digested by the SWIR method.

The digestion time was shortened because digestion procedures adapted in drinking water sample digestion are more moderate than that adapted in solid particles digestion (ISO et al., 1972; Yahaya et al., 2013; Huang et al., 2004). In terms of point-of-use drinking water samples digested by the other two methods, the experimental procedures were detailed in Chapter 3.

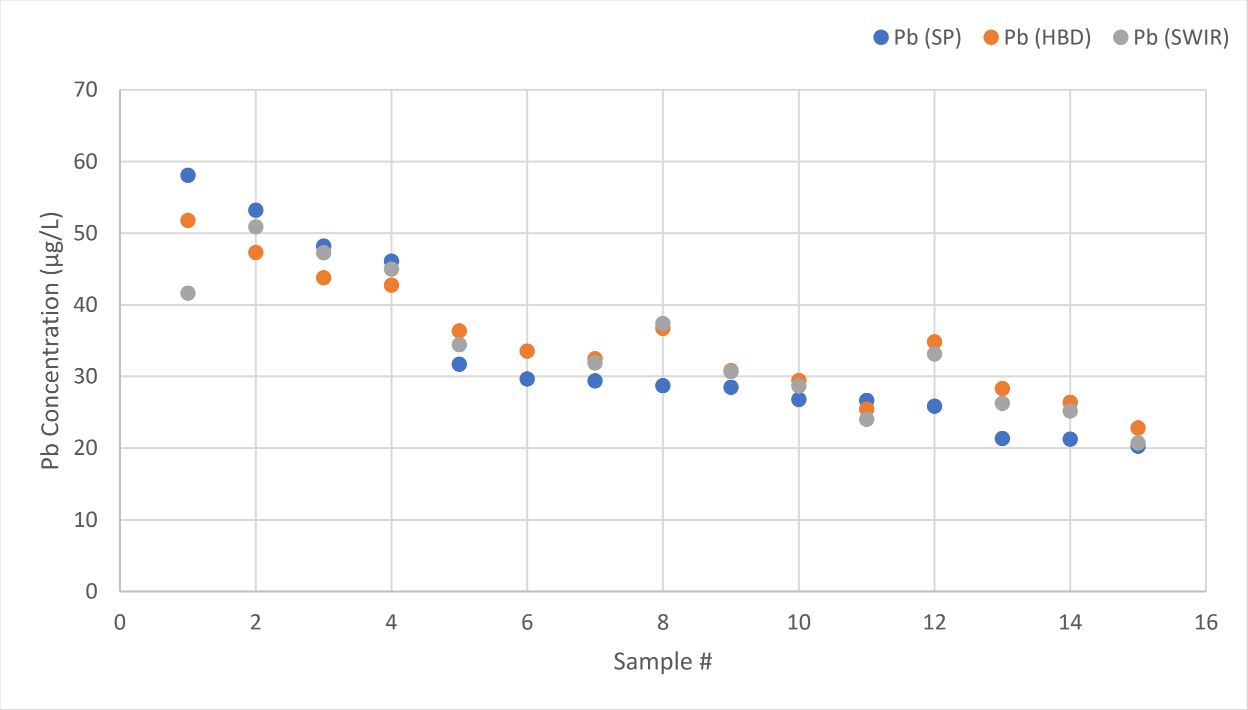

Figure 4. 1 The comparison of lead concentration recovered by standard preservation, hot block digestion, and SWIR digestion

Figure 4.1 compares the lead concentration recovered by three digestion methods. In general, three digestion methods recovered similar lead concentrations (on average) in digestion of 15 residential drinking water samples. Each sample was only performed for one analysis. The X axis stands for the number of samples. Lead concentrations in all 15 samples exceeded current maximum acceptable concentration (MAC) 10 µg/L of lead (Health Canada 2016). But it showed that 73.3% water samples (11 out of 15 samples) digested by hot block digestion and SWIR digestion were measured to contain higher lead concentration than samples preserved by standard preservation.

The mean lead recovery percentage of the SWIR method and hot block digestion were 106 ± 15.8% and 110 ± 15.7% respectively. Performed as rigorous digestion methods, these two methods are able to recover more lead from drinking water samples.

Figure 4.2 and 4.3 compares the lead concentrations in 15 residential drinking water samples recovered by SWIR method with lead recovered by standard preservation and hot block digestion, respectively.

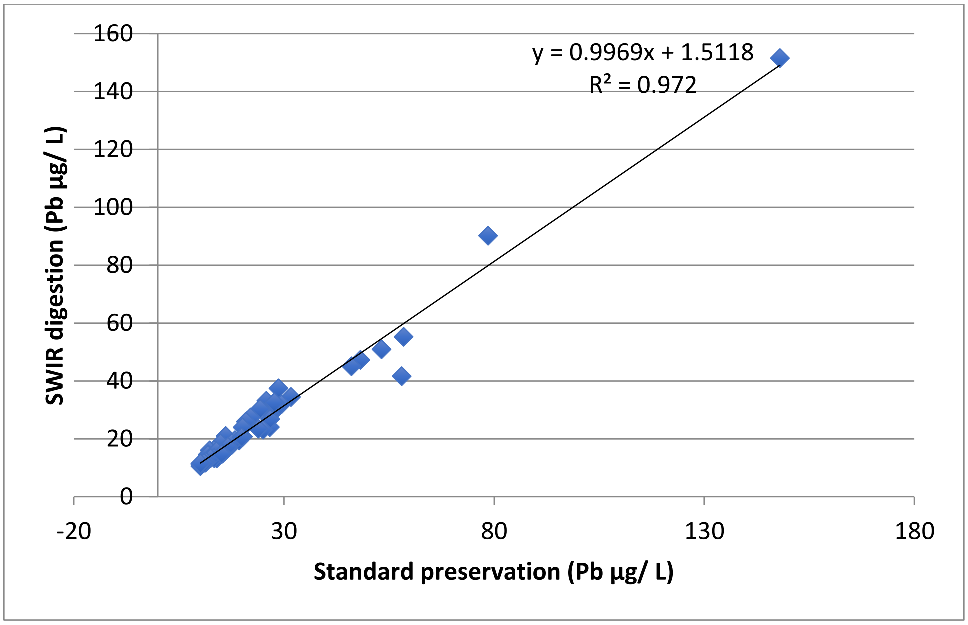

Figure 4. 2 Lead recovery comparison between SWIR method and standard preservation

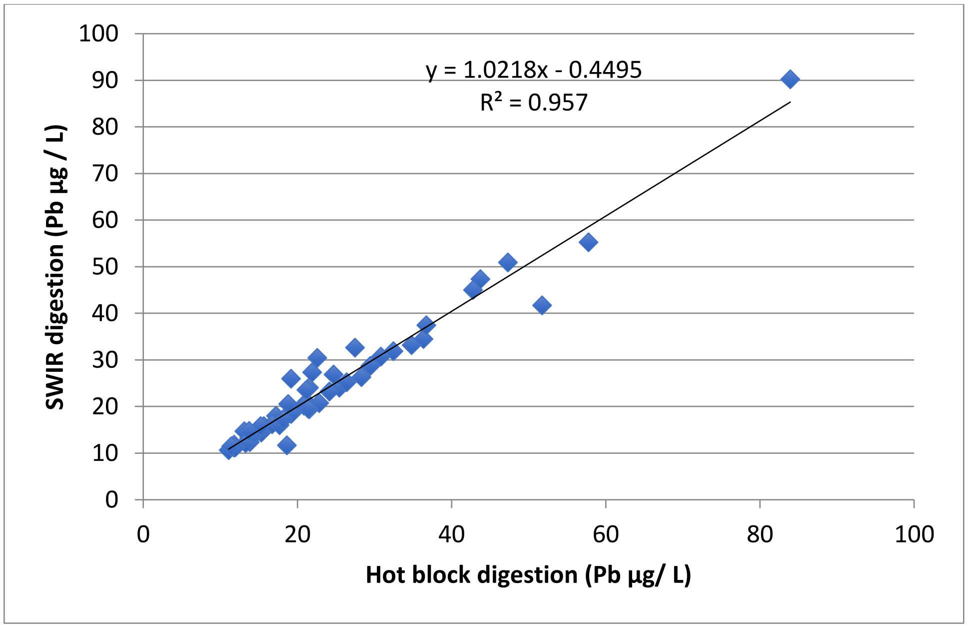

Figure 4. 3 Lead recovery comparison between SWIR method and hot block digestion

Figure 4.2 demonstrates that the lead recovery of the SWIR method was on average similar to the recovery of standard preservation. Figure 4.3 shows that the lead concentration recovered by SWIR digestion was similar to that recovered by hot block digestion.

According to the comparison shown in Figure 4.2 and 4.3, the concentrations of lead recovered by three digestion methods were similar. However, the digestion efficiency of the SWIR method was better than the other two digestion methods in terms of the consumption of nitric acid and digestion time. In terms of acid consumption, SWIR and standard preservation consumed less acid than hot block digestion. In addition, covering the wide opening of the SWIR digestion flask by a nitrile glove tightened with a twist tie , prevented acid fumes being released into the working area and air contaminants getting into aliquots. The sample loss was also controlled and less than the sample loss in hot block digestion process. Because the aliquots digested by SWIR digestion were the same as aliquots digested by standard preservation, there was only 0.2% *v/v* nitric acid and no extra added. Whereas, an extra 5% *v/v* nitric acid was added in to the aliquots digested by hot block digestion. Moreover, the digestion period of the SWIR method was only 5 minutes, which was much more effective than hot block digestion (2 hours) and as well as standard preservation (16 ~ 24 hours)

Therefore, the results of the evaluation of the SWIR method showed that SWIR was able to achieve a similar recovery of lead, but with much less digestion time (5 minutes) and less acid consumption (0.2% *v/v*). Based on the factors affecting digestion efficiency (ISO et al., 1972; Yahaya et al., 2013; Huang et al., 2004; Idera et al., 2014), the next phase of experiments in this study was to optimize the SWIR method to achieve a higher recovery rate in a shorter time frame.

4.2.2 Initial SWIR optimization

In this phase of experiment, the goal was to optimize the performance of SWIR digestion by adjusting the operational settings based on the three main factors affecting digestion efficiency, including radiation intensity , digestion time and concentrations of acid (Oliva et al., 2003; Yahaya et al., 2013; Huang et al., 2004; ISO et al., 1972). The correlation between lead recovery and these factors was investigated. In accordance with the highest recovery, the corresponding operating conditions was employed in the following phases of experiments.

Power intensity can affect the temperature profile in SWIR digestion. Moreover, temperature during SWIR digestion process was supposed to be comparable to the temperature of hot block digestion and be consistent at different power intensities. In order to keep the temperature profile consistent between each power intensity, the changes in temperature were monitored in each experiment. One complete operational cycle consisted of two sections; the first section was 80 seconds running at 400W (100%) and the other was digestion at target power intensity for the rest of the time. Therefore, there were two temperature records in each run. The first temperature profile was monitored after the 80 sec running and the second profile was measured after the whole digestion process was complete, which were 0.5h and 2h in this study. Table 4.1 shows the details of operating cycles at different power intensities as well as the corresponding temperature records.

Table 4. 1 Operation cycles and corresponding temperature profiles of digestion at 100W and 400W

	Operate cycle	**Temperature (ºC)**
100W (25%)	80sec on (at 400W) 3min off	80.3 ± 2.5 ºC (SD)
	Repeat: 25min on (at 100W) 1.5min off	0.5h: 81.2 ± 3.5 ºC (SD) 2h: 84.6 ± 1.5 ºC (SD)
400W (100%)	80sec on (at 400W) 3min off	80.3 ± 2.5 ºC (SD)
	Repeat: 20sec on (at 400W) 3min off	0.5r: 79.2 ± 2.5 ºC (SD) 2h: 86. ± 0.9 ºC (SD)

The mean temperature of aliquots reached 80.3 ± 2.5 ºC (SD) after 80 seconds digestion which was consistent, and then samples were cooled in-situ for 3 minutes. Afterwards, for digestion at 100W (25%), aliquots were irradiated in a repeating cycle of 25 min running and 1.5min cooling, whereas for digestion at 400W (100%), the repeating cycle included 20 sec running and 3 min cooling. The mean temperature after 0.5h digestion was 81.2 ± 3.5 ºC (SD) at 100W (25%) and 79.2 ± 2.5 ºC (SD) at 400W (100%) respectively. For the experiment with 2h digestion, after digestion, the mean temperature reached 84.6 ± 1.5 ºC (SD) at 100W and 86.0 ± 0.9 ºC (SD) at 400W respectively. The temperature data profile showed that mean temperatures of aliquots under different operating conditions were comparable. Consistent temperatures could be maintained during the digestion process at different power intensities and violent boiling could be also avoided. Therefore, these specific operating cycles were employed in the following experiments.

The correlation between lead recovery and three determinants (radiation intensity consumptions of nitric acid, and digestion time) is compared in Figure 4.4. Triplicate measurements were performed to compare the significance on lead recovery between each determinant.

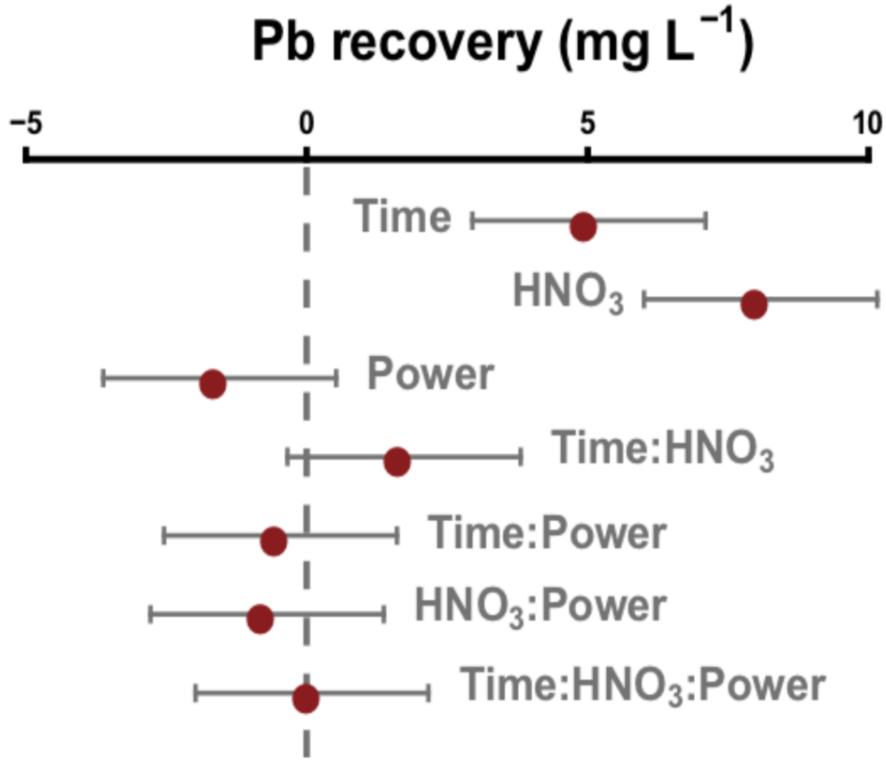

Figure 4. 4 The correlation and comparison of lead recovery and the concentration of HNO_3 , digestion time and power intensity.

Figure 4.4 shows that digestion time and the acid concentration were significant determinants of Pb recovery by SWIR digestion, whereas power intensity of irradiation was not. Nitric acid concentration was the greatest determinant. On average, increasing nitric acid concentration from 0.2% to 5% *v/v* significantly increased Pb recovery by 8.39 ± 2.35 mg/L (95% CI). The increase of digestion time from 0.5h to 2 h accompanied an increase in Pb recovery by 4.87 ± 2.35 mg/L (95% CI).

However power intensity was not positively related with an increase in Pb recovery; increasing power intensity from 100W (25%) to 400W (100%) decreased Pb recovery by 1.24 ± 2.35 mg/L

(95% CI) (not statistically significant) over the 2 h digestion process. Lower Pb recovery was possibly due to the much shorter irradiation time at 400W (100%). The total irradiation time at 400W (100%) was 85.5 W h for 2h digestion, whereas the total energy supplied at 100W (25%) over 2h was 192.2 W h. Because of much stronger irradiation intensity at 400W (100%) , flash boiling was more likely to occur and difficult to control, making it the major drawback of SWIR digestion. The specific operating cycle at 400W (100%) comprised longer cooling time but shorter irradiation time; therefore, much less energy was provided at 400W (100%). In this case, digestion by SWIR at 400W (100%) was not performed in the further recovery comparison experiments.

In order to maintain the highest Pb recovery by SWIR, digestion time was kept at 2h and the concentration of HNO_3 was determined to be 5% *v/v* in the following optimization experiments.

In the following SWIR optimization experiments, the effect of power intensity on Pb recovery was explored by comparing the result of digestion at 140W (35%) and 300W (75%). Since the significance of acid concentration and digestion time has been confirmed in this study, experiments were performed with 5% *v/v* nitric acid for 2h. And this operation setting was kept in the following experiments in this study.

The first step of digestion methods at different power intensities was the same, which was irradiating aliquots at 400W (100%) for 80 sec to bring to the target temperature and then cooling aliquots for 3min to prevent violent boiling. Afterwards, for digestion at 140W (35%), the aliquots were digested in a repeating cycle of 35min running and 1min cooling for 2h; for digestion at 300W (75%), the repeating cycle consisted of 40sec running and 2min cooling. Over 2h digestion, the aliquots digested at 140W and 300W reached 94.8 ± 2.3 ˚C (SD) and 95.3 ± 0.6 ˚C (SD), respectively.

Table 4. 2 Operational cycle and temperature records at 140W and 300W

	Operational cycle	**Temperature (ºC)**
140W (25%)	80sec on (at 400W) 3min off	80.3 ± 2.5 ºC (SD)
	Repeat: 25min on (at 140W) 1.5min off	2h: 94.8 ± 2.3 ˚C (SD)
300W (75%)	80sec on (at 400W) 3min off	80.3 ± 2.5 ºC (SD)
	Repeat: 40sec on (at 300W) 3min off	2h: 95.3 ± 0.6 ˚C (SD)

The results of Pb recovery are summarized in Figure 4.5, which compares the lead concentration recovered by SWIR at 4 different power intensities. Figure 4.5 shows that the lead concentration recovered at 140W (35%) and 300W (75%) was 17.5 ± 10.4 mg/L (SD) and 27.1 ± 2.49 mg/L (SD), respectively, which were much higher than at both 100W(25%) and 400W (100%). The highest concentration of lead was recovered from PbO_2 suspensions by SWIR digestion at 300W (75%) (27.1 ± 2.49 mg/L (SD)), whereas 400W (100%) could only recover 13.2 ±3.9 mg/L (SD) lead. The decrease of lead recovery at 400W could possibly be attributed to the less total digestion time at this high power intensity (400W(100%)).

In addition, high relative standard deviation values were observed at lower power intensity settings, which was possibly because of inconsistent irradiation. This finding was consistent with the previous conclusion that the power intensity is not one of the significant factors affecting digestion efficiency. The increase of the power intensity was not always accompanied with an increase of lead recovery.

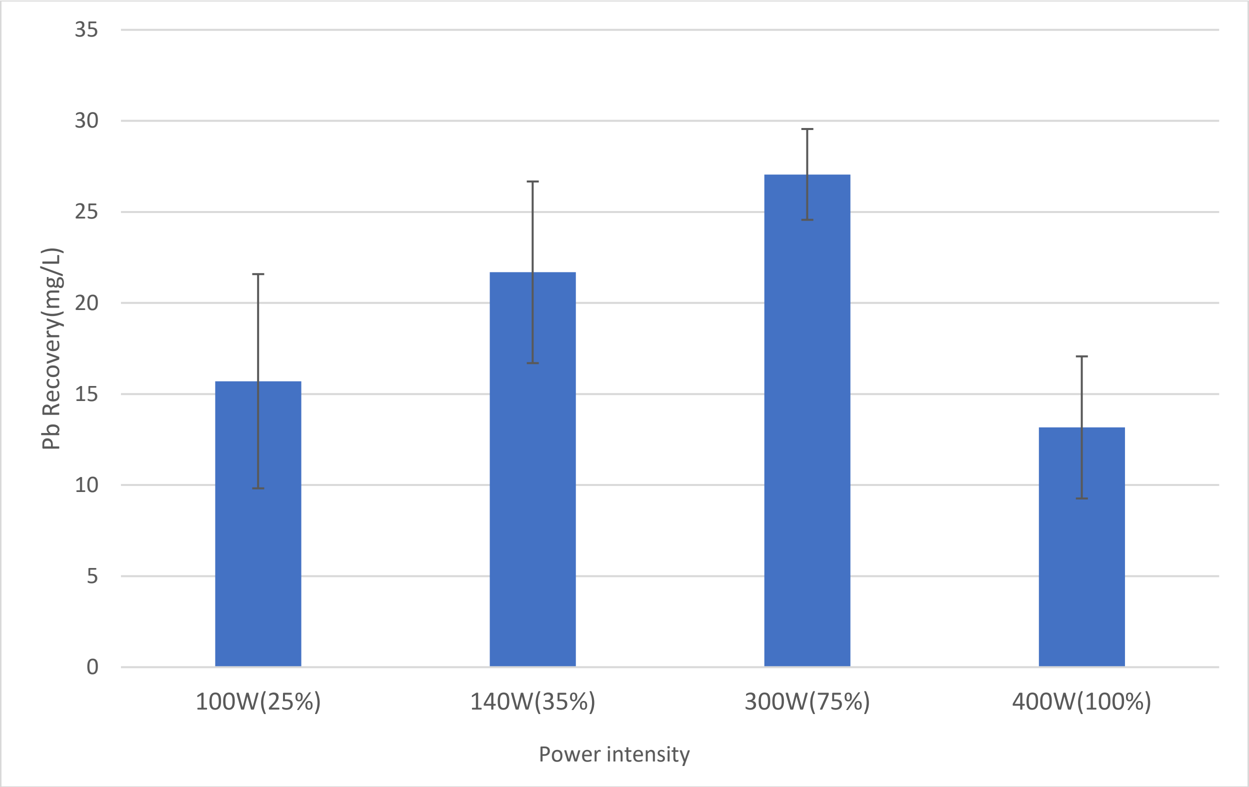

Figure 4. 5 Comparison of lead recovery between four different power intensity

Overall, compared with digestion at the other three power intensities digestion at 300W (75%) with 5% *v/v* HNO_3 for 2h was found to result in an optimal outcome of SWIR because of the highest recovery rate was achieved under this operation setting. Thus, SWIR, which will be operated under the best-performance cycle, along with hot block digestion and standard preservation will be compared on particulate lead recovery in the following experiments.

4.2.3 Recovery comparison of PbO_2 digestion

PbO_2 was selected as the target lead particulate which was the same as the SWIR optimization experiment. This phase of the experiment compared the performance of particulate lead digestion by the SWIR method (at 300W (75%)) , hot block digestion and standard preservation.

Figure 4.6 compares the mean lead recovery rate by three digestion methods, and shows SWIR digestion at 300W (75%) exceeds hot block digestion and standard preservation by factors of about 6 and 28, respectively. The target solution includes 38.9 mg Pb per liter; the SWIR method recovered an average of 27.1 mg Pb/L (69.42%) at 300W (75%), whereas hot block digestion just recovered an average of 4.6 mg Pb/L (17.75%). The mean recovery of lead by standard preservation was the lowest which was just 1.0 mg Pb/L, 2.46% of the total lead. The lowest concentration of lead was recovered by standard preservation, which was consistent with the finding noted by Haas et al., (2013) that less than 2% lead (IV) oxide was dissolved. This finding is because higher-oxidized metal is relatively inert in diluted nitric acid solution at room temperature (Haas et al., 2013).

With the same amount of acid consumption and same digestion time, SWIR digestion is more efficient on digesting PbO_2, providing much higher recovery than conventional methods.

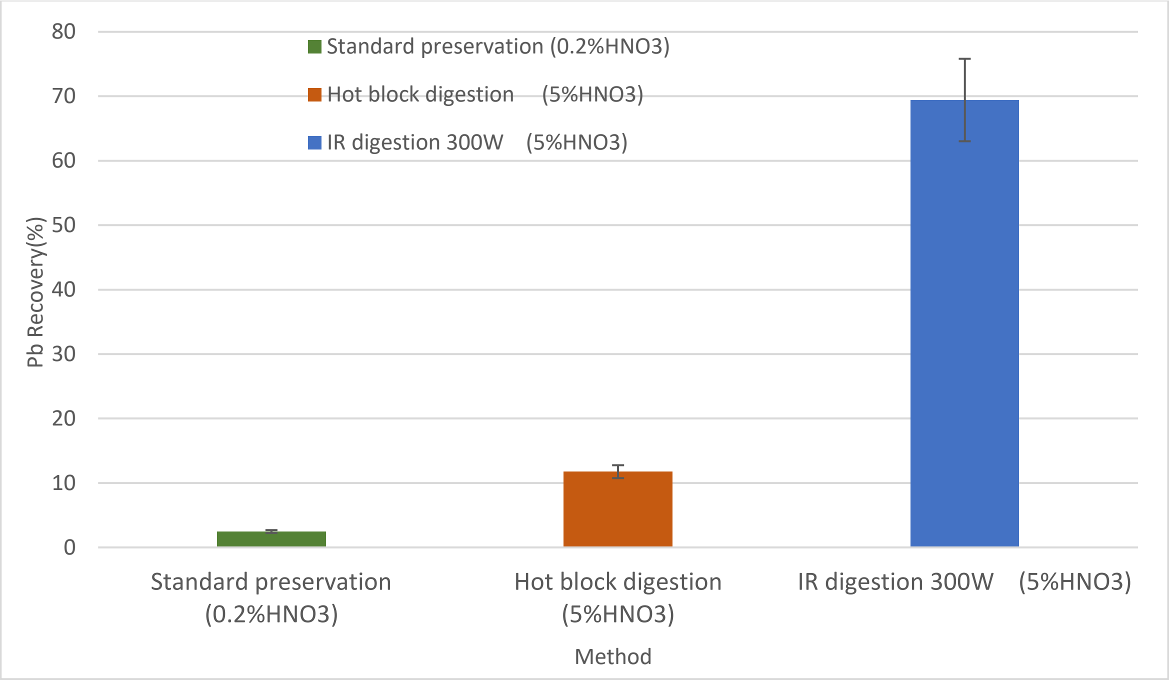

Figure 4. 6 Comparison of PbO_2 digestion by standard preservation, hot bloc digestion and SWIR digestion at 300W (with HNO_3 only)

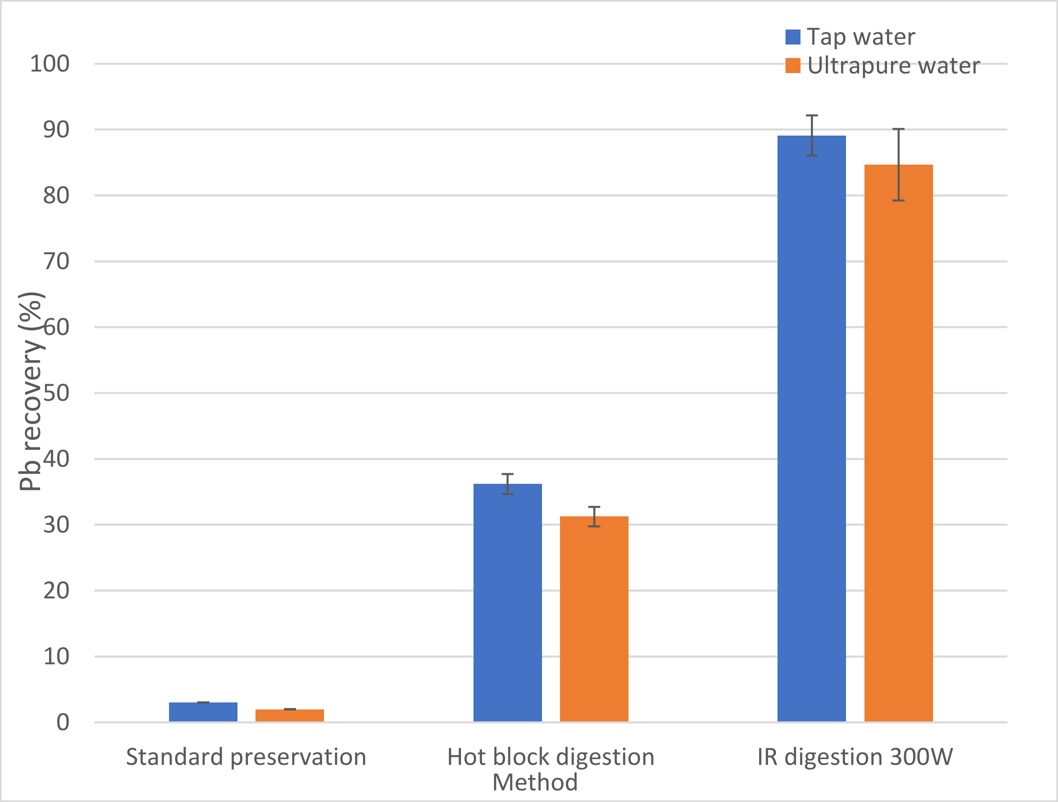

Figure 4. 7 Recovery comparison between PbO_2 digestion in ultrapure water and tap water

Figure 4.7 compares the recovery of digestion with two water matrices. As explained in Chapter 2, the dissolution of lead (IV) oxide can be affected by natural organic matter, the occurrence of carbonate and the changes in pH (Lin et al., 2008; Dryer et al., 2007; Xie et al., 2010). Thus, the digestion efficiency of the three methods was investigated by digesting PbO_2 in a different water matrix: municipal tap water substituted for ultrapure water. The concentration of PbO_2 suspension was 48.5 mg/L. The mean recovery of PbO_2 digestion in municipal tap water by the three methods were all higher than digestion in ultrapure water.

The mean recovery by the SWIR method increased from 84.7% to 89.1%, which was the highest among the three digestion methods. The tap water matrix had 22.5 mg/L $CaCO_3$, 1.6 mg/L total organic carbon, and circumneutral pH value (pH=7.3) The higher recovery rate from the tap water matrix compared to the ultrapure water matrix was consistent with previous observations from Washington D.C. drinking water crisis in 2003 (Lin et al., 2008). A dramatic increase in lead concentrations was detected in drinking water samples over the period. This increase might have been due to the common occurrence of reducing agents in municipal tap water, such as natural organic matter (NOM) (Lin et al., 2008; Dryer et al., 2007). With the presence of NOM and carbonate, reductive dissolution of tetravalent lead by organic matter and ligand-promoted dissolution by carbonate will occur with PbO_2 (Xie et al., 2010).

Comparing across digestions procedures, the SWIR method could recover the most lead from either tap water or ultrapure water compared with hot block digestion and standard preservation.

4.2.4 Comparison of PbO_2 digestion with acid mixtures

In previous phases of the experiments, only nitric acid was applied in PbO_2 digestion. With an increase in nitric acid consumption to 5% *v/v*, the highest recovery of lead was 69.4% which was digested by SWIR digestion. In order to determine the effect of different types of acid, the mixture of hydrochloric acid (HCl) and HNO_3 was applied by hot block digestion and the SWIR method, substituted for HNO_3 only.

The concentration of HCl showed great influence on lead recovery in the study of Haas et al., (2013). That study compared the recovery from solution with varying concentrations of HCl (0 % *v/v*, 1% *v/v* and 2% *v/v*) and demonstrated that 1% *v/v* was adequate in fully dissolving lead from PbO_2 particles without heating. In this phase of experiment, 0.5% *v/v* HCl was used for hot block digestion and SWIR digestion but was not used for standard preservation. In terms of the concentration of HNO_3, hot block digestion and SWIR digestion applied 0.2% *v/v* , which was the same as the concentration of the aliquots preserved by standard preservation.

The dissolution of PbO_2 and reduction of Pb (IV) to Pb (II) can occur with the addition of HCl. And the resulting salt $PbCl_4$ will be soluble in the matrix during digestion.

$$PbO_2 + 4\ HCl \rightarrow PbCl_4 + 2\ H_2O$$
$$PbCl_4 \rightarrow PbCl_2 + Cl_2 \qquad \text{(Equation 4-1)}$$

According to stoichiometry, the molar ratio of PbO_2 and HCl is 1:4. In this study, 45 mg pf PbO_2 was weighted to make a suspension, which is about 1.881×10^{-4} mol Pb in the suspension. Since the concentration of HCl is 0.5% *v/v* , 2.448×10^{-3} mol HCl was applied in each 15 ml aliquot. Accordingly, the molar ratio of the actual doses of PbO_2 and HCl greatly exceeds 1 : 4. Therefore, digested with addition of HCl, PbO_2 particles are supposed to be fully dissolved turning into free metal ions which can pass through 0.45 μm filter paper. In this case, after digestion, centrifuged aliquots were filtered before being analyzed by ICP-MS, in order to determine the effect of HCl.

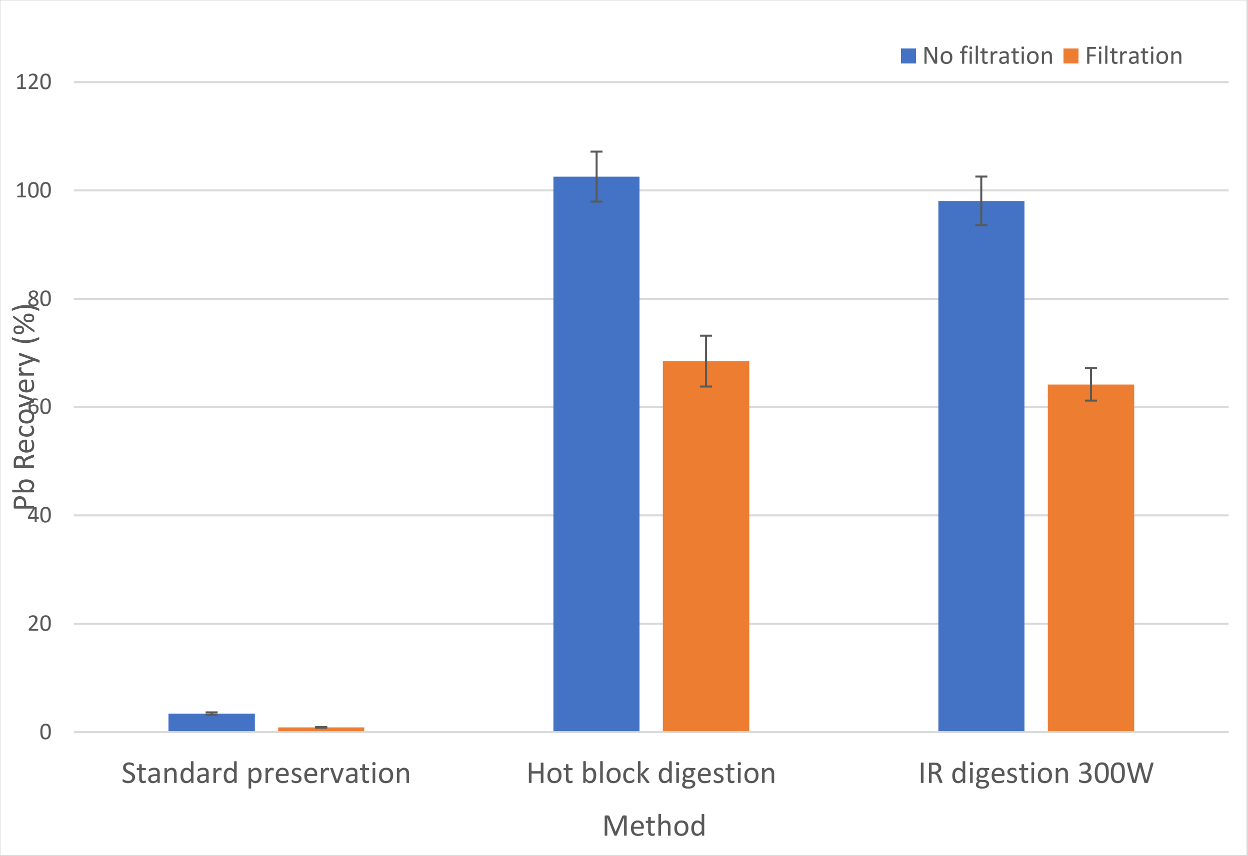

Figure 4. 8 Comparison of PbO_2 digestion with acid mixtures (HNO_3 and HCl) and evaluation of the effect of filtration procedure

Figure 4.8 compares the lead recovery of the three digestion methods by adding acid mixtures of HNO_3 and HCl. Results show that hot block digestion recovered 102.6% lead from the PbO_2 suspension by digestion with acid mixtures of HNO_3 and HCl. which is the highest among the three methods . The SWIR method recovered 98.1% lead, 4.47% lower than the recovery rate by hot block digestion. Theoretically, both hot block digestion and the SWIR method are supposed to achieve at least 100% recovery of lead, based on the stoichiometry principles. The reason why the SWIR method recovered less Pb may be attributed in part to the inconsistent dosing of the heterogenous suspension and the adsorption on glassware used in the SWIR method. As for standard preservation, lead recovery (3.44%) achieved in this study is consistent with previous investigation of the digestion efficiency of standard preservation in which HCl was not added to preserve samples (Hass et al., 2013).

Figure 4.8 also compares the effect of filtration on lead recovery by each method. The filtration approach after digestion involved filtering digested aliquots through 0.45 µm filter paper, in order to separate the particulate lead particulates in the supernatant. The fraction after filtration by 0.45 µm filter paper refers to the fraction of dissolved lead. However, after filtration, the lead concentrations digested by the three methods was found to be lower than filtration not applied. The lead recovery by hot block digestion decreased from 102.6% to 68.5%, while the recovery by the SWIR method decreased from 98.1 to 68.2%. In terms of the aliquots preserved by standard preservation, only 0.88% lead were measured by ICP-MS, 2.56% lower than the concentration measured without filtration. The relatively low recoveries may have been attributed to the loss within the filtration components. But theoretically adsorption can be prevented in low pH matrices. This contradiction pointed out an assumption that the lead concentrations measured by ICP-MS after digestion consists of lead particles with two size fractions. Not all the lead detected by ICP-MS was existing in the dissolved form; there was a fraction with particle size larger than 0.45 µm that could be measured.

These results demonstrate that although three digestion methods were able to fully dissolve more than 64% of lead from PbO_2 suspension, digested by acid mixtures of HNO_3 and HCl, but there was still a fraction (about 34%) of PbO_2 particles, broken into small pieces and presenting in the quantifiable colloidal forms.

4.3 Recovery comparison of different compounds digestion

This section discusses the lead recoveries of different types of compounds digested by standard preservation, hot block digestion, and the SWIR method. Apart from PbO_2 particles, digestion efficiency of other significant lead corrosion by-products such as lead (II) sulfate ($PbSO_4$), lead scales, and chloropyromorphite ($Pb_5(PO_4)_3Cl$), were investigated. In addition, iron particulates play an important role in releasing lead particulates into water, thus, hematite (iron (III) oxide, Fe_2O_3) and magnetite (iron (II,III) oxide, Fe_3O_4) were also selected to evaluate the digestion efficiency of the three methods.

The experimental procedures for the three digestion methods of different compounds digestion were all the same as the procedures performed previously. The suspension of different compounds were made at a concentration of 45 mg/L and preserved by standard preservation for 24 hours.

4.3.1 Comparison of PbSO4 digestion

5% *v/v* HNO_3 was added in to the aliquots which were digested by hot block digestion and the SWIR method, taken from the suspension preserved by standard preservation. Aliquots of the preserved samples were taken and 5% v/v HNO3 was added. These aliquots were digested by hot block digestion and the SWIR method.

Figure 4.9 shows the comparison of lead recoveries of $PbSO_4$ digested by the three methods. Both standard preservation and hot block digestion show adequacy in fully recovering lead and achieving 101.6% and 100.2% recovery, respectively. This finding demonstrated that diluted nitric acid solution at a concentration of 0.2% *v/v* along with a 24-hour holding period, can fully recover lead from $PbSO_4$. In this case, hot block digestion is not necessary to pretreat samples containing $PbSO_4$ solids.

However, only 83.1% lead was measured in the aliquots which were digested by the SWIR method, showing the lowest lead recovery among the three methods. The low recovery rate might be due to the adsorption on the inner walls of the digestion flask as well as incomplete dissolution by SWIR. In addition, highest standard deviation value (13.5%) was observed, whereas the values obtained from standard preservation and hot block digestion were 1.25% ad 1.05%, respectively. The large variability might have been attributed to inconsistent dosing. Due to the incomplete dissolution of the suspension, large particles might be still present and settle down quickly when taking aliquots out of the sample bottle. Therefore, it is difficult to ensure the same amount of target compound is successfully taken in each aliquot.

Overall, the SWIR method is not recommended for $PbSO_4$ digestion since the recovery achieved by this method was relatively low (83.1%). Standard preservation is the most efficient pretreatment step for samples containing high concentration of $PbSO_4$, because this pretreatment method can achieve the highest recovery of lead from the digestion of $PbSO_4$ under its straightforward operation procedures.

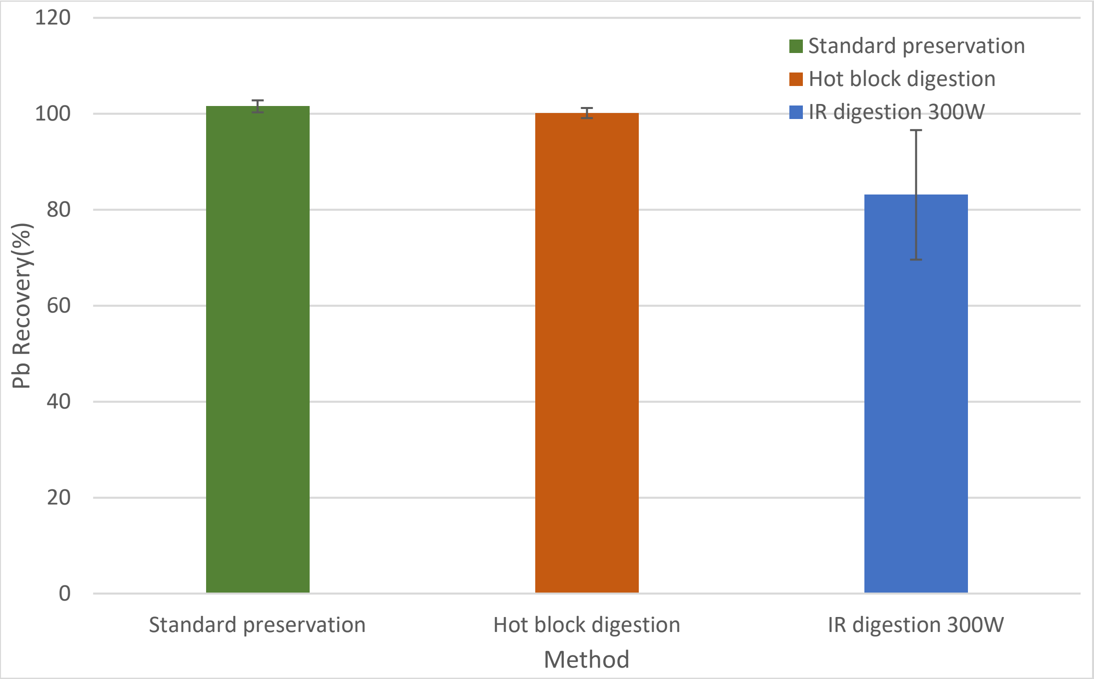

Figure 4. 9 Comparison of lead recoveries of $PbSO_4$ digestion by standard preservation, hot block digestion and the SWIR method

4.3.2 Comparison of hematite (Fe_2O_3) and magnetite (Fe_3O_4) digestion

In this experiment, the suspension of Fe_3O_4 and Fe_2O_3 were made and preserved by following the same procedures which were employed previously. For digestion by hot block digestion and the SWIR method, aliquots were prepared in two ways. One set of aliquots was dosed with extra 5% *v/v* HNO_3 prior to digestion, and the other set was dosed with extra 2% *v/v* H_2O_2 and no extra HNO_3 was added. This was to investigate the effect of the reducing agent (H_2O_2) on the iron recovery. Each comparison was performed in triplicate.

Figure 4.10 shows the comparison of iron recoveries after digesting Fe_3O_4 and Fe_2O_3 digestion by the use of HNO_3 only and the use of the reducing agent only through the three different digestion methods. The error bars in the figure stand for the standard deviation. In 0.2% *v/v* HNO_3 solution for 24 hours, both the iron recoveries of Fe_3O_4 and Fe_2O_3 were lower than 2%, which was the lowest among three digestion methods. The recovery of Fe_3O_4 was 1.66%, slightly higher than that of Fe_2O_3 (1.49%). The relatively low recovery of iron showed that the standard preservation method could miss more than 98% of iron if it is present in drinking water in forms of Fe_3O_4 or Fe_2O_3.

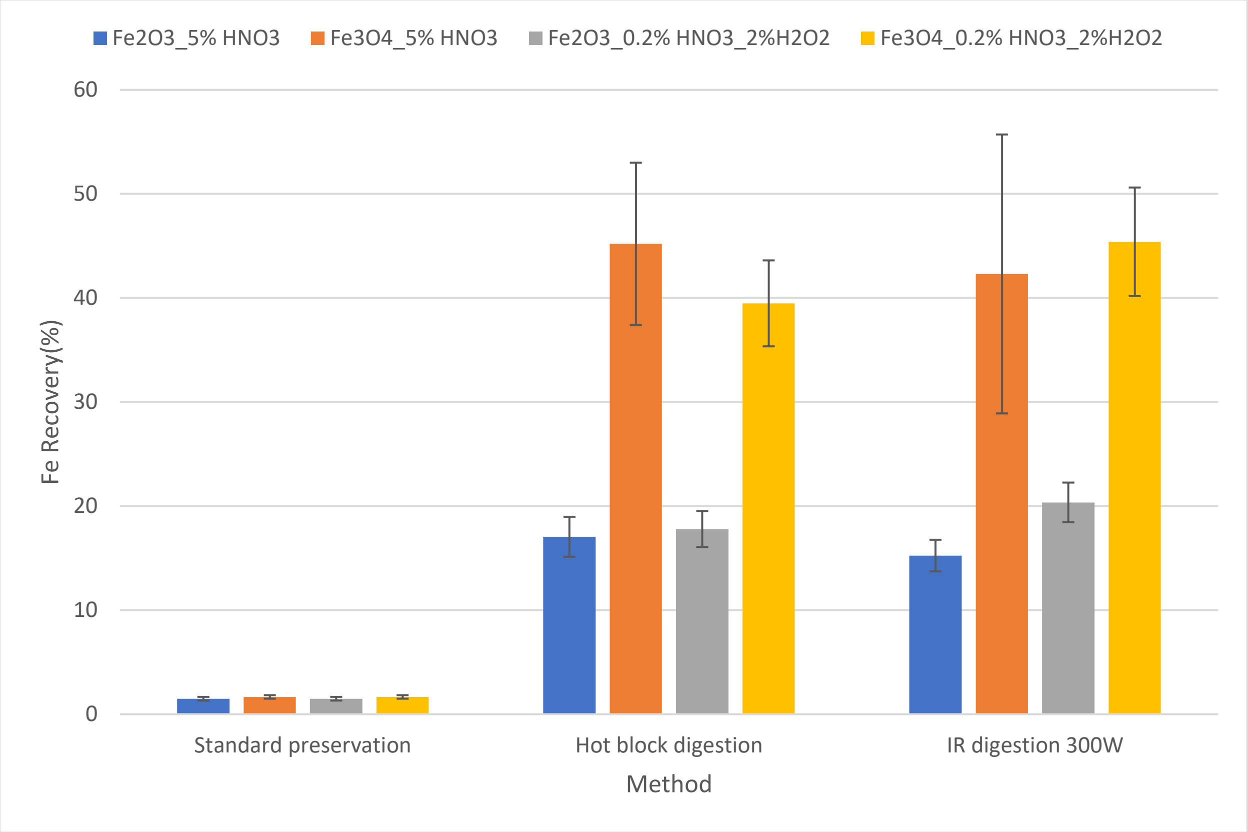

Figure 4. 10 Iron recoveries comparison of hematite and magnetite digestion.

For the Fe_2O_3 digestion with HNO_3 only, hot block digestion and the SWIR method recovered similar fractions of iron, which were 17.1% and 15.2%, respectively. After the addition of the reducing agent (H_2O_2), the recoveries by both methods slightly increased. The recovery of iron by hot block digestion increased from 17.1% to 17.8%, showing only 0.72% was improved. While the iron recovery by the SWIR method increased up to 20.4% from 15.2% , the increases in iron recovery by both methods after adding the reducing agent were not significantly synergetic (p value = 0.90 (HBD) and 0.94 (SWIR)).

For the Fe_3O_4 digestion with HNO_3 only, the iron recoveries by hot block digestion and the SWIR digestion were also similar. 45.2% of iron was recovered by hot block digestion, slightly higher than the recovery by the SWIR method which was 42.3%. Nevertheless, greater standard deviation value was observed in aliquots digested by the SWIR method. The addition of H_2O_2 accompanied an increase in iron recovery by the SWIR method from 42.3% to 45.4%. However, a decrease of 5.72% of iron measured in aliquots digested by hot block digestion (from 45.2% to 38.5%) was observed. And this finding showed that in the digestion of Fe_3O_4 by hot block digestion, the addition of reducing agent (H_2O_2) was not able to increase the recovery of iron.

Overall, with HNO_3 only or with H_2O_2, iron recovery of Fe_2O_3 and Fe_3O_4 digestion by hot block digestion and SWIR digestion were all similar. However, when digestion with HNO_3 only, hot block digestion can achieve slightly high recovery rate than SWIR digestion, whereas SWIR digestion can achieve slightly higher recovery rate than hot block digestion by adding H_2O_2.

When only compare the Fe_2O_3 digestion by hot block digestion between the effect of HNO_3 only and the effect of H_2O_2, it is obvious that the iron recovery rates were pretty close. However, the trend of Fe_2O_3 digestion by SWIR digestion was slightly different. The iron recovery rate by addition of HNO_3 only was lower than the addition of H_2O_2. In addition, the similar trend was observed in Fe_3O_4 digestion. For Fe_3O_4 digestion by hot block digestion, after addition of H_2O_2, the iron recovery decreased. For Fe_3O_4 digestion by SWIR digestion, after addition of H_2O_2, the iron recovery increased. These results provide an assumption that SWIR digestion can recover more iron from iron particulates by adding reducing agents, like H_2O_2, while hot block digestion can achieve higher iron recovery rate by adding HNO_3 only.

4.3.3 Comparison of lead scale digestion

In the comparison experiments of lead scale digestion, lead scale suspension was prepared by weighing 45 mg lead scale pieces and adding them into 1 L 0.2% *v/v* HNO_3 solution. Aliquots digested by hot block digestion and the SWIR method were prepared by following the experimental procedures introduced previously. 5% *v/v* HNO_3 was added prior to digestion.

Figure 4.11 compares the lead recovery rate by the three methods. The measurements were performed in triplicate. And in Figure 4.11, the error bars stand for the standard deviation values. It demonstrates that standard preservation is able to recover a higher concentration of lead from lead scale suspension, which is 45%. Following standard preservation is the SWIR method, which can recover 34.8% lead. The lowest lead concentration was only 24.7%, measured in the aliquots digested by hot block digestion. Lead recoveries by the three digestion methods were all lower than 50%. This means that rigorous digestion based on standard preservation with addition of 5% *v/v* HNO_3 cannot fully dissolve lead scale pieces if they occur in drinking water. For full dissolution of lead scale, stronger acid or acid mixtures have to be considered and digestion time has to be extended.

Moreover, large standard deviation values were observed from Figure 4.11. The high variability of the three methods might have been partially attributed to inconsistent sample dosing when each aliquot was prepared. This is because the lead scale pieces were too large to be fully dissolved during the 24-hour holding period and too large to be drawn and transferred into each aliquot. In this case, it was not able to ensure each aliquot contains the same amount of lead. Therefore, large variability was observed in each method.

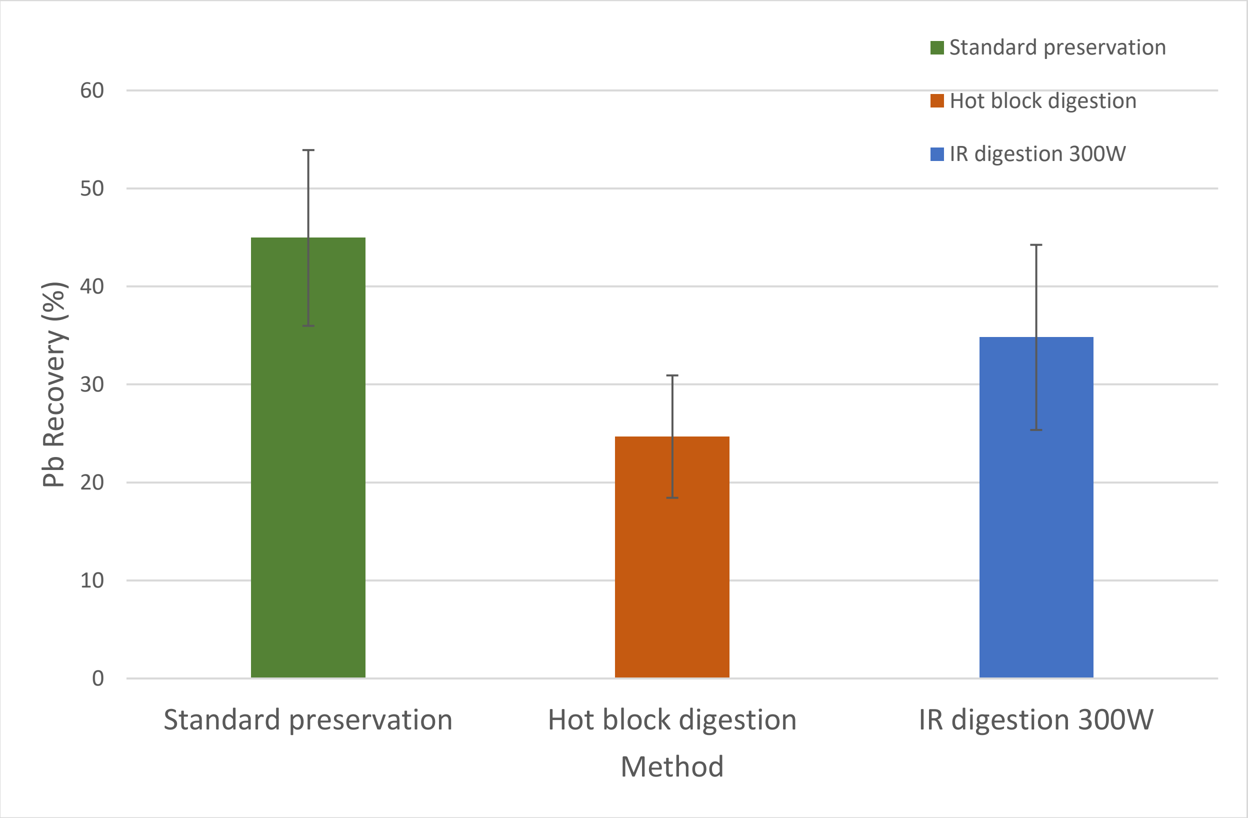

Figure 4. 11 Comparison of lead recoveries of lead scale digestion by three methods

4.3.4 Comparison of chloropyromorphite ($Pb_5(PO_4)_3Cl$) digestion

In this experiment, chloropyromorphite was smashed and then weighed to obtain 45 mg to make the suspension. The suspension was held by following the procedures of standard preservation before digestion. Because of the high insolubility of chloropyromorphite, for preparing the aliquots digested by hot block digestion and the SWIR method, 0.5% *v/v* HCl was added, and the concentration of HNO_3 was kept at 0.2% *v/v*.

Figure 4.12 shows that the highest lead concentration was recovered by standard preservation, which was 46.2 ± 3.75%. The lead recovery by the SWIR method was 42.7 ± 5.23%, similar to standard preservation. Hot block digestion recovered the least lead from chloropyromorphite, and only 24.9 ± 5.31% lead was recovered. In terms of the standard deviation values, they were all lower than the values observed from lead scale digestion.

Apart from the recovery rate, the acid consumption by standard preservation was also much less than the other two digestion methods, which was only 0.2% *v/v* HNO_3 applied. In addition, the operating procedures were more simple; chloropyromorphite suspension was held for 24 hours and then centrifuged before being analyzed by ICP-MS.

Overall, standard preservation is the best method to pretreat the drinking water samples containing chloropyromorphite because the acid consumption is less and pretreatment procedures are more simple and recovery rate is higher.

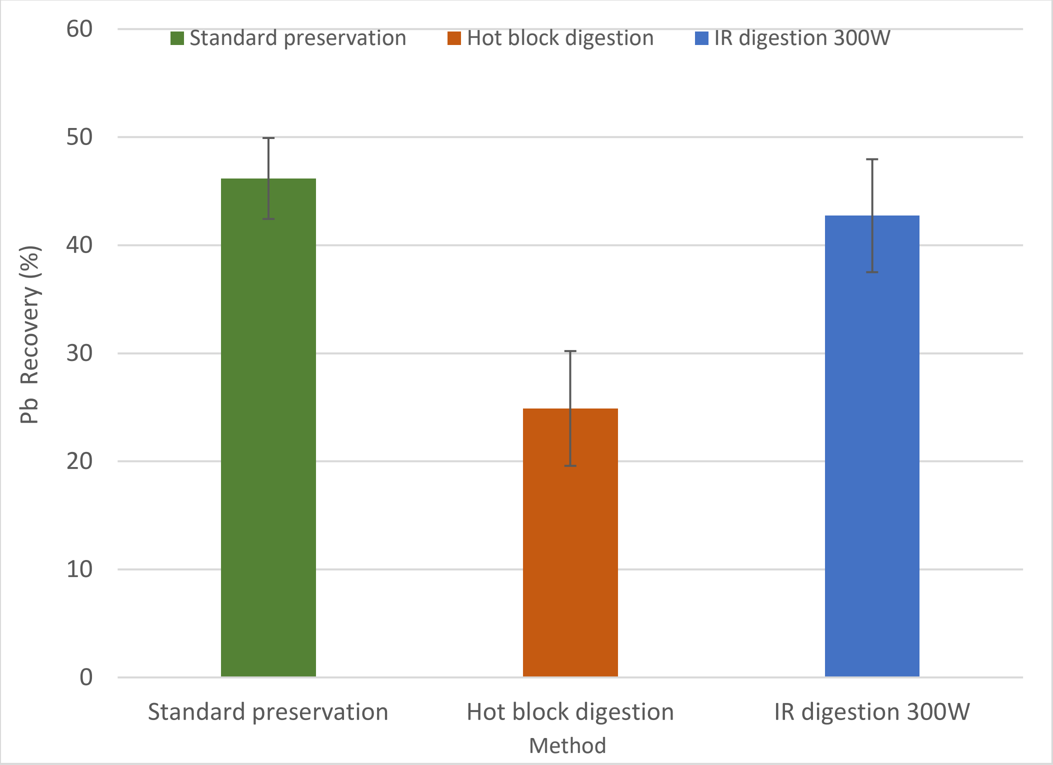

Figure 4. 12 Comparison of lead recoveries of chloropyromorphite digestion by three methods

Chapter 5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

The purposes of this study were to evaluate and optimize the digestion ability of the SWIR method, a new drinking water sample pretreatment method, and compare this new method with established methods, such as standard preservation and hot block digestion. Experiments consisted of three major phases based on the different objectives.

The first phase of experiments was designed to investigate the digestion ability of the SWIR method. In this phase, lead recovery of residential water digested by the SWIR method under default settings was compared with the other two methods. And then the SWIR method was optimized based on the adjustment of operational settings in order to obtain a consistently high result. The second phase was the investigation of digestion efficiency of three methods on PbO_2 suspension digestion. In the second phase, a PbO_2 suspension was digested under different conditions, such as addition of HCl and the substitution of tap water for ultrapure water. The third phase in this work further compared lead recoveries of different lead particulates and iron particulates digestion by the SWIR method with standard preservation and hot block digestion.

The key findings were summarized in the following sections.

5.1.1 Evaluation of the SWIR method

The SWIR method, standard preservation and hot block digestion recovered similar concentrations of lead from 15 residential water samples digestion. But the acid consumption by the SWIR method was the same as that by standard preservation (0.2% *v/v*), much less than that by hot block digestion (5% *v/v*). Because the wide opening of the digestion flask used in the SWIR method was covered with a nitrate glove and tightened, the acid fumes released and volumes lost were relatively less than hot block digestion which applies continuous conductive heating to digest sample. In addition, the digestion time of SWIR digestion was 5 minutes, whereas the digestion period of hot block digestion lasts 2 hours. Thus, if the SWIR method can be well developed, it could possibly perform better than standard preservation and hot block digestion as well.

5.1.2 Optimization of the SWIR method

Digestion time and nitric acid concentration were significant determinants of lead recovery for the SWIR method, but the power intensity of radiation was not. The greatest factor was the concentration of nitric acid, increasing the concentration from 0.2% *v/v* to 5% *v/v* accompanying an increase of 8.39 ± 2.35 mg/L (95% CI) in lead recovery. And an increase in digestion time from 5 minutes to 2 hours accompanied a 4.84 ± 2.35 mg/L (95% CI) increase in lead recovery. However, there was a 1.24 ± 2.35 mg/L (95% CI) (not statistically significant) decrease in lead recovery when the power intensity was increased from 100W (25%) to 400W (100%).

Operating the SWIR methods for 2 hours at 300W (75%) with addition of 5% *v/v* nitric acid has the highest lead recovery, that 27.1 ± 2.49 mg/L of lead were recovered.

5.1.3 Lead recovery comparison of PbO_2 digestion

The key findings from PbO_2 digestion under different conditions are summarized in Table 5.1 below.

Table 5. 1 Key findings from PbO_2 digestion by standard preservation (SP), hot block digestion (HBD) and the SWIR method (IR)

	Reagents		**Key Findings**
PbO_2 Digestion in ultrapure water	Standard preservation (SP)	0.2% *v/v* HNO_3	• The SWIR method recovered 69.4% of lead when it was operated at 300W (75%) for 2h. • The recovery via the SWIR method exceeded recovery by standard preservation and hot block digestion by factors of approximately 28 and 6 respectively.
	Hot block digestion (HBD)	5% *v/v* HNO_3	
	The SWIR method (SWIR)	5% *v/v* HNO_3	
PbO_2 Digestion In Tap Water	SP	0.2% *v/v* HNO_3	• Greater lead recovery by all three digestion methods was observed. • Mean recovery by the SWIR method increased to 89.1%
	HBD	5% *v/v* HNO_3	
	SWIR	5% *v/v* HNO_3	
PbO_2 Digestion with acid mixtures	SP	0.2% *v/v* HNO_3	• With addition of HCl, lead recovery by hot block digestion and the SWIR method both increased (102.6% and 98.1% respectively) • The fraction of dissolved lead recovered by hot block digestion was 66.8% and by the SWIR method was 65.5%.
	HBD	0.2% *v/v* HNO_3 & 0.5% *v/v* HCl	
	SWIR	0.2% *v/v* HNO_3 & 0.5% *v/v* HCl	

Note: SP = Standard preservation, HBD = hot block digestion, SWIR = Short wave infrared digestion

5.1.4 Recovery comparison of lead particulate and iron particulate digestion

The key findings of two species of lead particulates and two types of iron particulates are summarized in Table 5.2 below.

Table 5. 2 Key findings from lead particulate and iron particulate digestion by standard preservation (SP), hot block digestion (HBD) and the SWIR method (IR)

	Reagents		**Key Findings**
$PbSO_4$ Digestion	Standard preservation (SP)	0.2% *v/v* HNO_3	• The recovery of lead by standard preservation and hot block digestion was 101.6% and 100.2% respectively. • The lead recovery via the SWIR method was the lowest (83.1%)
	Hot block digestion (HBD)	5% *v/v* HNO_3	
	The SWIR method (SWIR)	5% *v/v* HNO_3	
Fe_2O_3 and Fe_3O_4 Digestion	SP	0.2% *v/v* HNO_3	• Overall, the iron recovery of Fe_3O_4 digestion was higher than the recovery of Fe_2O_3 digestion. • For Fe_2O_3 digestion, the addition of the reducing agent (H_2O_2) was accompanied by slight increases of iron recovery by hot block digestion and the SWIR method. • For Fe_3O_4 digestion, the addition of the reducing agent (H_2O_2) was accompanied by a 3.09% increase of iron recovery by the SWIR method; however, the iron recovery by hot block digestion decreased by 5.72%.
	HBD	5% *v/v* HNO_3 / 0.2% *v/v* HNO_3 & 0.5% *v/v* H_2O_2	
	SWIR	5% *v/v* HNO_3 / 0.2% *v/v* HNO_3 & 0.5% *v/v* H_2O_2	

	Reagents		**Key Findings**
Lead Scale Digestion	SP	0.2% *v/v* HNO_3	• Standard preservation can recover the highest concentration of lead, (45%) followed by the SWIR method (34.8%), while the recovery by hot block digestion was the lowest (24.7%). • Lead recoveries by all three methods were all lower than 50%.
	HBD	5% *v/v* HNO_3	
	SWIR	5% *v/v* HNO_3	
$Pb_5(PO_4)_3Cl$ Digestion	SP	0.2% *v/v* HNO_3	• The lead recovery from chloropyromorphite digestion by all three methods was similar to the lead recovery from lead scale digestion (lower than 50%). • Standard preservation was the most efficient method of chloropyromorphite digestion, which can recover the highest concentration of lead (46.2%) but using less acid. • The lowest lead recovery was 24.9% by hot block digestion.
	HBD	0.2% *v/v* HNO_3 & 0.5% *v/v* HCl	
	SWIR	0.2% *v/v* HNO_3 & 0.5% *v/v* HCl	

Note: SP = Standard preservation, HBD = hot block digestion, SWIR = Short wave infrared digestion

5.2 Recommendations

In this work, high lead concentrations were occasionally detected in the blank samples from the SWIR method. These were presumed to be leftover contamination on the inner walls of digestion flasks from previous runs. And soaking digestion flasks in the acid bath overnight was not able to remove contaminants. For future studies, one recommendation would be adding 2% *v/v* H_2O_2 into acid bath which contains 10% *v/v* HNO_3. As well, other digestion components used by the SWIR method are recommended to be acid washed with extra 2% *v/v* H_2O_2.

Future studies should be conducted with a more consistent dosing procedure and closer attention paid to sample transfer. This is because high standard deviation values were sometimes observed from hot block digestion and the SWIR method. In addition, it is difficult to have homogenous aliquots, due to partial dissolution of the suspension. Filtration of supernatant after digestion is not recommended for future research since significant target analyte loss was observed. For future studies, other compounds which are ubiquitous, such as manganese, iron, copper, lead carbonates and lead phosphates, should be considered. Different water matrices apart from tap water should also be considered to further investigate the digestion efficiency of all three methods.

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