Design of a Flow-Through Extraction Cell for Rapid Determination of Toxic Metals (Arsenic, Cadmium, Chromium, Copper, Mercury, Lead, Tin, Zinc) from Soils and Sediments

Julie Asselin

A Thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Master of Science.

February 2006

Department of Chemistry
McGill University
Montreal, Quebec
Canada

Your file Votre référence
ISBN: 978-0-494-24605-4
Our file Notre référence
ISBN: 978-0-494-24605-4

Abstract

The goal of this study was to design, characterize and test a flow-through extraction cell for rapid determination of toxic metals present in soil and sediment samples.

Based on a design elaborated by Jean Bouffard, a Teflon cell was first machined, but it appeared to be leaky and hard to disassemble without breaking the fritted glass discs. To overcome these difficulties, a poly ether ether ketone (PEEK) cell was machined and several parts were modified. Even though the shape and seal of the components seemed to be affected when heated, the cell was working at room temperature and proved promising for future work.

Finally, the EPA (Environmental Protection Agency) method 1311 was applied on some real samples, and the extracts were analyzed in order to get reference results that could eventually be compared to results given by extracts obtained with the flow-through cell.

Résumé

Le but de cette étude était de concevoir, caractériser et tester une cellule d'extraction à flot forcé pour déterminer rapidement la présence de métaux toxiques dans des échantillons de sol et de sédiments.

Conçue à partir d'un modèle élaboré par Jean Bouffard, une cellule en Téflon fut d'abord fabriquée, mais il s'est avéré qu'elle fuyait et était difficile à désassembler sans briser les disques de verre fritté. Pour remédier à ces problèmes, une cellule en poly éther éther cétone (PEEC) fut construite en modifiant plusieurs pièces. Même si la forme et l'étanchéité des composantes semblaient affectées par la chaleur, la cellule fonctionnait à la température de la pièce, promettant ainsi une future utilisation.

Finalement, quelques échantillons ont été analysés en utilisant la méthode 1311 de l'agence de protection environnementale (APE). Les résultats obtenus pourront éventuellement être comparés aux résultats qui seront générés par la cellule à flot forcé.

Acknowledgements

I would first like to thank my research supervisor, Eric Salin for his support, encouragement and comprehensiveness.

A Pierre-Luc, mon conjoint, merci de m'avoir supportée et encouragée tout au long de ces années d'étude supplémentaires et d'avoir cru en moi.

Merci a mon fils, Jérôme, qui, sans le savoir, m'a donné la force de terminer l'écriture de cette thèse avant sa naissance et qui, par la suite, m'a gentiment laissée terminer les corrections en dormant très souvent.

A ma mère, merci de m'avoir supportée financièrement et de m'avoir encouragée à poursuivre des études supérieures.

To Dr. Laurie Chan and his students for letting me perform experiments in their lab. I would like to address a special thank to Donna Leggee, the lab mommy, who helped me a lot with my analyses.

To Mr. Alfred Kluck and Mr. Bill Bastien who machined the cell and gave me suggestions for the designs.

I would like to thank Cameron Skinner who also helped me with the design and for giving me advices on fittings, tubing and connections.

To Erica Salin, our "poor" slave during summer 2003, who helped me for the second round of extractions.

To David Burns, who had the idea of using a toaster oven instead of a microwave oven to heat the cell.

To Dominique P. Chan, who reviewed the whole document for English wording, thanks for your time, help and friendship.

Finally, to my friends in the lab and outside, thank you for your good humor, support, friendship, and for all the time you listened to my complaints about this thesis.

Table of Contents

List of Tables

List of Figures

Chapter 1 : Introduction and Literature Review

Organometals are among the most toxic chemicals present in aquatic and terrestrial environments. Some are naturally formed *in situ* by bacteria (*e.g.* methyl mercury MeHg), some others (tributyltin - TBT and dibutyltin - DBT) are introduced intentionally into ecosystems. Mercury occurs naturally in elemental organic and inorganic forms. Much of the Hg in the environment is inorganic and as such is strongly bound to sediment and organic matter, making it unavailable to organisms. Cinnabar, HgS, is the only important natural source of mercury and is found along lines of previous volcanic activity. The mercury cycle is relatively complex and involves soil, atmospheric and water systems (see Figure 1-1).

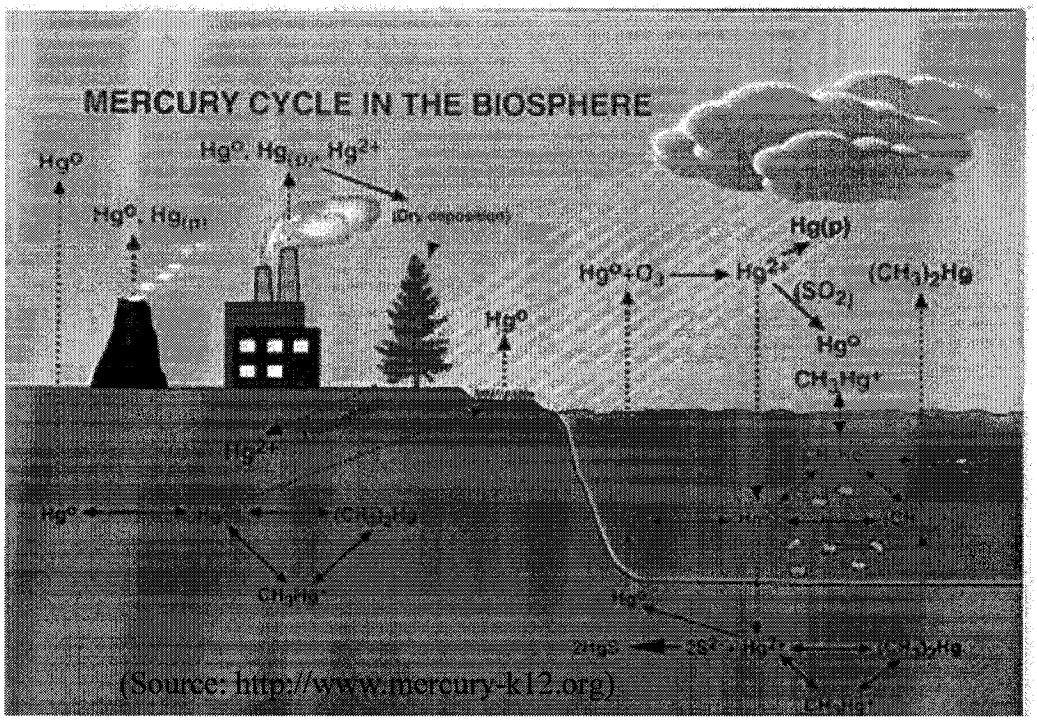


Figure 1-1: Mercury cycle in the biosphere

Mercury is an unreactive substance, being attacked only by concentrated HBr, HI or aqua regia[1]. Inorganic Hg can be methylated to form organic compounds (*e.g.* MeHg), which can biomagnify through food chains. Exposure to MeHg has been a problem among humans who are at the top of the food chain, because it is

neurotoxic. MeHg and other organomercurials are more readily absorbed in the gastrointestinal tract than Hg^{II} salts because of their greater ability to permeate biomembranes. These compounds concentrate in the blood and have a more immediate and permanent effect on the brain and central nervous system, no doubt acting by binding to the –SH groups in proteins. Naturally occuring anaerobic bacteria in the sediments of sea or lake floors are able to methylate inorganic mercury (Cobalt-Methyl groups in vitamin B_{12} are able to transfer the Me to Hg^{II}) which is then concentrated in plankton and so enters the fish food chain. The Minamata disaster[1] in Japan, when 52 people died in 1952, occurred because fish, which formed the staple diet of the small fishing community, contained abnormally high concentrations of mercury in the form of MeHgSMe. It was observed that birds were falling from the sky, cats "committed suicide", and people began to notice a strange disease that caused numbness in limbs and lips, slurring of speech, vision constriction, uncontrollable shouting, involuntary movements, and unconsciousness. Overall, more than 3000 people suffering from degeneration of the nervous system were diagnosed with what was later called the Minamata disease.[2] This was found to originate from a local chemical works where Hg^{II} salts were used (inefficiently) to catalyse the production of acetylene from acetaldehyde, and the effluent was then discharged into the shallow sea. Evidence of a similar bacterial production of organomercury is available from Sweden where methylation of Hg^{II} in the effluent from paper mills has been shown to occur.[1] The use of organomercurials as fungicidal seed dressings has also resulted in fatalities in many parts of the world when the seed was subsequently eaten[1]. Derivatives of tin (Sn) have been known for their biocidal properties for over a century and have been used as pesticides in anti-fouling paints and agriculture.[3] In spite of a large body of information on fate and effects of organotins in aquatic environment[4], the effects of these substances are poorly documented.[5] Based on that, it is obvious that these compounds have to be detected and identified rapidly. The major problem is that the most common extraction procedures (ASTM [American Society for Testing and Materials], EPA [Environmental Protection Agency]) take approximately 18 hours[6] (analysis and

sample preparation not included), and in our opinion, this is too consuming of time and resources and it needs to be improved.

1.1 Digestion versus Extraction (availability)

Geologists are interested in finding a great deal about the sample, often the exact total elemental composition. For that reason, they perform "digestion" on their samples. By using strong acid mixtures, they are able to attack the sample matrix to break all the bonds in the sample. Environmentalists though, want "available" or "bio available" species, leading them to use "extraction" techniques. Their interest lies on the identification of the environmentally available concentrations of potential contaminants in the sample, those which can be taken up directly by plants and animals and then enter the food chain. In other words, their interest is in elements likely to be liberated (to leach) or to spread in the environment due to the action of naturally induced physico-chemical effects including weathering. Two different approaches exist with respect of the environmental analysis of soils and sediments. The first approach consists in the determination of the sum of all elemental concentrations that could eventually leach out from a given sample. In other terms, the goal is to identify the composition of the fraction of the soil that is susceptible to weathering. Typical analytical methods[7,8] for the analysis with respect to this first approach consist of extracting the soil sample with 1:1 nitric acid or with a mixture of 1:1 nitric acid and 1:1 hydrochloric acid, and sometimes with the addition of hydrogen peroxide. This extraction mixture is potent enough to dissolve the totality of "leachable" elements without attacking the siliceous matrix of soils. The second approach consists of an evaluation (or prediction) of the concentration of elements that would be observable in contaminated waters that would flow from the soil, such as effluents from a waste disposal site. It does not represent the concentration of environmentally available elements in the soil, but attempts to predict what the concentrations of elements observed in waters (and by extension, other parts of the ecosystem) will be after they have been in contact with the soil sample. These methods[6,9,10] typically involve the mechanical

agitation of soil in a pH adjusted aqueous solution. Variations of the method may involve the addition of other reagents such as complexation agents. The extracts obtained after agitation are filtered to separate them from the soil or sediment sample, and the aqueous solutions are then digested, typically using nitric acid or a combination of nitric and hydrochloric acids.[11]

1.2 Elemental Analysis Techniques

1.2.1 Flame Atomic Absorption (FAA)

People started using flame atomic absorption spectrophotometry in the early 1960s for the determination of metals. This technique is based on the absorption of radiation by neutral, ground-state atoms produced by an atomizer. The most popular flames used are air-acetylene and nitrous oxide-acetylene flames. Since the nitrous oxide-acetylene flame is hotter than the air-acetylene one, it provides higher atomization efficiencies and better detection limits for refractory elements, and minimizes interference effects. The line source typically used is a hollow cathode lamp. The sample is generally introduced as a liquid, so for solid samples, dissolution procedures must first be applied. Flame atomic absorbtion is adequate for determination of most elements at concentrations of 0.001% (w/w) or above in solid samples after dissolution by acid digestion. The major disadvantage of this technique is that it is a single-element one, therefore it is not so practical.[12]

1.2.2 Electrothermal Vaporization (ETV)

When using electrothermal atomizer techniques, a discrete sample is placed in a furnace, and the furnace is electrically heated to create a transient cloud of atomic vapor. The absorption of this atomic vapor is investigated to establish the amount of analyte in the sample. This is performed in three distinct steps: the drying or desolvation step, in which the solvent contained in the sample is evaporated to leave a solid residue, the ash step, used to transform organic matter to ashes or

into water and carbon dioxide, and to vaporize volatile inorganic components, and finally, the atomization step, in which the sample is vaporized and atomized to produce the vapor mentioned earlier. All of these steps are accompanied by a progressive elevation of the temperature inside the furnace. One of the advantages of this technique is that the dilution factor of an analyte is about 1000 times less (or the atomic number density of the analyte produced from a given solution is about 1000 times greater) than the one obtained with the flame atomic absorption technique. However, this increased number density brings a disadvantage: the concentration of other gaseous components from the sample matrix is correspondingly larger. Thus, interference effects can be more severe in a furnace compared to a flame.[12]

1.2.3 Inductively Coupled Plasma Spectrometry

Inductively coupled plasma (ICP) spectrometry[12] has risen to prominence in the last thirty years due to the remarkable environment provided by the atmospheric pressure argon plasma used. The plasma is generated without electrodes so it is essentially completely clean. Unlike a flame or furnace, the argon environment provides none of the species that commonly cause spectral and matrix problems, primarily oxygen in flames and graphite in furnaces. ICP-AES (atomic emission spectroscopy, sometimes abbreviated OES for optical emission spectrometry) was the first ICP technique to be extensively developed commercially. Detection limits are often in the low ppb (10^{-9}g/mL) range and the high temperatures of the ICP keep matrix effects remarkably low. Over the last fifteen years, ICP-MS (Mass Spectrometry) has come of age, providing detection limits which are now in the low ppt (10^{-12}g/mL) range. The remarkable detection limits of both AES and certainly MS often allow important elements to be monitored at natural levels, a capability necessary for following changes in the environment. Due to the high temperatures of the plasma (5,000-7,000°K) which excite or ionize most elements in the periodic chart, both techniques are inherently multielement. Now semiconductor based detection systems for ICP-AES have the physical capability

of monitoring all metallic species simultaneously. The scanning systems for ICP-MS are so fast that are also capable of what is essentially simultaneous monitoring.

Additionally, it is important to consider the high throughput that these systems offer. In theory, samples can be put through as rapidly as every 30 seconds, with a rapid clearing sample introduction system or low levels of matrix constituents. In practice, 30 samples or standards per hour is more common. The throughput and multielement capability distinguish these systems from their other competitor in the elemental analysis arena: electrothermal (furnace) vaporization (ETV) atomic absorption (AA). A further difference between the ICP and ETV-AA techniques is the relative freedom from matrix effects. In particular, ICP-AES (which uses ground state atomic emission as compared to ions in MS) is extremely durable while the lower temperatures of the ETV often result in incomplete atomization while the graphite furnace components can lead the formation of carbide forming refractor species like CaC.

1.2.4 X-Ray Fluorescence

X-Ray Fluorescence is a technique capable of multielement analysis; however, the detection limits are generally only of the order of 10^{-1} ppm, and the level of quantitation is therefore much higher, making this technique unsuitable for the study of toxic metals in soils and sediments.

1.3 Leaching or Extraction Procedures

1.3.1 EPA method 1311: TCLP

The EPA method 1311: Toxicity Characteristic Leaching Procedure (TCLP)[6] is used to determine the mobility of both organic and inorganic analytes present in a soil or sediment sample. Essentially, it involves mixing the sample with an extraction solution at a specific pH based on the pH of the sample analyzed, and

then agitating continuously for 18 to 20 hours at room temperature. Once this step is completed, a filtration of the sample is performed and prior to analysis, depending of what kind of instrumentation is used to determine the concentration of analyte(s), the sample is further prepared by adding digestion and/or dilution steps. Then the sample can be analyzed, thus making this technique quite time consuming and labor intensive.

1.3.2 Microwave Extraction

The microwave extraction method is a powerful and rapid (approximately 10 minutes) multi-element acid extraction/dissolution technique which uses microwaves along with nitric acid (HNO_3) or a mixture of hydrochloric and nitric acids (HCl / HNO_3) to leach the elements from the sample. If one wants the total composition of the samples, the strength of the acid mixture should be increased and the technique becomes a microwave digestion. Both methods use closed vessels to heat the extraction solvent to 2 to 3 times its atmospheric boiling point. The elevated temperature of the solvent increases the solubility of the analyte of interest and lowers the viscosity of the solvent, allowing it to better penetrate the matrix. Despite the fact that it is a fast technique, it has also some disadvantages: the closed vessel can lead to high pressures which can be dangerous if not well controlled, some matrices are more problematic than others, and the extract needs to be cooled, filtered and possibly diluted prior to analysis.

1.3.3 Accelerated Solvent Extraction

In March 2002, Dionex Corporation (Sunnyvale, CA, USA) introduced their new Accelerated Solvent Extractor (ASE®). The accelerated solvent extraction is a technique for extracting solid and semisolid samples with liquid solvents. The ASE uses conventional liquid solvents at high pressures and temperatures to increase the efficiency of the extraction process. High pressures are used to keep the solvent below its boiling point so the extraction becomes safe, while increased temperatures hasten the extraction process, leading to very short extraction times

(12 to 20 minutes approximately). The flow-through extraction cell also uses these principles. The main difference between their instrument and the one designed for this project is the type of chemicals it can extract. Also, their instrument meets all the requirements for extraction of a different EPA method. It complies with U.S. EPA SW-846 Method 3545A for Pressurized Fluid Extraction while ours will eventually comply with U.S. EPA method 1311 mentioned above. While they are using the ASE to extract semi-volatiles, total petroleum hydrocarbons, organochlorine and organophosphorous pesticides, polychlorinated biphenyls, dioxins and furans, chlorinated herbicides, pharmaceutical/natural products, plastics/polymers, and food, our system was specifically built to extract metallic species. It would be impossible to use their system for our extraction needs since the extraction cell is made out of stainless steel, which would contaminate our samples.

1.3.4 Soxhlet Extraction

The Soxhlet is an apparatus for cleaning samples using the distillation extraction method. In the Soxhlet apparatus (also called extractor, or chamber), the sample soaks in hot solvent that is periodically siphoned off, distilled and returned to the sample. The process continues until the siphoned-off solvent becomes clear. The process can take up to 48 hours; 4 hours with the automated Soxhlet. This method is very efficient, with near 100% recovery, but the extraction times are comparable to those of the EPA method 1311, which should be shorter in order to attain the goals of this project.

1.3.5 Chelating Agent Extraction

The chelating agent extraction method seems to have gained a lot of popularity recently in the scientific community. Several groups have tried to extract metals with various types of chelating agents. A chelant is a ligand that contains two or more electron-donor groups so that more than one bond is formed between the metal ion and the ligand.[13] The chelant solution removes the heavy metals (Cd,

Cu, Pb, Zn, Fe, Cr, As, and Hg) simultaneously.[14] The use of chelating agents to wash soils has many advantages: metals are extracted with high efficiency; the metal complexes formed with the chelant have high thermodynamic stabilities, a good solubility and a low adsorptivity on soils.[15,16] On the other hand, when the chelating agent is used in excess to guarantee that enough molecules are present to bind with the targeted metals, some molecules might be precipitated, adsorbed by the soil, or might form complexes with other cations (Ca, Mg, Fe, Al and other trace heavy metals), thus reducing the agent's ability to extract the desired elements.[17] Another crucial parameter to keep in mind in soil washing processes is the kinetics of metal desorption/dissolution as it can affect the treatment duration and cost.[18,19,20]

Using a multiple-stage batch extraction, soils from Aberdeen Proving Ground's J-Field were successfully treated, passing both the Toxicity Characteristic Leaching Procedure (TCLP) and EPA Total Extractable Metal Limit, by Peters.[14] He used EDTA (ethylenediaminetetraacetic acid), citric acid, and nitrilotriacetic acid (NTA) to extract copper, lead, and zinc from these soils and found that they were all successful in removing these metals. He also found that, in general, some other chelating agents tested like gluconate, oxalate, Citranox, ammonium acetate, and phosphoric acid, were inefficient in complexing and removing the heavy metals from the soils. Here again we are facing multiple extractions, which means long times.

The extractability of heavy metals Cd, Pb and Zn in contaminated soils by Na_2-EDTA was evaluated by Mahvi *et. al.*[17] They tried to extract these metals with different concentrations of Na_2-EDTA (0.005, 0.01 and 0.1 M). A ratio of 2.5:1 (liquid/solid) was employed for all experiments. The procedure used for the extraction was very similar to the one employed in the EPA method 1311: TCLP, except that the extraction time was much shorter. They placed their solutions on a mechanical shaker at room temperature and shook them for 2 hours at 180 rpm. Other extraction times up to 48 hours were used, but the amount of metal

extracted after two hours was not significantly higher. After this 2-hours period, the samples were allowed to settle for approximately 15 minutes and then centrifuged and filtered. The filtrate was then acidified to a pH lower than 2.0 for heavy metal analysis. This experiment was performed on single-metal and multi-metal contaminated soils. The results showed that EDTA worked better in a single-metal contaminated soil. The general trend observed was that heavy metals were removed more effectively with 0.1 M solutions of Na_2-EDTA. However, this solution extracted preferentially Pb over Cd and Zn. On the other hand, if the concentration of Na_2-EDTA was decreased to 0.005 M, Cd and Zn were extracted with a higher efficiency than Pb.

Here again, even if the extraction time is relatively short, the preparation of the extracts for analysis still involves several steps such as settlement time, filtration and acidification. Moreover, the efficiency of using EDTA to extract heavy metals has been proven only for Pb, Cd and Zn. It might not be possible to use it for the extraction of other toxic metals.

Tandy *et. al*[18] used other chelating agents to try to overcome some of the disadvantages of EDTA, especially that EDTA has a low biodegradability in the environment. They studied the following biodegradable chelating agents and compared them to EDTA: [S,S]-ethylenediaminedisuccinic acid (EDDS), iminodisuccinic acid (IDSA), methylglycine diacetic acid (MGDA), and nitrilotriacetic acid (NTA). The metals extracted were Cu, Pb and Zn, and their experiments showed that the optimum extraction time was 24 hours, which is still time consuming. In soil washing, they found that at neutral pH, EDDS was more efficient to extract metals from soils than EDTA because the competitive binding with calcium was much less significant.

Teik-Thye *et. al.*[21] performed a single-step extraction procedure to compare the extraction efficiencies of the chelating agents EDTA, sodium nitrolotriacetic acid (NTA) and calcium trisodium diethylenetriaminepentaacetic acid (DTPA) versus

those of HNO_3, $CaCl_2$, and deionized water. The procedure was performed on an acidic soil in order to extract Pb, Cd and Cr. It was found that greater than 80% of Cd and 94% of Pb could be removed within 30 minutes with the chelating agents, while deionized water showed poor extraction efficiency (below 10%), and $CaCl_2$ showed an average extraction efficiency (~45%) for the same metals. The lead and cadmium could even be removed within 15 minutes of extraction time. Other researchers like Bermond and Ghestem[22], Steele and Pichtel[23], Abumaizar and Smith[15] have also reported that extraction times lower than 30 minutes were adequate to extract a considerable fraction of heavy metals from contaminated soils. As for chromium, the percentage removed from the soil with all of the extracting agents was below 10%. This low recovery was also observed by Neale *et. al.*[24], Abumaizar and Smith[15], and Wasay *et. al.*[25] The heavy metal speciation in the soil could be linked closely to the extraction efficiency.

Clifford *et. al.*[26] studied the feasibility of extracting toxic metals from soil using anhydrous ammonia. They wanted to extract common metal contaminants such as lead (Pb), mercury (Hg), cadmium (Cd), copper (Cu), and zinc (Zn). Their choice of pure anhydrous liquid ammonia for extraction of contaminants from soil samples was based on the fact that it forms strong, soluble ammonia complexes with many toxic metals, and that it is inexpensive to use. They tested this approach with three different devices: a pressurized Soxhlet extractor, a plug flow extractor, and a pressurized stirred batch reactor. They found that they all gave basically the same performance, which suggests that the metal removed was readily extractable. An extraction efficiency of 60 to 70% was achieved for Cd, Cu and Zn present in soils spiked and aged for four months to two years with 50 000 mg/kg of the metal nitrate. Lead and mercury removals were low (< 15%) with pure ammonia. In their opinion, the ammonia extraction of toxic metals does not show great potential for cleaning an entire contaminated site. However, to determine the practical effectiveness of ammonia extraction as a pretreatment for soil remediation, additional tests would need to be performed, and the criterion for

success should be a Toxicity Characteristic Leachate Procedure (TCLP) test on the extracted soil, which leads back to the long and labor-intensive method.

1.3.6 Supercritical Fluid Extraction (SFE)

Supercritical fluid extraction (SFE) is based on the principle that solubilities in a supercritical fluid increase dramatically with increasing density, and that different solutes have different solubilities at the same conditions. Supercritical fluids are produced by heating a gas above its critical temperature or compressing a liquid above its critical pressure. The critical temperature of a substance is the temperature above which a liquid phase cannot exist, regardless of pressure. The vapour pressure of a substance at its critical temperature is its critical pressure. At temperatures and pressures above but close to its critical temperature and pressure (the critical point), a substance is called a supercritical fluid.

Under these conditions, the molar volume is the same whether the original form was a liquid or a gas. Supercritical fluids have densities, viscosities and other properties that are intermediate between those of the substance in its gaseous and in its liquid state. Carbon dioxide is the most commonly used supercritical fluid because of its low critical temperature (31°C), inertness, low toxicity and reactivity and high purity at low cost. Carbon dioxide does not dissolve polar compounds so when extracting that type of compound, methanol, cyclic ethers, water or formic acid can be added to the carbon dioxide.

Supercritical fluids can be used to extract analytes from samples. The main advantages of using supercritical fluids for extractions is that they are inexpensive, contaminant free, and less costly to dispose of safely than organic solvents.

The main components of an SFE instrument are a pump, an extraction chamber, a recovery chamber and a collection device. In order to generate a carbon dioxide supercritical fluid, carbon dioxide is pressurized above its critical pressure in a

pump. The mixture to be separated is placed in the extraction chamber and put in contact with the supercritical fluid. One of the species (let's call it component A) in the mixture dissolves better in the critical fluid and leaves the residue enriched in the other components. The loaded solvent is then transferred to a recovery chamber, where component A is recovered by lowering the solvent's density. This density change can be achieved by raising the temperature at constant pressure but more often it is achieved by reducing the pressure at constant temperature. After depressurizing, two methods have been adopted for collection of the extracted analyses, these are on-line or off-line SFE.

In on-line SFE, the extracted analytes are directly coupled to a chromatographic separation system (SFC) such as gas chromatography (GC) or high performance liquid chromatography (HPLC) with appropriate detection. Directly coupled GC is limited to volatile compounds while SFE-SFC can be used for higher molecular weights. The off-line approach allows the extraction and concentration of analytes for subsequent HPLC analysis.

SFE is an important method for large-scale purification of complex liquid or solid matrices, such as polluted streams, but it can also be used for laboratory-scale extractions for analytical purposes. The major advantage of this method is that the supercritical fluid can easily be removed after extraction by lowering the temperature or pressure or both. The supercritical fluid becomes a gas, and the extracted species condense into a liquid or solid. The problem of removing the extracting liquid is eliminated.

Wang *et. al.*[27] used this technique to extract toxic heavy metals (Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, and Cr^{6+}) from solid and aqueous matrices, using supercritical CO_2 and dithiocarbamate chelating agents. The addition of a ligand to the supercritical CO_2 was necessary since the direct extraction of metal ions by CO_2 only is inefficient because of the charge neutralization requirement and the weak solute-solvent interaction. By adding a ligand, the chelated metal ions become

relatively soluble in supercritical CO_2.[28-32] To obtain a successful extraction of metal species in supercritical CO_2, the following factors are crucial: solubility of the chelating agent, solubility and stability of the metal chelate, density of the supercritical fluids, chemical form of the metal species, and sample matrix. In their experiment, the ligand lithium bis(trifluoroethyl)dithiocarbamate (LiFDDC) and supercritical CO_2 were used to extract the metal ions mentioned above from a sand matrix that was spiked with the same metal ions. The supercritical fluid extraction was undertaken at 200 atm and 60°C for a 10-minute static extraction followed by a dynamic flushing that lasted 15 minutes for all the ions except Cr^{3+} and Cr^{6+}, which were subjected to a 30-minute static extraction followed by a 45-minute dynamic flushing. For an extraction performed with CO_2 only, the recovery of the spiked metal ions was less than 2%. When LiFDDC was added to the procedure, the extraction efficiencies of all the ions except the chromium species were between 90 and 92%. To enhance the extraction efficiency for polar solutes, they also added to CO_2 (liquid phase) 5% methanol (v/v), to increase the polarity of the fluid phase. By doing so, the extraction efficiencies for the divalent metals raised to higher than 95%.

Cui *et. al*[33] used 8-hydroxyquinoline, methanol and Triton X-100 with supercritical CO_2 to extract metal ions, Cu^{2+} in particular. Also, to find the optimal conditions for the extraction, they varied the pressure, the temperature and the volume of CO_2 added, and kept a static extraction time of 20 minutes.. They found that the optimal conditions were a pressure in the range of 30 to 35 MPa, a temperature of 60°C and a volume of CO_2 of 35 mL. They also noticed, like Wang *et. al.*[27], that the addition of methanol to the supercritical CO_2 was greatly affecting the extraction efficiency. In their case, it increased from 11.38% to 83.60%. Furthermore, following the addition of methanol, they also added a surfactant, Triton X-100. The extraction efficiency of Cu^{2+} rose again to reach 96.62%.

1.3.7 The BCR Sequential Extraction Procedure

Soils consist of heterogeneous combinations of organic and inorganic substances and the binding mechanisms for metals vary with the composition of the soil. The ecological effects of heavy metals in soil are closely related to the distribution of species in the solid and liquid phases of the soil.[34] Depending on their origin, trace elements exist in different mineral forms and chemical compounds, and in different combinations with mineral and organic components of soil and sediments which may vary according to various conditions. For example, pH has an influence on the trace metal forms, and other parameters affecting their concentration levels, mobility, transformation, and accumulation processes in the ecosystem are redox conditions, oxidation states, temperature, the presence of organic matter, and microbiological activity. All these factors strongly influence the biogeochemical cycles of elements in the environment.[35] In acidic soils, mostly simple cations and complexes of chlorides and sulphates can be found, while in neutral and slightly alkaline conditions carbonate complexes dominate.[36]

Chemical speciation can be defined as the process of determining and identifying specific chemical species or binding forms; it allows one to determine the availability and mobility of the metals in order to understand their chemical behaviour and fate. Most speciation schemes rely on the use of one or more separation steps, followed by element-specific detection.[34] Chemical speciation is of interest in environmental analytical chemistry because the way the trace elements act in natural systems depends on the forms, as well as the amounts, present in that system.[37] Since the behaviour of the elements in a soil-water-plant system depends on their forms, the determination of trace metals in soils is often performed by single or sequential extraction. The procedures involve subjecting a solid sample (soil or sediment) to successive attacks with reagents possessing different chemical properties (acidity, redox potential, or complexing properties) in which each extract includes a part of the trace metals associated with the sample.[36] The BCR (Community Bureau of Reference, which is now called

Standards, Measurements and Testing program (SM & T) of the European Union) sequential extraction procedure has been widely applied to soil and sediment samples (terrestrial or marine originated), and standard reference materials by a number of investigators.[37-44] This procedure provides measurements of extractable metals from media such as acetic acid (step one, for exchangeable metals), hydroxylammonium chloride (step two, for reducible metals) and hydrogen peroxide plus ammonium acetate (step three, for oxidizable metals).

Takalioglu *et. al.*[35] performed a sequential extraction procedure on different highway soils collected in Turkey. They were monitoring nine heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn). For the first step, to extract the exchangeable metals, the samples were shaken in an end-over-end fashion at 400 rpm, at room temperature, for 16 hours. The extracts were collected after 20 minutes of centrifugation. For the second step, to extract metals bound to iron and manganese oxides, the extraction procedure was the same as that described for the first step, except the samples were centrifuged for 15 minutes instead of 20. For the last step, to extract metals bound to organic matter and sulphides, the samples were digested for one hour at room temperature with hydrogen peroxide and then for another hour at 85°C. Another aliquot of hydrogen peroxide was added and the digestion repeated. The solution was then heated to near dryness and a solution of ammonium acetate added. The sample was centrifuged and the supernatant separated. Each extract obtained was evaporated close to dryness and completed to 5 mL with nitric acid. This procedure is known to provide excellent results regarding the concentration of heavy metals in each fraction of a sample, but as can be seen, it implies a very long time (two steps of approximately 16 hours each, one of approximately 4 hours, plus the analysis of the collected fractions) before the results are known.

1.3.8 EPA method 3545A: Pressurized Fluid Extraction (PFE)

EPA's pressurized fluid extraction method[45] is similar to Soxhlet extraction, except that the solvents are used near their supercritical region where they have high extraction properties. It is a procedure for extracting water insoluble or slightly water soluble organic compounds from soils, clays, sediments, sludges, and waste solids. The method uses elevated temperatures (100 - 180°C) and pressures (1500 – 2000 psi) to achieve analyte recoveries equivalent to those from Soxhlet extraction, using less solvent and taking significantly less time than the Soxhlet procedure. Typically, it uses a commercially available, automated extraction system like the Dionex system mentioned above. There is one disadvantage though: the cells are made of stainless steel, which could contaminate the samples if metals are to be determined.

1.3.9 Electrodialytic Remediation Technique (EDR)

Electrodialytic remediation is particularly useful for fine grained harbor sediments where conventional soil remediation technologies, like extraction techniques, are impractical or even impossible to use.[46,47] Initially, it was described for remediation of heavy metal polluted soil.[48] The basic concept of this technique relies on the application of a low voltage direct current that acts as the cleaning agent.[49] In the applied electric field, ions in the liquid phase of the sediment electromigrate toward the electrodes with the opposite charge. In their article "*Electrodialytic Removal of Cu, Zn, Pb, and Cd from Harbor Sediment: Influence of Changing Experimental Conditions*", Nystroem *et. al.*[49], investigated the decontamination potential of the electrodialytic method for the removal of heavy metals (Cu, Zn, Pb, and Cd) from contaminated sediments. They found that to decontaminate the slightly contaminated sediment sample they had, the most efficient experimental conditions for the EDR were a liquid to solid ratio of 8 (once the sediment is air-dried, HCl is added as a desorbing agent to reach this ratio) and a current of 70 mA applied during 14 days. The percentages of metals removed were 65, 90, >90, and ~100% for Cu, Zn, Pb, and Cd, respectively. With

these parameters, the decontaminated sediments passed the OSPAR ecotoxicological assessment criteria (EAC) for marine sediments.[50] Despite the fact that this technique gave good results, 14 days is a really long period to decontaminate such a small portion of a contaminated site.

1.4 Sample Preparation Problems

The most important stage in multielement analysis using ICP-AES and ICP-MS is sample preparation. Sample solution integrity and reliability of preparation protocols dictate whether results are valid. Errors in sample preparation are the main source of uncertainty in the entire analytical process. Almost all of the leaching or extraction procedures described above are used to prepare samples prior to analysis by ICP-AES or MS. Some of the disadvantages that can be seen when using one of these methods are a loss of volatiles, a poor recovery, the cost of reagents when large quantities need to be used, a possibility of contamination and a long preparation time. In order to overcome these issues, an ideal sample preparation method would have to use inert material to eliminate the contamination of the sample, the manipulation of the sample and the use of reagent would be reduced to a minimum, the device containing the sample would be closed and directly connected to the ICP-AES or MS to avoid loss of volatiles, and it would be more time-efficient than the methods described previously. These are thus part of the specific objectives of this study.

1.5 Objectives

The overall objective of this study is to develop new methods and instrumentation for rapid extraction of toxic metals from soil and sediment samples.

The specific objectives are :

1. To study the feasibility of automated extraction.

2. While developing the above processes for Hg and Sn, to monitor the processes for all toxic metals to provide a preliminary indicator as to the potential universality of these approaches.

3. Our long-term goal is to provide Canadian scientists the ability to rapidly and inexpensively monitor metallic species in the environment, thus enabling more analyses.

1.6 References

1. N. N. Greenwood, A. Earnshaw, *Chemistry of the elements*, second edition, School of Chemistry, University of Leeds, U.K., 1202-1226, (1998).

2. P.Stratta, A. Messuerotti and C. Canavese, *Environmental Health Perspectives* **109 (8)**, A361, (2001).

3. S. de Mora (ed)., *Tributyltin: case study of an environmental contaminant*, Cambridge University Press, UK, 301 pp, (1996).

4. S. de Mora and É. Pelletier, *Environ. Technol.* **18**, 1169-1177, (1997).

5. R.H.H. Pieters, M. Bol and A.H. Penninks, *Toxicology* **91**, 189-202, (1994).

6. EPA method 1311, *Toxicity Characteristic Leaching Procedure*, revision 0, July 1992.

7. EPA method 3050B, *Acid Digestion of Sediments, Sludges, and Soils*, revision 2, December 1996.

8. EPA method 3051A, *Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils*, revision 1, January 1998.

9. EPA method 1310A, *Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test*, revision 1, July 1992.

10. EPA method 1312, *Synthetic Precipitation Leaching Procedure*, revision 0, September 1994.

11. EPA method 3015A, *Microwave Assisted Acid Digestion of Aqueous Samples and Extracts*, revision 1, January 1998.

12. J.D. Ingle, Jr., S.R. Crouch, *Spectrochemical Analysis*, Prentice-Hall, Inc., New Jersey, USA, pp. 590, (1988).

13. S.R. Cline, B.R. Reed, *J. Environ. Eng.* **121 (10)**, 700-705, (1995).

14. R.W. Peters, *Journal of Hazardous Materials* **66**, 151-210, (1999).

15. R.J. Abumaizar and E.H. Smith, *J. Haz. Mater.* **B70**, 71-86, (1999).

16. L.M. Lo and X.Y. Yang, *Water, Air, and Soil Poll.* **109**, 219-236, (1997).

17. A.H. Mahvi, A.R. Mesdaghinia and D. Naghipoor, *Pakistan Journal of Biological Sciences* **8 (8)**, 1081-1085, (2005)

18. S. Tandy, K. Bossart, R. Mueller, J. Ritschel, L. Hauser, R. Schulin and B. Nowack, *Environ. Sci. Technol.* **38**, 937-944, (2004).

19. T. Lim, J. Tay and J. Wang, *J. Environ. Eng.*, 59-63, (2004).

20. B.E. Reed, P.C. Carrier and R. Moore, *J. Environ. Eng.*, 48-50, (1996).

21. L. Teik-Thye, T. Joo-Hwa and W. Jing-Yuan, *Journal of Environmental Engineering* **Vol. 130, No. 1**, 59-66, (2004).

22. A. Bermond and J.P. Ghestem, *Heavy metals release in soils*, H.M. Selim and D.L. Sparks, eds., Lewis Publishers, Boca Raton, Fla., 131-147, (2001)

23. M.C. Steel and J. Pichtel, *J. Environ. Eng.*, **124(7)**, 639-645, (1998).

24. C.N. Neale, R.M. Bricka and A.C. Chao, *Environ. Prog.* **16(4)**, 274-280, (1997).

25. S.A. Wasay, S. Barrington and S. Tokunaga, *Water, Air, and Soil Poll.* **127(1/4)**, 301-314, (2001).

26. D.A. Clifford, M. Yang, and T. Nedwed, *Waste Management*, Vol. 13, 207-219, (1993).

27. S. Wang, U. Lin and C.M. Wai, *Separation Science and Technology* **38(10)**, 2279-2289, (2003).

28. K.E. Laintz, C.M. Wai, C.R. Yonker, R.D. Smith, *J. Supercrit. Fluids* **4**, 194-198, (1991).

29. K.E. Laintz, C.M. Wai, C.R. Yonker, R.D. Smith, *Anal. Chem.* **22**, 2875-2878, (1992).

30. Y. Lin, R.D. Brauer, K.E. Laintz, C.M. Wai, *Anal. Chem.* **65**, 2549-2551, (1993).

31. C.M. Wai, Y. Lin, R.D. Brauer, S. Wang, W.F. Beckert, *Talanta* **40**, 1325-1330, (1993).

32. Y. Lin, N.G. Smart, C.M. Wai, *Trends Anal. Chem.* **14(3)**, 123-133, (1995).

33. Z.J. Cui, J.C. Liu, L.C. Gao, Y.Q. Wei and J.Z. Zhang, *Chinese Chemical Letters* **10(6)**, 525-528, (1999).

34. W. Lund, *Fresenius J. Anal. Chem.* **337**, 557-564, (1990).

35. S. Tokalioglu, S. Kartal and G. Birol, *Turk J. Chem.* **27**, 333-346, (2003).

36. A. Kot and J. Namiesnik, *Trends Anal. Chem.* **19**, 69-79, (2000).

37. C.M. Davidson, P.C.S. Ferreira and A.M. Ure, *Fresenius J. Anal. Chem.* **363**, 446-451, (1999).

38. M.D. Petit and M.I Rucandio, *Anal. Chim. Acta* **401**, 283-291 (1999).

39. Z. Mester, C. Cremisini, E. Ghiara and R. Morabito, *Anal. Chim. Acta* **359**, 133-142, (1998).

40. Y.M. Luo and P. Christie, *Int. J. Environ. Anal. Chem.* **72**, 59-75, (1998).

41. C.M. Davidson, A.L. Duncan, D. Littlejohn, A.M. Ure and L.M. Garden, *Anal. Chim. Acta* **363**, 45-55, (1998).

42. M.D. Ho and G.J. Evans, *Anal. Commun.* **34**, 363-364, (1997).

43. R.P. Thomas, A.M. Ure, C.M. Davidson, D. Littlejohn, G. Rauret, R. Rubio and J.F. Lopez-Sanchez, *Anal. Chim. Acta* **286**, 423-429, (1994).

44. G. Rauret, J.F. Lopez-Sanchez, A. Sahuquillo, E. Barahona, M. Lachica, A.M. Ure, C.M. Davidson, A. Gomez, D. Lück, J.Bacon, M. Yli-Halla, H. Muntau and Ph. Quevanviller, *J. Environ. Monit.* **2**, 228-233, (2000).

45. EPA method 3545A, *Pressurized Fluid Extraction (PFE)*, revision 1, January 1998.

46. W.H. Rulkens, R. Tichy and J.T.C. Grotenhuis, *Water Sci. Technol.* **37**, 27-35, (1998).

47. C.N. Mulligan, R.N. Yong and B.F. Gibbs, *J. Hazard. Mater.* **85**, 145-163, (2001).

48. L.M. Ottosen, I.V. Kristensen, A.J. Pedersen, H.K. Hansen, A. Villumsen and A.B. Ribeiro, *Sep. Sci. Technol.* **38**, 1269-1289, (2003).

49. G.M. Nystroem, L.M. Ottosen and A. Villumsen, *Environ. Sci. Technol.* **39**, 2906-2911, (2005).

50. OSPAR, Agreement 1997-14: *Agreed ecotoxicological assessment criteria for trace metals, PCBs, PAHs, TBT and some organochlorine pesticides.*, Annex 6, ref 3.14, (1997).

Chapter 2 : Preliminary Studies

2.1 Abstract

The first work on a capsule concept was done in Dr. Salin's lab by Guy Légère. He developed a large tube microwave digestion system with capsule sample introduction. The capsule was made from an ultra-clean polyacrylamide gel in order to analyze soils, botanicals, and biological samples. An analysis of the digested samples proved that the dissolution of analytes achieved with this method was as efficient as a conventional digestion in a microwave bomb at the same digestion temperature. Then, based on these studies, Jean Bouffard worked on the development of a new digestion technique for the rapid speciation and determination of toxic metals in soils and sediments. The goals of Jean Bouffard's research project were to provide proof that microwave capsule extraction followed by aqueous digestion would be a more advantageous technique than traditional modes of soil extract analyses. His experimental results in terms of extraction and reproducibility of the method he proposed did not yield results as good as traditional methods, but did provide the basis for this project. As the work is unpublished, it is presented here so that a logical sequence to the work is available.

2.2 Guy Légère's Capsule-Based Microwave Digestion

Légère developed a large tube microwave digestion system with capsule sample introduction[1]. This pressurized microwave digestion system used capsule sample introduction, reagent addition, and controlled venting during the digestion. The digestion tube featured built-in cooling, an infrared temperature sensor, an in-line pressure sensor, automatic venting, and a new type of valve, called the "Flange Valve". This valve was designed for introducing capsules into the digestion tube and to ease the cleaning of the tube parts that were in contact with the sample.

The digestion tube was composed of Teflon PFA®, which had the capability of operating at high pressure (200 psi) and high temperature (200°C). He used water, salt solutions, and concentrated nitric acid to characterize the system.

Légère developed a process to make the capsules from ultra-clean polyacrylamide gel so that he could use these to analyze soils, botanicals, and biological samples. The concept involved the collection of the sample on-site with the capsule. This step would be the last manual handling step. The capsule would then be inserted into and pushed through the digestion tube with a device equipped with a soft gas-tight Teflon® end attached to a flexible rod. The capsule would then dissolve during the microwave digestion process without contaminating the sample. This device was also used at the end of the procedure to remove digestate from the digestion tube.

An analysis of the digested samples proved that the dissolution of analytes achieved with this method was as efficient as a conventional digestion in a microwave bomb at the same digestion temperature.

2.3 Jean Bouffard's New Digestion Technique

When soils and sediments are contaminated by inorganic species such as heavy metals, these can be present in diverse chemical forms with different physico-chemical properties, concentrations and toxicity. Most elemental analysis methods can detect the global concentrations of all forms of compounds, only organic compounds, or only inorganic compounds. Moreover, it is difficult to separate the different compounds to identify and quantify each of them. This process, called speciation, can be very time-consuming and expensive. Based on Guy Légère's capsule idea, Bouffard's[2] concept of a porous capsule-based digestion was a step towards speciating pollutants in soils and sediments with a process that is quite simple and less expensive to use.

The basis of this concept is the encapsulation of a sample in a porous capsule. In theory, a soil sample is inserted and sealed in the capsule. Then, they are both submerged in an extractive solution or solvent, which will progressively and selectively extract (leach out) analytes from the soil or sediment sample to the bulk of the solution. The effectiveness of the extraction can be varied by adjusting different variables. These include:

1. The composition of the extractive solution or solvent (pH, water or organic solvent, polarity). These solutions can also contain complexation agents or other reagents that will accelerate or slow down the extraction (oxidizers, reducers and complexing ions, ionic strength of the solution, etc.).
2. The application of energy (mechanical or thermal agitation of the capsule and its content, temperature control, various types of irradiation like microwave and ultrasound, etc.) to the system in order to speed up the extraction kinetics.

A well chosen set of variables should permit a selective extraction of the desired compounds from the sample.

One of Bouffard's capsule designs, see Figure 2-1, consisted of a fluoropolymer hollow cylinder body, with fritted glass disks placed at each end. He built and tested a prototype, but following his experiments, he found out that it was too large, hard to manipulate, and difficult to seal. This last defect was attributed to the Teflon®'s mechanical properties such as contraction, dilatation, and/or softening, that were modified by the high temperatures used. As a result, the fritted disks, which were tightly fit onto the cylinder body, were falling out during the digestion, thus breaking the seal of the capsule. While this design was found to be inadequate for Jean's project, it was modified, and some of its novel ideas were introduced in my design, which was well suited for a flow-through system.

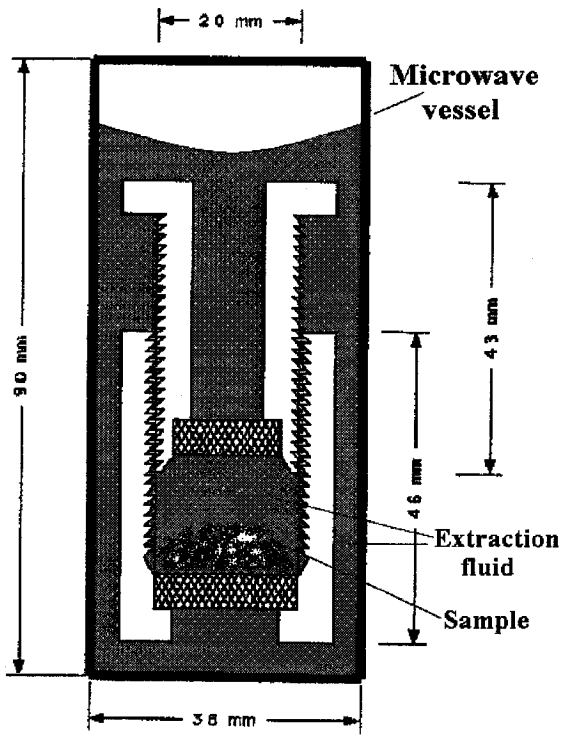


Figure 2-1: Jean's static system capsule

Another design, that was used in most of his experiments, was based on porous glass cylinders. The capsule consisted of a fritted glass hollow cylinder body, of about 10 mm ID, 16 mm OD and a length of 30 mm. Several methods were used to seal both ends of these cylinders, but only one was kept: sealing the extremities directly with fluoropolymer tape. The main advantages of these cylinders were their ease of use, their internal volume that exceeded the requirements, and their low cost. However, this cylinder design did not achieved the goals set. They held large dead volumes that could contribute to errors and they were relatively crumbly and easy to break. Sealing the capsule only with Teflon tape was sometimes difficult. The development of a permanent cap system that would not necessitate the use of Teflon tape to provide a good seal would be more efficient. Unfortunately, since the fritted material was crumbly and didn't have a long lifetime, it was contributing to the failure of the seal of the capsule. Finally, he thought that the considerable thickness of the cylinder walls, in combination with its composition, could have been responsible for the energetic and/or kinetic barrier to the equilibration of the concentrations from both sides (inside / outside) of the capsule.

The main procedure used during the experiments was as follows: the soil sample was introduced into the capsule and the capsule was then sealed and placed in a microwave digestion vessel. For the extraction phase, an aqueous acetate buffer (pH ~ 4.93) and an internal standard solution were added to the vessel which was then sealed and placed in a microwave oven. The temperature was increased from room temperature to 170°C in 5 minutes, followed by a 25 minutes plateau at 170°C. For the digestion phase, the capsules were then taken out of the solution and a mixture of nitric and hydrochloric acids was added to the solution. Microwave energy was applied again and the temperature was increased from room temperature to 140°C in 1 minute, then from 140°C to 175°C in 9 minutes and maintained there for 10 minutes. The digested solution was finally analyzed by ICP-AES (inductively coupled plasma – atomic emission spectroscopy).

In order to characterize the properties of his system, variations to the above mentioned main procedure were used and the following parameters were studied: temperature during the extraction phase, extraction time during the extraction phase, heating rate (applied power) during the heating of the extraction phase, pH of the extraction solution, nature of the work-up of the extract (direct analysis, acidification, acidification and aqueous digestion), porosity of the capsule walls, forced flow / flushing out of the solution (using air, deionized water) through the capsule after extraction, and finally, the residence time of the capsule in contact with the extraction solution after microwave irradiation.

2.3.1 Extraction Temperature Experiments

The maximum temperature reached during the extraction phase was varied to obtain 100, 125, 150, and 170°C. Once the extraction was done and the capsule removed from the oven, the aqueous sample was normally digested and analyzed by ICP-AES. Unclear trends were noted, like a rough augmentation in concentrations, when the extraction temperature was raised from 100 to 170°C. An augmentation was seen in most of the cases, but with the noise in the data mostly attributed to the lack of reproducibility in the experiments, no clear function shape could be attributed with certainty to this temperature versus extraction efficiency model. Temperature variable influence showed partial linearity, with positive, near zero or slightly negative slopes, depending on the element / line observed. Arsenic was an interesting case though, because at high temperatures, its concentration was decreasing. This behavior was probably caused by volatile losses. It was thus a possibility that the extraction efficiency increased when the temperature was raised, but when it reached a certain temperature range, a plateau was attained.

2.3.2 Extraction Time Experiments

As with the extraction temperature experiments, a sequence of single-sample data points were collected in which all of the parameters of the main procedure were kept the same, except for the extraction time. Samples were collected after 1, 2, 3, 5, 10, 15, 20, 25, and 30 minutes of extraction. Results obtained after 2 and 3 minutes extraction periods tended to be inconsistent, most likely due to errors in the manipulations. It was also established that data points taken at 1, 5, 10, 15, 20, and 30 minutes were giving consistent data, so the other data points were not used. A sigmoidal curve was observed for the extraction efficiency versus time function, for almost all the analytes. Occasionally, the concentrations seemed to stabilize at longer extraction times, which was exactly what would have been expected when an equilibrium was reached and concentrations remained constant. For some other analytes (Mg, Fe, Ca and Ba), it did not appear that equilibrium had been reached even after 30 minutes of microwave irradiation. The increase in concentrations usually happened after 10 to 20 minutes, and lasted approximately 5 minutes before an area of stability was reached. Two possibilities could have explained this behavior: the energy applied to provide extraction or the kinetics of diffusion. However, it was unknown whether one was better than the other. Arsenic showed a descending sigmoidal curve. Again, the loss of volatile species was suggested, as for the temperature studies. The non-equilibrium state that was still observed at extraction times longer than 30 minutes for many analytes corroborated the findings that the concentrations of the solutions inside and outside of the capsule were not at equilibrium.

2.3.3 Low Temperature Extraction for Volatiles Experiments

The observations made in the previous experiments about the depletion of the arsenic concentrations suggested the possibility that volatiles were lost during the extraction process. This loss happened most likely in the microwave digestion vessel headspace, but also possibly through permeation / diffusion through the Teflon walls of the capsule. Experiments were done on a series of six samples to

determine if a lower temperature program (50°C) combined with a longer extraction period (180 minutes) would reduce these losses and improve the extraction efficiencies of the volatile elements. Results showed that the extraction recoveries obtained were not better than those obtained with the main procedure's conditions, even for the volatile species like arsenic, tin and mercury. Since neither the regular nor the low temperature extractions seemed appropriate to give reasonable extraction yields without risking the loss of volatile species, the use of a system with no headspace might be mandatory.

2.3.4 Extraction pH Experiments

Some changes were applied to the main procedure to increase and decrease the pH of the extraction solution (pH higher and lower than the sodium acetate buffer, pH ~ 4.93), so extractions were performed with acidic and neutral solutions. To prepare an acidic extraction solution at a pH of 2.89, 250 µL of glacial acetic acid were added to 45 mL of water. As for the neutral extraction solution, pure water was used. It was observed that an augmentation of the acidity of the extraction solution led to a more efficient extraction.

2.3.5 Work-up Conditions Experiments

The main procedure was modified twice in order to determine if the aqueous digestion phase, which usually followed the main extraction step, was essential or not. Besides the main digestion process, the first experiment consisted of removing totally the digestion phase, and in the second one, the digestion phase was kept, except that after the addition of the acid mixture, no further microwave energy was applied. In the light of the results obtained, it seemed that the extraction only and the extraction followed by the digestion combined with microwave power gave high analyte concentrations. The extraction followed by digestion with no microwave energy gave lower concentrations of analytes. There was a possibility that the high concentrations observed were due to a depression of the internal standard in the samples. Since a higher than average

signal of the internal standard was observed for the extraction-acidification, it was normal that lower concentrations were obtained, and it would confirm the hypothesis. Conversely, for the experiment conducted with an extraction only, the internal standard's signal was quite low, thus leading to concentrations that were higher than anticipated. Therefore, Bouffard concluded that the work-up procedure on the extracted analytes did not have a well known effect, but regardless of this, he believed that the digestion phase combined with microwave energy was indispensable to the analysis to obtain adequate concentrations of the internal standard.

2.3.6 Fritted Glass Porosity Experiments

Bouffard acquired fritted glass capsules with different porosities and with pore sizes varying from 5 to 175 microns. The pore size and the thickness of the fritted material were judiciously chosen and combined to avoid the leak of solid particles through the frits. Obviously, the time taken by a solution to flow through a frit is directly linked to the pore size. In the case of the gas dispersion tube, the necessary time, following a partial immersion in water at room temperature, to achieve an equilibrium between the outer and the inner water levels varied from 3 seconds for the largest pores to more than 20 minutes with the smallest pore sizes. Based on these facts, it can be assumed that the ionic diffusion and the bulk solution convection movement were affected (slowed down) by the fritted glass surface. All of the capsule designs were conceived around this rule. Extracts obtained from extraction experiments performed on gas dispersion tubes with different porosities were compared. All other parameters remained unchanged. In the light of these experiments, it was concluded that for the majority of the elements, their extraction was directly dependent of the pore size of the fritted material, and that with larger pore sizes, a plateau was attained.

2.3.7 Diffusion Effects Experiments

The basic rules behind the soil encapsulation principle involve a free or satisfactorily free diffusion of ions in order to reach two thermodynamic equilibria: one between the leachable elements present in the soil sample and the solution in the capsule, and one between the dissolved elements in the capsule and the bulk solution in the microwave digestion vessel. In the case of common leachable elements extraction or microwave digestions, only the first equilibrium needs to be taken into consideration. The irradiation provided by the microwaves helps in obtaining this status. On the other hand, if either one or even both of the equilibria cannot be achieved, the idea of the encapsulation may still be applicable. The system would have to be controlled in order to get reproducible levels of achievement each time the experiment is performed. In addition, correction factors would have to be applied so the developed method could be comparable to the standard method to which we refer. Experiments performed at the beginning of Bouffard's project showed that in most cases, the first equilibrium was obtained or partially obtained with a reproducible level of completion, while the second one was almost never achieved.

The porous fritted glass material from which the cylinders, tubes and fritted disks walls were made, worked as a barrier against both flows of liquid through diffusion and convection, and possibly against ionic diffusion in solutions. Glass material with a great surface area could have played the role of an ion-exchanger and of a substrate for the deposit of polar substances. Furthermore, adsorption and mechanical enclosure also stopped the compounds on these surfaces. There was a strong possibility that organic substances, such as fumic and humic acids, often present in soils and acting as complexing agents, could have adsorbed on the glass surfaces and constituted a trap for ions in the walls of the capsules. Another observed fact, the formation of nucleation centers caused by bubbles on the fritted material surfaces, could possibly have isolated the inner and outer solutions.

The hypotheses concerning the non-establishment of a diffusive equilibrium were confirmed with multiple experiments designed to study the characteristics of diffusion through the walls of the porous capsule. Based on the physico-chemical properties of pure compounds, model extractions were carried out to find out the location of these compounds at the end of the procedure. To authenticate the results obtained with the pure compounds, experiments were executed on real soil samples. Finally, controlled kinetics experiments were performed with soil samples, and it appeared that while the diffusion profile looked as if it was following the trends observed in previous experiments, the time required to reach an equilibrium was of the order of hundreds of hours, which was much longer than the one assumed.

The concentrations of leachable elements obtained by using encapsulation and with no encapsulation were compared to assess the relative diffusion rates through the capsule walls. For all of the experiments, Bouffard realized that the concentrations obtained by a direct extraction were greater than those from the encapsulated samples. He also noted that the proportion of the extracted elements were dependent of the solubility of the original sample. In addition to the experiments performed on pure compounds, experiments were carried out on the usual soil samples to find out the spatial distribution of the analytes around the capsule placed in the microwave digestion vessel after the extraction procedure. This meant the proportion of analytes that were present in the bulk solution outside the capsule, in the solution inside the capsule, and immobilized (absorbed or adsorbed) in/on the capsule walls. He found that the concentrations of analytes inside the capsule were much greater than outside the capsule, and that, unexpectedly, the capsule walls were enclosing an exceptionally high concentration of analytes, at all times higher than the ones outside the capsule and occasionaly greater than the concentrations of the inner solution. This confirmed that the concentrations were not distributed equally compared to what should have been observed in the case of equilibrium, meaning that the capsule walls played a major role in the acquisition of these results. The walls could have been acting in

two ways to concentrate the analytes. In the first scenario, the evaporation of the water trapped in the walls would increase the concentration of non-volatile species, while in the second scenario, an assortment of phenomena like ion-exchange, ion adsorption and/or binding could have taken place on the surfaces of the capsule walls.

A diffusion kinetics experiment was conducted and resistance to diffusion was finally detected, confirmed and characterized. In order to get these results, the capsules were taken out of the extraction solution before proceeding to the digestion step, but the time the sample and the capsule were in contact with the extraction solution was varied with timepoints of 0, 24, 48 and 72 hours. Jean observed that even after a 72 hour-extraction, the diffusion was far from reaching the equilibrium, thus establishing without a doubt a resistance to diffusion in the capsule.

Based on this, an experiment was created to eradicate, if possible, the resistance which prevents the diffusion, through the capsule walls, and equilibration, between the inside and outside of the capsule, of analyte concentrations. Microwave extractions were performed using the main procedure except that right after the extraction, air was blown into the capsule with the help of a rubber pipette bulb to expel the solution present in the capsule in the external solution. Another set of samples was processed similarly, but before blowing air inside, the capsules were loaded with deionized water. The water was thus forced out, rinsing efficiently the capsule's content. The solutions obtained were then normally digested. The experimental results achieved showed enhanced extraction yields, which were nearer to the ones obtained with reference samples, and an improvement in the reproducibility of the method. There was evidence of greater levels of extracted analytes in the samples rinsed with water, but regarding the reproducibility, it was not superior to the samples in which only air was blown.

2.3.8 Conclusions

The idea behind Bouffard's research project was to demonstrate that a microwave capsule extraction followed by an aqueous digestion step would be a favorable method compared to long-established soil extraction analyses. His experimental results showed that even if the extraction and the reproducibility of the suggested technique were not quite as good as what was obtained with the conventional methods, it could still be used and improved with more work. A variety of enhancements were executed from the primary designs and the main procedure, and the characteristics of the suggested technique are now closer to the ones of the conventional methods. The two major reasons for the inappropriateness of the microwave capsule extractions were recognized as a probable ion-exchange / binding / adsorption of the capsule walls material (fritted glass), and as a lack of convection or forced circulation of solutions inside the capsule during the extraction stage.

This is where the design of the flow-through cell comes into action. The flow-through approach is a good starting point because, based on Jean's static system results, it would minimize equilibria concerns.

2.4 References

1. G. Légère, E.D. Salin, *Applied Spectroscopy* **49(4)**, 14A-22A, (1995).
2. J. Bouffard, *Development of a New Digestion Technique for the Rapid Speciation and Determination of Toxic Metals in Soils and Sediment*, Summer reseach project report, 37 pages, (2001).

Chapter 3 : Construction, Operation and Characterization of the Flow-Through Cell System

3.1 Abstract

In this section, the construction, operation and characterization of two designs of flow-through cells (Teflon and poly ether ether ketone (PEEK) models) were investigated, as well as a system configuration to perform a soil extraction. The apparatus can be used in several ways by circulating or re-circulating the extraction fluid in different ways. For the Teflon cell prototype, the main problem encountered was leaks at the fittings connections and around the upper frit part of the cell. With this prototype, it was also sometimes hard to bring out the bottom frit without having to break it. For the second (PEEK) cell prototype, there were two main problems. The cell was leaking through the bottom holes roughly 50% of the time and it was difficult to take all the pieces apart after they had been heated and then cooled. It was concluded that even if the PEEK model had some problems, it solved all the problems that were encountered with the Teflon model, it was sometimes possible to operate it without leaking and under pressure, and that it could reach higher temperatures somewhat faster than the Teflon cell.

3.2 Introduction

The system designed must be chemically inert. This is important to avoid contamination of the samples. Second, it should retain the solid portion of a sample inside a capsule. It should allow liquid and dissolved material to leave or enter the cell easily, and it should accommodate 0.25 to 1.0 g of sample. Its mechanical properties should sustain pressures of the order of 200 psi[1] and be physically rigid. For the thermal properties, it would sustain temperatures around 200°C and provide a much faster way of extracting the sample without digesting it. It would minimize manipulations as much as possible, and permit the re-circulation of the fluid in and out the cell to avoid diluting too much the sample. Finally, the global analysis process would be much faster than the actual EPA method. In this study, several types of materials, valves and fittings were investigated. Also, different configurations of the cell itself and the circulation path of the fluid were investigated, in order to reach the above mentioned specifications.

3.3 General Concept

The first system configuration envisioned is presented in Figure 3-1:

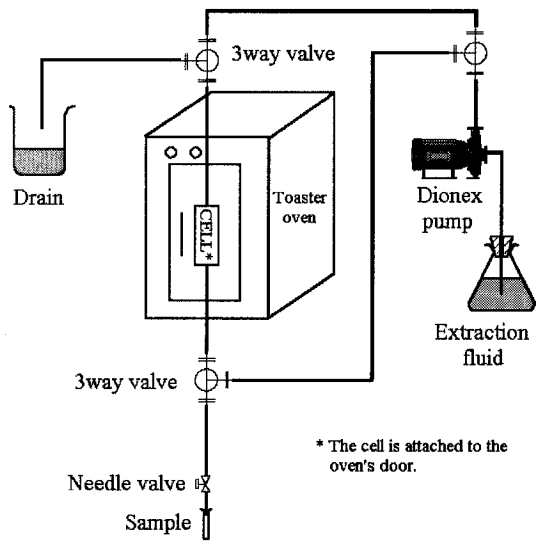


Figure 3-1: Flow-through system.

This configuration could be used in many different ways. For example, in Figure 3-2, the three-way valves can be changed for tees and on/off valves. The flow of solution could go in different directions depending on the desired effect or result. Tubing, valves and tees can be heated, cooled or left at room temperature depending on the need.

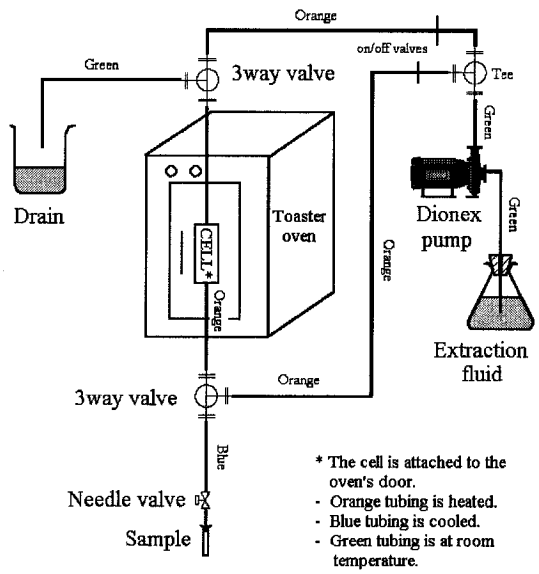


Figure 3-2: Flow-through system.

In Figure 3-3, the cell is filled from the top by keeping the bottom 3-way valve and needle valve closed. When the pressure starts to increase on the pump display, it indicates that the cell is full.

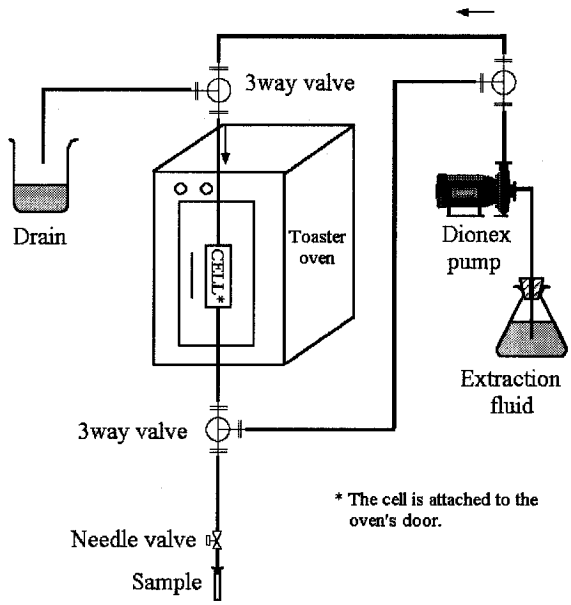


Figure 3-3: Flow-through system.

In Figure 3-4, the cell is filled from the bottom and when it is full, the excess solution goes into the waste.

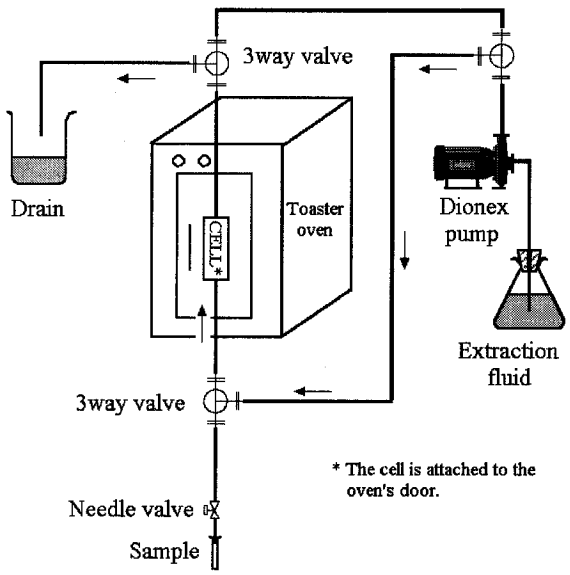


Figure 3-4: Flow-through system.

In Figure 3-5, the solution is recirculated through the cell, from top to bottom or inversely.

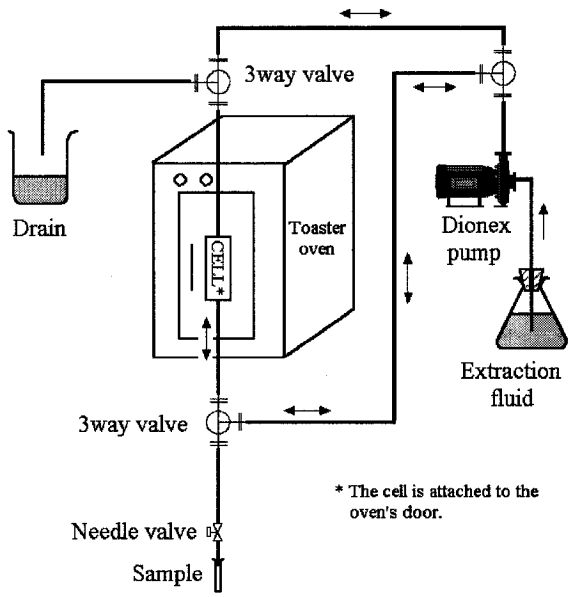


Figure 3-5: Flow-through system.

Figure 3-6 is a picture of the apparatus with the Teflon cell.

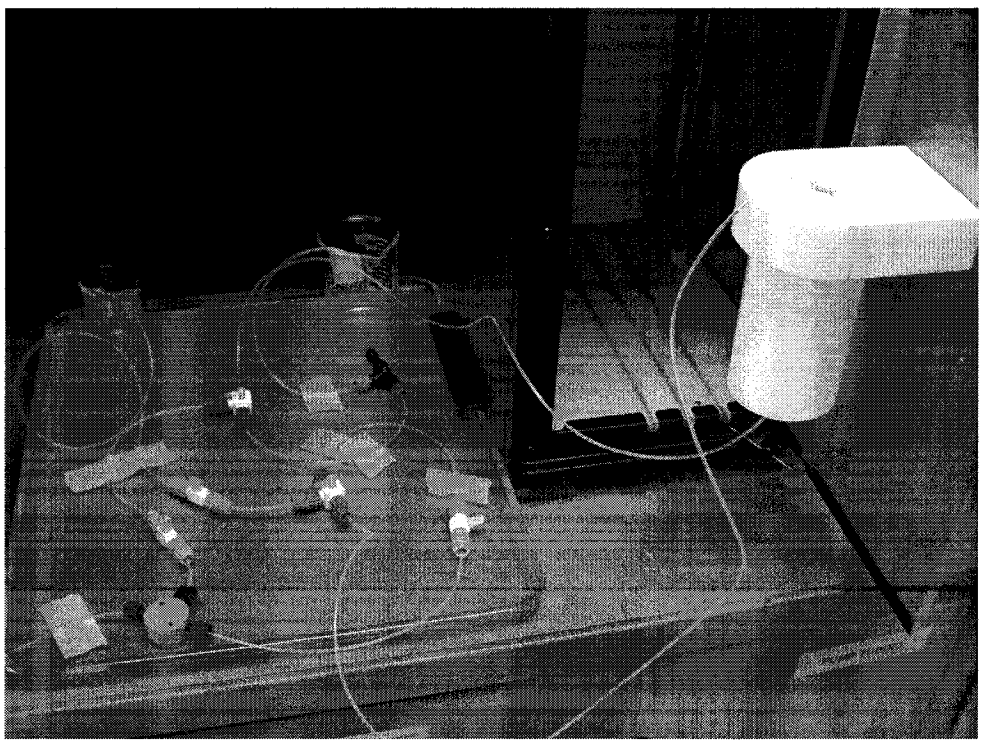


Figure 3-6: Flow-through apparatus.

3.3.1 Equipment

3.3.1.1 Pump

All pressure experiments were done on the various parts of the cell using an HPLC gradient pump, model GPM-2, serial number 892154 (Dionex Corporation, Sunnyvale, CA, USA). Different settings could be adjusted. There were ten different programs that could be saved for future use. The flow rate scale was from 0.0 mL/min to 9.9 mL/min with increments of 0.1 mL/min. There were four solution lines and the percentage of each line to be used could be set. There was also a feature that allowed us to set low and high pressure limits alarms, thus enabling the pump to stop automatically when one of these limits was reached. The actual pressure inside the system could be read from a digital display.

3.3.1.2 Oven

All temperature experiments were conducted using a toaster oven, a Kenmore model from Sears (Montreal, QC, Canada), and a thermocouple type J, 0.010" diameter, 36" of length, glass insulated, PN 5SC-GG-J-30-36 from Omega Engineering, Inc. (Stamford, CT, USA), linked to a Digi-Sense® thermocouple thermometer, model number 8528-20, serial number 529130, from Cole-Parmer Instrument Company (Chicago, IL, USA). An experiment was conducted with no cell to see how long it took for the inside of the oven to reach the temperature indicated on the front panel. Only three temperature settings were used for this experiment: 100, 125 and 150°C. Results are shown in Table 3-1 and Figure 3-7.

Table 3-1: Temperature readings from the inside of the toaster oven.

Time (minutes)	Temperature set at (°C)		
	100	125	150
0.00	22.7	25.4	26.2
0.25	-	27.9	27.9
0.50	-	37.6	36.6
0.75	-	54.1	51.4
1.00	-	77.8	71.5
1.25	-	107.4	95.6
1.50	-	143.5	122.8
1.75	-	176.7	157.9
2.00	-	198.8	189.9
2.25	182.0	-	214.5
2.50	-	-	227.0
3.00	156.5	181.0	215.1
4.00	137.5	155.1	179.0
5.00	113.5	127.2	145.3
6.00	96.5	111.2	132.9
7.00	92.4	106.9	123.5
8.00	87.1	103.0	117.6
9.00	86.8	101.5	115.7
10.00	85.6	99.7	115.5
11.00	88.1	98.8	114.0
12.00	86.9	100.0	115.3
13.00	85.2	100.9	-
14.00	86.6	98.5	115.6
15.00	-	98.5	113.2
16.00	-	117.4	112.4
17.00	-	105.7	112.6
18.00	-	94.3	113.2
19.00	-	96.5	112.3
20.00	-	95.9	113.0
21.00	-	96.0	111.5
22.00	-	97.5	110.8
23.00	-	98.6	109.4
24.00	-	98.7	111.0
25.00	-	99.3	110.1

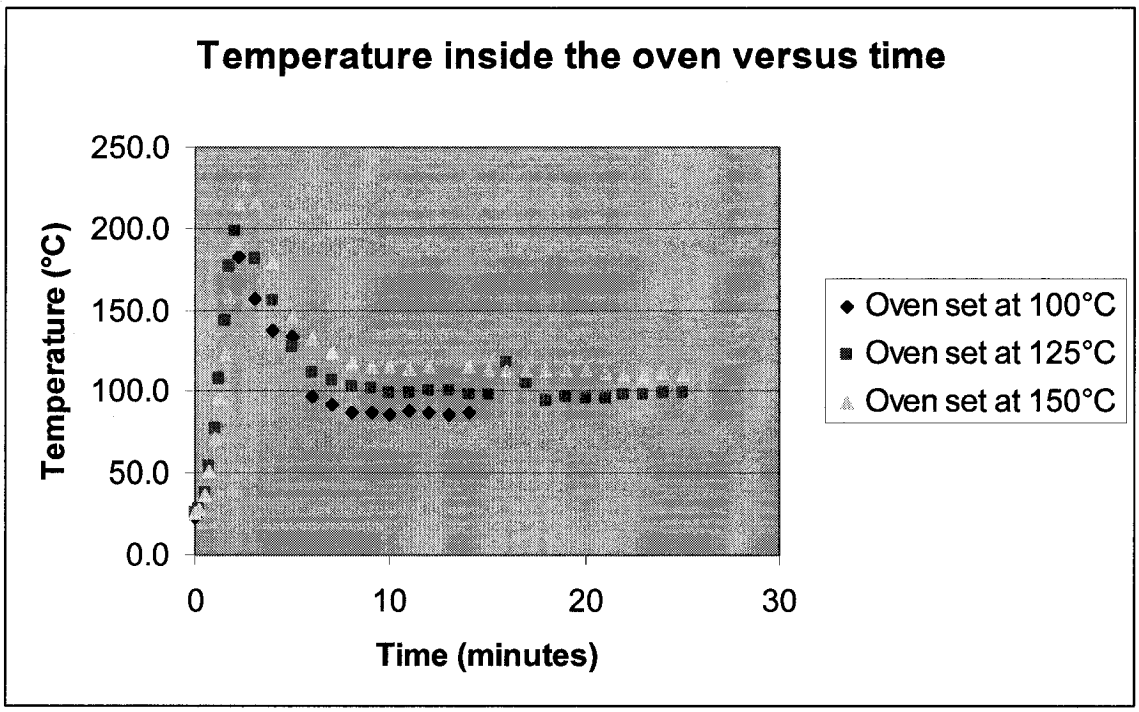


Figure 3-7: Temperature inside the oven as a function of time.

During these experiments, it was observed that the oven's elements were heating intermittently. Once the temperature of the oven was turned on, the elements heated rapidly to red-hot. Then, they seemed to stop heating. In Figure 3-7, it can be seen that the temperature was quite high at the beginning stage and then it decreased slowly to reach a plateau. It was assumed that the boost given at the beginning was to reach the set temperature rapidly. After that phase, the elements were turning on and off at regular intervals to maintain the expected temperature.

3.3.1.3 Tubing

Polytetrafluoroethylene (PTFE) tubing, 1/16" OD x 0.030" ID, PN VTTF30S25F, was purchased from Chromatographic Specialties (Brockville, ON, Canada). This particular type of tubing was chosen first to match the Teflon of the cell and also because it had a high degree of rigidity as well as the highest working temperature of all fluoropolymer tubing (up to 287°C).

Later, PEEK polymer tubing, 1/16" OD x 0.010" ID, PN 1531, and 1/16" OD x 0.030" ID, PN 1533, were acquired from Upchurch Scientific (Oak Harbor, WA, USA) to match the PEEK cell and fittings. This type of tubing was biocompatible, chemically inert to most solvents, flexible and could easily be cut to desired lengths. It could safely withstand 20-30% nitric acid at room temperature and was pressure rated to 7000 psi (tested with water at room temperature by the manufacturer).

3.3.1.4 Fittings

PEEK fittings, standard 1/16", 10-32, 1 piece (nut and ferrule attached), PN C44550201, were purchased from Chromatographic Specialties (Brockville, ON, Canada). It was later found that these fittings had a disadvantage: after they were inserted on the tubing and screwed in place, it was impossible to remove the tubing to change it, thus making these fittings non re-usable.

3.3.1.5 Valves

The first valves that were ordered were Omnifit valves (see Figure 3-6) from Thomson Instruments (Clear Brook, VA, USA). The 2-way valves, PN 1101, and the 3-way valves single key had their bodies machined from a single piece of Teflon for strength and maximum inertness. The valves had no dead space within and were autoclavable. They also had only one moving part/channel and were rated to 400 psi.

Then, a needle valve, also called micro-metering valve, PN P-446 was purchased from Upchurch Scientific (Oak Harbor, WA, USA). This valve had a sturdy PEEK construction, was able to control flow rates as low as 3.5 µL/minute and came complete with PEEK 10-32 fingertight fittings. It was also pressure rated to 800 psi and had 0.020" thru-holes.

Later, when it appeared that the pressure to be used might exceed 400 psi, the 2- and 3-way Omnifit valves were replaced by 4-port switching valves, bulkhead-mount version, PN V-101L, right angle flow, and shut-off valves, PN P-732, from Upchurch Scientific (Oak Harbor, WA, USA). Each of the 4-port switching valves had a low swept volume, could withstand pressures to 500 psi, was chemically inert and biocompatible. The PEEK and fluoropolymer construction resulted in a valve that was said to be as durable as it was economical. The valves had 0.040" thru-holes and came complete with flangeless ferrules and nuts for 1/16" OD tubing. To operate, each port must be either connected to a line of the system or plugged using a special plug. The built-in positioning detents allowed these valves to snap into place, ensuring the thru-hole was properly aligned. As for the shut-off valves, they were designed for holding pressures up to 600 psi and were injection molded from PEEK with a Kel-F rotor, making them highly resistant to chemical attack. They were also biocompatible because of their all-polymer flow path. Semirigid polymer tubing, such as PEEK or Teflon, 1/16" OD, could be connected to the valves. Finally, they had a 0.020" thru-hole, and the maximum internal volume, with the valve fully open, was 2.5 μL, thus minimizing dead volumes.

3.3.1.6 Fritted glass discs

Sintered glass filter discs made by ACE Glass, were ordered from Lasalle Scientifique Inc. (Lasalle, QC, Canada), in various sizes (15 mm and 20 mm OD) and porosities (A: 145-174 μm, B: 70-100 μm, C: 25-50 μm, and D: 10-20 μm). The glass fiber structure of ACE filters resulted in a more abrasion resistant surface. Being fused together on a greater surface area, the particles did not detach from the filter body as easily as spheroid granules. Since they were made entirely of glass, they were highly resistant to thermal shocks and chemical attacks.

3.3.1.7 Miscellaneous

A couple of PEEK tees, with standard 1/16", 10-32 fittings, PN C441030 were ordered from Chromatographic Specialties (Brockville, ON, Canada). These tees were to be combined with 2-way valves or shut-off valves to replace a 3-way valve.

A static mixing tee, PN U-466, was purchased from Upchurch Scientific (Oak Harbor, WA, USA), in order to mix the "fresh" extraction fluid with the "recirculated" fluid when the system would be in the recirculating mode. It had a PEEK body with three two-piece fingertight fittings and a 10 μm UHMWPE (Ultra High Molecular Weight Polyethylene) frit in the center port that aids mixing. It had a low swept volume of 2.2 μL, including the frit volume, and was designed for flow rates of 0.5 to 3.0 mL/minute and a maximum pressure of 6000 psi.

3.4 Teflon Cell Prototype

3.4.1 Cell Design

It was decided to build the cell prototype with Teflon, because, at the beginning, it had appeared that it would be the most chemically inert material that would not contaminate our samples. It was easy to machine, showed an excellent resistance to aging and degradation, had high non-stick properties, its melting point was at 621 degree Fahrenheit (327°C) and its upper service temperature was 260°C.

In Figure 3-8 below, the first design that was imagined can be seen.

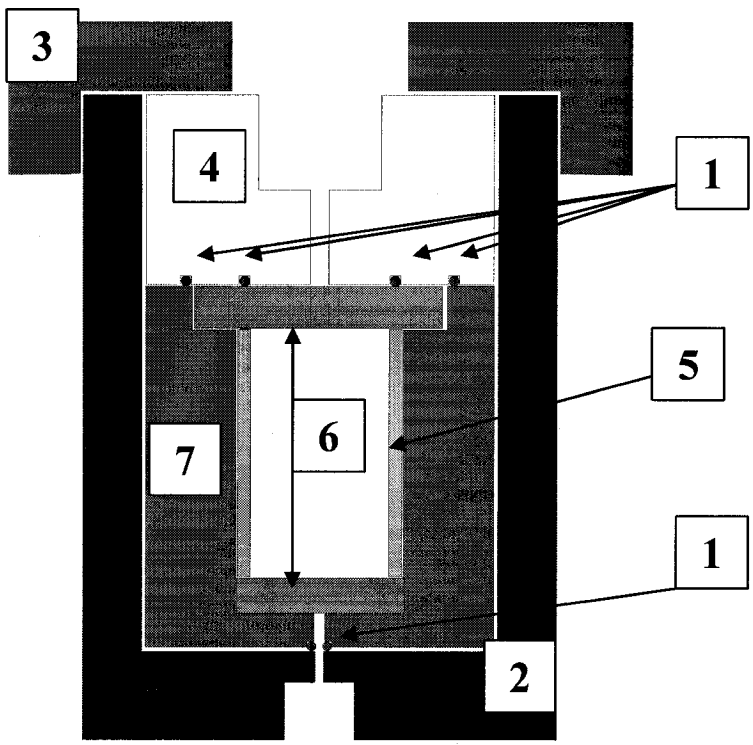


Figure 3-8: First cell design in Teflon.

1. These circles were o-rings inserted into part number 4 and used to avoid having liquid outside of the cell.
2. This part was a PTFE (polytetrafluoroethylene, most commonly called Teflon) holder. The tubing would screw in at the bottom. Dimensions: 5.85 cm OD, 3.48 cm ID, height of 10.30 cm.
3. This was the PTFE or SS316 (stainless steel) cap that would screw into the holder. It would hold everything tight. There was a small slit going from the middle to the outside to allow the removal of the cap without unscrewing the tubing. Dimensions: 7.804 cm width, 10.584 cm length, 2.881 cm depth.
4. The top part of the cell. The tubing would screw into it. We only had to pull the tubing to remove the top part. This part also pushed on the top frit to hold it in place. Dimensions: 3.48 cm OD, 1.605 cm height.
5. Here was the PTFE sleeve used to push on the bottom frit to hold it in place. Dimensions: 1.51 cm OD, 1.26 cm ID, 6.008 cm height.
6. These parts were the two (2) sintered glass filter discs.
7. The bottom part of the cell. On the top, there were two holes in which we could insert screws to remove this. Dimensions: 3.48 cm OD, 1.51 cm most inner ID, 1.996 cm ID and 7.319 cm height. When this part would be out, we only had to insert a very small metal rod through the bottom to remove the 2 frits, the sleeve and the sample, and we could easily put new frits and sample.

Figure 3-9 is a picture of all the disassembled parts of this Teflon cell. This cell had already been modified a little bit though by the addition of a top frit holder (dimensions: 2.014 cm OD, 1.538 cm ID, 1.224 cm most inner ID and 0.372 cm height).

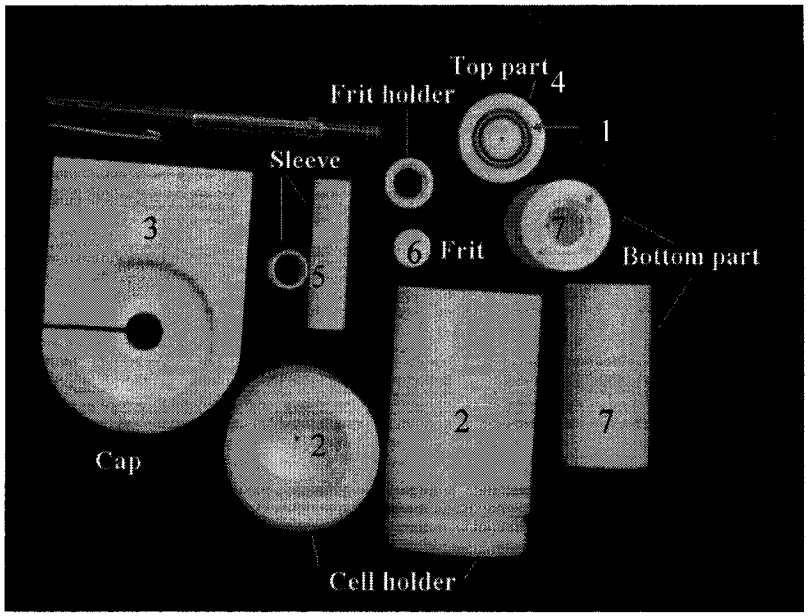


Figure 3-9: Disassembled parts of the Teflon cell.

3.4.2 Cell Performance

The first experiment that was performed on this cell was a temperature experiment. The goal of this experiment was to determine how long it took to the inside of the cell to reach a set temperature. The cell was put together with all the pieces, except the top frit, and a thermocouple (J-type) was inserted into it where the tubing should be attached, at the top of the cell. The temperature at time zero was recorded, and then, the oven's door was closed and the temperature set. A stop-watch was started and a temperature reading was taken every 5 minutes during 180 minutes (3 hours). This temperature experiment was repeated with different temperature settings (100°C, 150°C, 175°C, 200°C, 220°C, and "broil"). Results are presented in Table 3-2 and Figure 3-10.

It was observed that in all cases, a plateau was reached after approximately 120 minutes (2 hours), but that the attained temperature was around 15% below the set temperature. This could probably be explained by the fact that Teflon is an insulator, meaning that it does not conduct heat, that it tries to keep the heat

outside. This was why it took so long to reach a plateau. Despite that, it gave a fairly good idea of what the temperature inside the cell would be during the extraction of a real sample without having to open it. Of course, this could only be assumed if the cell is at ambient pressure. This scheme might change totally once a pressure would be applied to the system.

Table 3-2: Temperature readings obtained inside the Teflon cell.

Time	Temperature (°C)					
(minutes)	100	150	175	200	220	broil
0	24.5	23.8	24.0	22.0	22.0	22.8
5	26.6	28.2	28.6	29.8	34.5	33.6
10	30.5	34.6	34.2	35.0	36.3	42.0
15	37.0	46.0	46.0	50.0	52.1	53.4
20	42.8	56.0	56.7	63.7	69.2	72.9
25	46.6	64.8	66.2	76.3	81.0	89.5
30	51.9	75.7	74.8	87.5	93.7	103.4
35	55.8	79.1	82.5	97.5	104.7	118.3
40	58.6	85.0	89.7	106.5	114.4	130.6
45	61.9	90.5	96.0	114.2	123.0	141.9
50	65.0	95.2	101.7	121.1	130.8	151.9
55	67.7	99.3	106.8	127.4	137.7	161.2
60	69.7	103.0	111.4	132.8	143.8	169.3
65	72.1	106.2	115.8	137.6	148.9	176.1
70	73.9	109.1	119.4	141.7	153.9	182.6
75	75.4	111.5	122.7	145.6	157.9	187.9
80	77.2	113.8	125.6	148.7	161.7	192.5
85	78.2	115.8	128.2	151.4	165.0	196.5
90	79.5	117.5	130.4	153.8	167.9	200.1
95	80.6	119.2	132.5	155.9	170.5	203.3
100	81.7	120.7	134.3	157.9	172.9	205.7
105	82.4	121.8	135.9	159.5	175.0	208.0
110	83.3	123.0	137.4	160.8	176.4	210.0
115	84.0	124.0	138.4	162.1	178.0	211.6
120	84.7	124.9	139.6	163.0	179.2	213.1
125	85.3	125.6	140.5	164.0	180.3	214.4
130	85.8	126.3	141.3	164.6	181.2	215.3
135	86.3	126.9	142.1	165.7	182.4	216.4
140	86.7	127.3	142.6	165.7	183.1	217.2
145	87.0	127.6	143.1	166.1	184.3	218.0
150	87.3	127.9	143.7	166.3	184.7	218.6
155	87.7	128.2	144.0	166.4	185.2	219.3
160	87.9	128.3	144.4	166.5	185.5	219.6
165	88.1	128.6	144.7	166.6	185.9	220.1
170	88.2	128.7	145.0	166.7	186.0	220.6
175	88.4	128.9	145.1	166.9	185.9	221.1
180	88.6	128.9	145.3	167.0	186.1	221.4

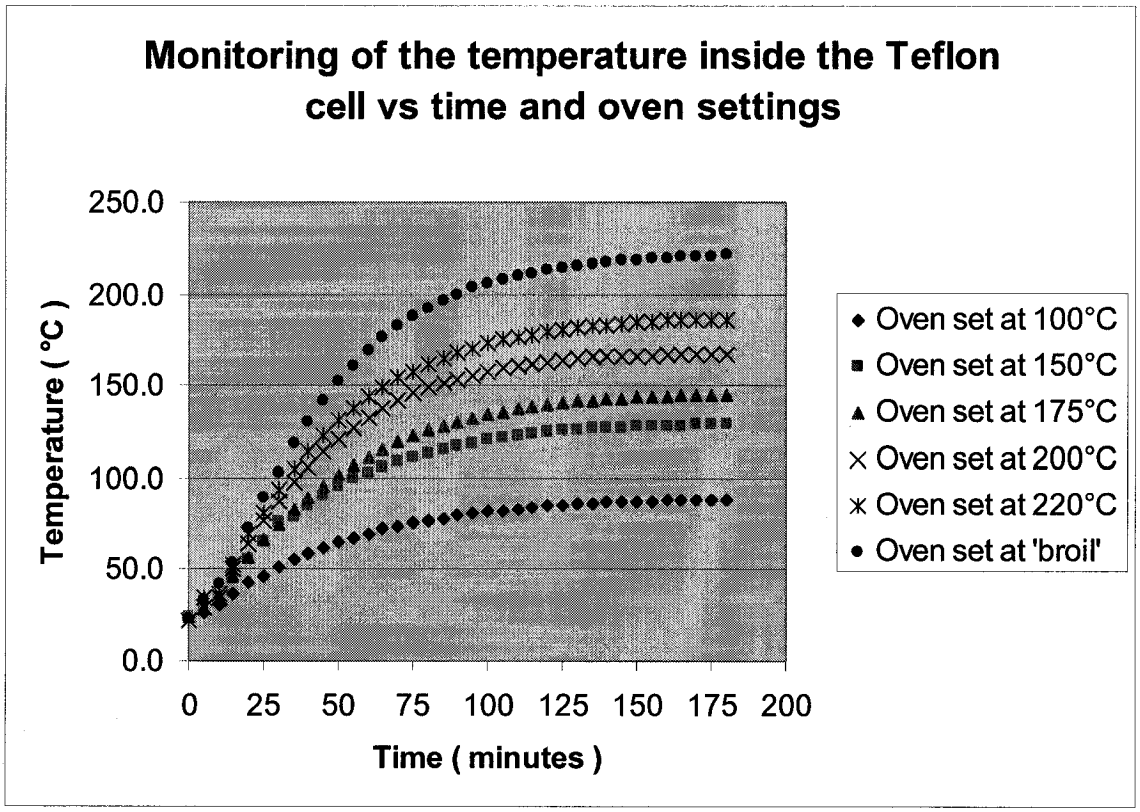


Figure 3-10: Teflon cell temperature versus time.

Later, the cell was tested in several different ways with water. A porosity B frit was used at the bottom and a porosity C at the top. The pump was set at 2.5 mL / min and the high pressure limit at 500 psi. Water was pumped through the bottom of the cell with a bottom frit in, but no top frit. The cell was successfully filled with water, but the top part leaked, see Figure 3-11, and some water got into the cell holder. The top part probably leaked because water was able to bypass the inner o-ring by diffusing through the frit. The pressure in the system was 0 psi. Then, water was pumped again through the bottom of the cell, but with both bottom and top frits in. It gave the same results as previously, and water wasn't coming out of the cell through the top tubing. Pumping water through the top of the cell with only the bottom frit in was tried, under the same conditions mentioned above. The cell was filled, water came out of the tubing at the bottom, but the top part still leaked and there was water again in the cell holder. The

bottom frit was changed for a porosity C frit and water was pumped through the bottom of the cell with no top frit. The cell was filled, the top part leaked, no water came out of the top tubing and there was water again in the cell holder.

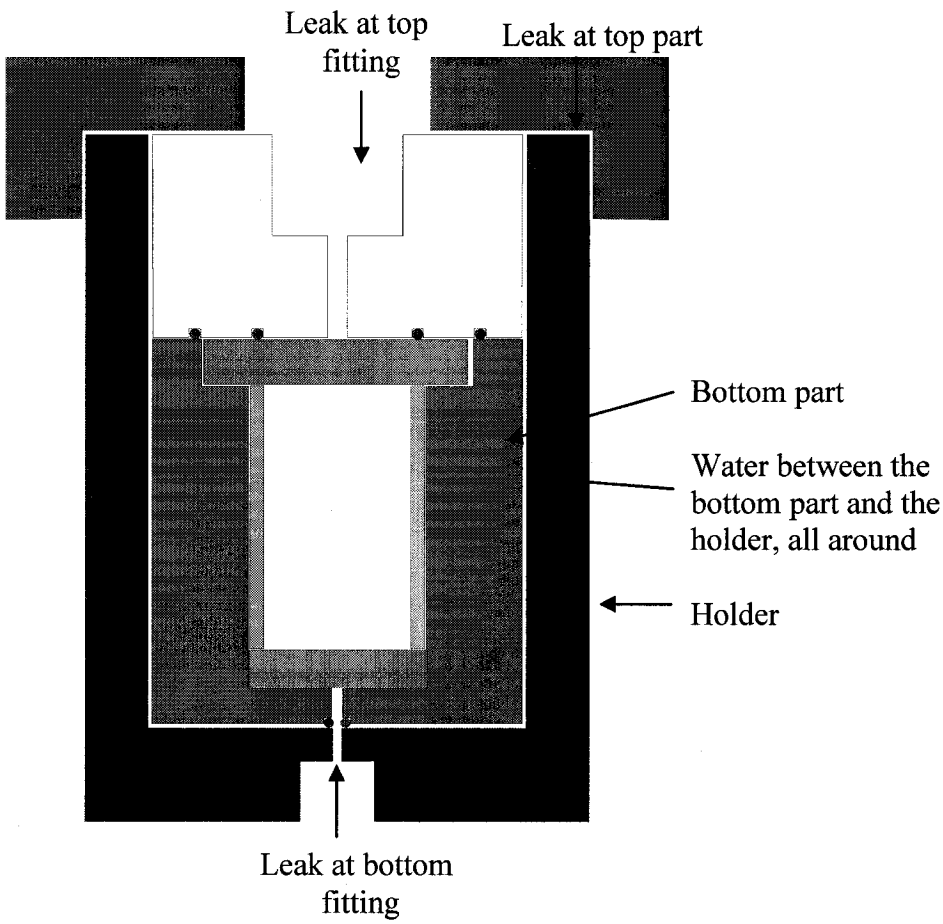


Figure 3-11: Position of the leaks on the Teflon cell.

Then, both the top and bottom frits were put back in, except that two coats of teflon tape were placed around the top frit, leaving the center part uncovered. By doing this, it was expected that the liquid would not bypass the o-ring by diffusing through the frit. Water was pumped through the top of the cell and it came out by the bottom tubing, proving that there was an improvement. It was impossible to know whether the cell was completely filled with water or not. There was still no pressure in the system and a little bit of water in the holder, but this time, the top part did not leak. Instead, a leak was detected at the top fitting. When the cell

was taken apart, using a small metal rod inserted through the hole under the bottom part of the cell to push both frits and the sleeve out, the two frits were broken. Maybe too much Teflon tape was used for the top frit, providing a very tight fit.

The top frit was changed for another porosity C frit and one coat of Teflon tape was wrapped around it instead of two. It was a little bit looser than previously. Water was pumped through the top with only the top frit installed. Liquid was coming out by the bottom tubing, but only after a while. Almost at the same time, the top fitting was leaking and a few seconds later, the top part also. The cell was filled and there was water again in the holder. The same thing was repeated, except that water was pumped through the bottom. No water was coming out of the top tubing, the cell was filled, the top part leaked, water was found in the holder, and there was almost no leaking from the top fitting.

At that point, it was decided that in order to get rid of the leak at the top of the cell, some modifications to the design were necessary. That was when the frit holder was designed (see Figure 3-9). With this holder, both the top and the bottom frit would be the same size (approximately 15 mm OD) instead of 20 mm for the top frit and 15 mm for the bottom one. In addition, a slight modification was done to the top part by changing the size and the disposition of the embedded o-rings, making the inner o-ring sit on the frit holder instead of on the frit, creating a better seal.

The same kind of experiments as above were repeated. Water was pumped through the top of the cell with bottom and top frits in (porosities C and B, respectively). Liquid came out by the bottom tubing. There was some water in the holder. The top part didn't leak, suggesting an improvement, but the top fitting was still leaking. When the cell was disassembled to look inside, the bottom frit was broken because a greater pressure had to be applied to take out everything.

The bottom frit was changed for a porosity D frit. Also, the top and bottom fittings were switched to see if the problem was the fitting itself or the connection. Water was pumped through the top of the cell. Now, no liquid came out by the bottom tubing, and both the top and bottom fittings leaked. The top part was still good with no leak. The bottom fritted glass disc was broken again for the same reason as above. The exact same experiment was repeated, but this time, the bottom frit was replaced by a solid disc of the same size to see if it was still hard to push everything out. Obviously, there was no water coming out of the bottom tubing. The top fitting leaked a lot, and just before the pump was stopped, the bottom fitting started to leak, probably because the cell was full of water and some was able to go under the solid disc. This time, it didn't take a great pressure in order to take everything apart. It is not known why it didn't behave the same with a regular fritted disc at the bottom, but it might only be because the solid disc was made of a stronger material than the fritted glass disc. As was suggested, once opened, the cell was full of water. In spite of this, the new top part did not leak and there was no trace of liquid past the outer o-ring, leading to no water in the cell holder. That was a great improvement. The experiment was repeated again by putting back another fritted glass disc of porosity B at the bottom that matched the porosity of the top frit. Before liquid was pumped through the cell, all of the components were disassembled to see if it was difficult. It was not a problem at all, everything went smoothly. Everything was put back together and water was pumped through the top of the cell. Water came out of the bottom tubing, the top part still worked perfectly, and the top fitting leaked again, but less than previously. The bottom fitting leaked too, except that it was not dripping. Once again, it was almost impossible to push everything out of the cell (both frits, sleeve, frit holder). The hypothesis for this problem was as follows: as everything was wet, maybe there was suction and this was why it was hard to push everything out of the cell.

Again, another design modification was mandatory. In order to avoid breaking the frit by pushing directly on it, another piece was needed, made of a harder material, so one could push on that piece instead of on the bottom frit. To be able to do this, the sleeve would have to be cut to give space for this new piece, and the bottom part of the cell would have to be modified so one could introduce a different pushing tool (2-, 3- or 4-prong tool) that would disperse the weight applied to push out everything towards the outside of that new part instead of in the middle only. That new designed part was a round disc with a small hole in the middle to allow the liquid to go out of the cell.

3.4.3 Conclusion

For this first cell prototype, see Figure 3-8 and Figure 3-9, the major problem encountered was leaks. The first leaks were located at the fittings connections with the cell. As Teflon was a softer material than the PEEK used for the fittings, it couldn't squeeze the fittings enough to grip the tubing, therefore leading to leaks. There was also a problem with leakage around the upper frit part of the cell. The last problem was that sometimes the bottom frit had to be broken to take it out of the cell.

A cell made out of PEEK was then considered for the next step.

3.5 PEEK (Poly Ether Ether Ketone) Cell Prototype

3.5.1 Cell Design

PEEK is a high temperature resistant engineered thermoplastic with excellent chemical and fatigue resistance plus thermal stability. PEEK exhibits superior mechanical and electrical properties. With a maximum continuous working temperature of 480° Fahrenheit (~250°C), PEEK has excellent retention of mechanical properties up to 570° Fahrenheit (~300°C) in a steam or high-pressure water environment. Superior chemical resistance allows PEEK to work effectively as a metal replacement in harsh environments. PEEK is inert to all common solvents and resists a wide range of organic and inorganic liquids.

As can be seen in Figure 3-12, for this second prototype, the shape of the fitting holes was modified to match the shape of the fittings; a spacer below the bottom frit was added, so one would not push directly on the frit to take it out, the top frit holder and the sleeve were merged into one piece, and holes were added in the bottom part of the cell and the holder so a 3-prong tool could be used to push everything out.

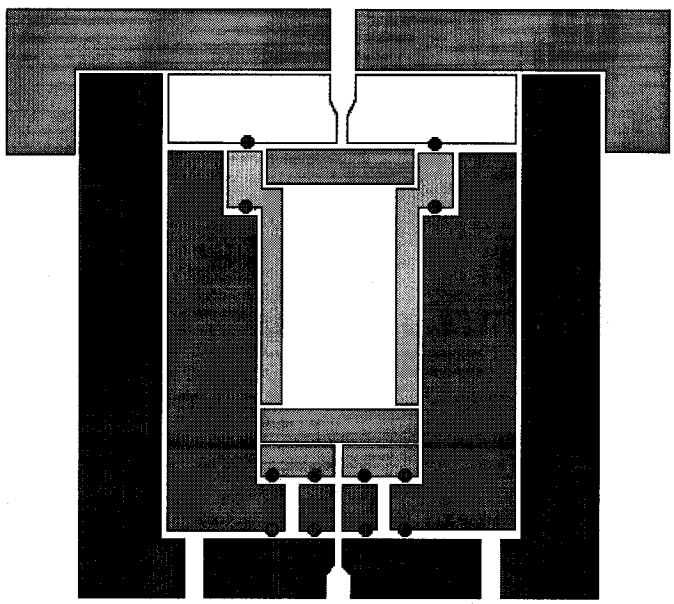


Figure 3-12: Second design of the cell with PEEK material.

3.5.2 Cell Performance

A temperature experiment was performed on this cell as with the Teflon cell. The goal of this experiment was to determine how long it took for the inside of the cell to reach a set temperature. Results were compared with those obtained with the Teflon cell. The cell was put together with all the pieces, except the top frit, and a thermocouple (J-type) was inserted in it where the tubing should be attached, at the top of the cell. The temperature at time zero was recorded, and then, the oven's door was closed and the temperature set at 220°C. A stop-watch was started and a temperature reading was taken each 5 minutes during 150 minutes (2.5 hours). This temperature experiment was repeated only with one different temperature setting, "broil", since these two temperatures would be the most probable temperatures that would be used for extraction experiments. Results are presented in Table 3-3 and Figure 3-13.

As for the Teflon cell, it was observed that in both cases, a plateau was reached after approximately 115 minutes (a little bit less than 2 hours), but that the attained temperature was around 13% below the set temperature. Despite that, it gave a fairly good idea of what the temperature inside the cell would be during the extraction of a real sample without having to open it. Of course, this could only be assumed if the cell is at ambient pressure. This scheme might change totally once a pressure would be applied to the system.

Table 3-3: Temperature readings obtained inside the PEEK cell.

Time (minutes)	Temperature (°C)	
	220	broil
0	25.8	23.4
5	27.9	24.3
10	51.2	41.4
15	78.3	69.9
20	98.5	96.1
25	114.7	115.1
30	127.8	131.6
35	138.4	145.1
40	147.1	156.1
45	154.9	165.6
50	160.7	173.2
55	165.5	179.2
60	169.3	184.3
65	172.7	188.7
70	175.8	192.4
75	178.5	195.5
80	180.9	198.2
85	182.9	200.3
90	184.4	201.9
95	185.9	203.5
100	187.0	204.7
105	188.3	206.5
110	189.3	207.6
115	190.1	209.6
120	190.8	212.1
125	191.2	213.0
130	191.4	213.2
135	192.1	213.3
140	192.7	213.2
145	192.8	213.2
150	192.7	212.9

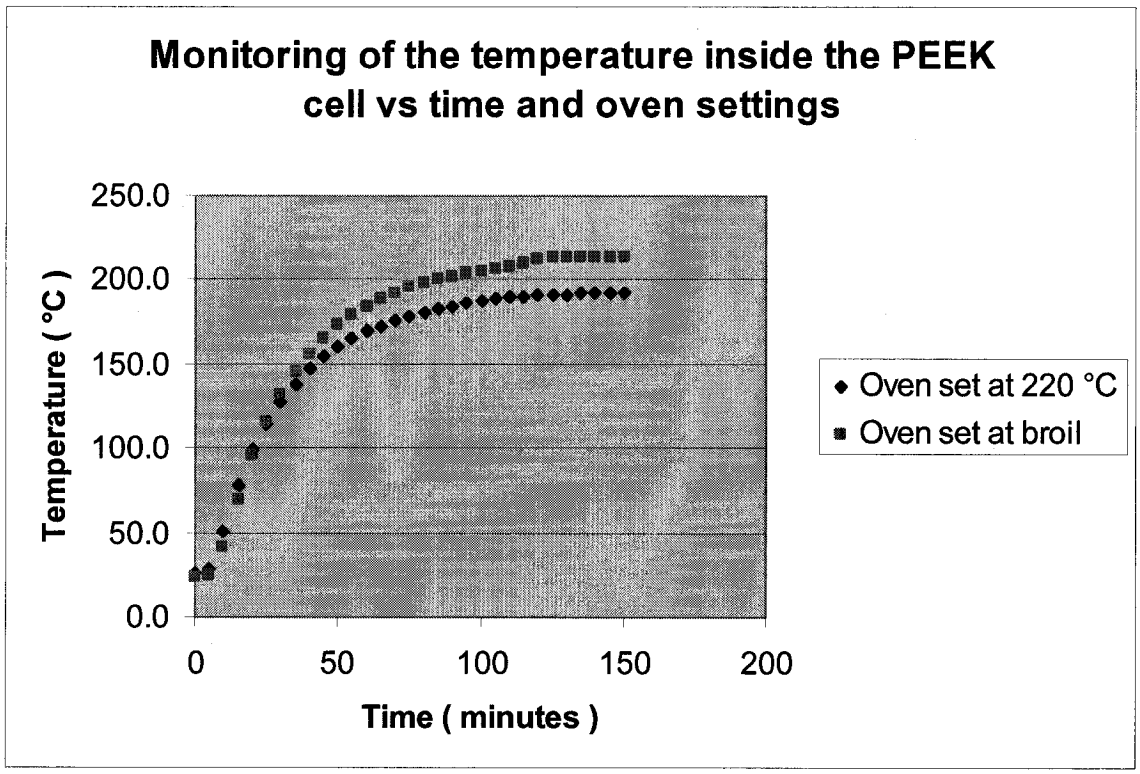


Figure 3-13: PEEK cell temperature versus time.

If the results obtained with the Teflon cell are compared against the results obtained with the PEEK cell, it can be seen that a plateau was reached a little bit faster with the PEEK cell and that the temperature inside the PEEK cell was slightly higher than in the Teflon cell. It thus proved that even if both PEEK and Teflon are insulators, PEEK was better at conducting temperature than Teflon and therefore was more suitable for the extraction experiments than Teflon. See the comparison of temperatures at 220°C in Figure 3-14 and at "broil" in Figure 3-15.

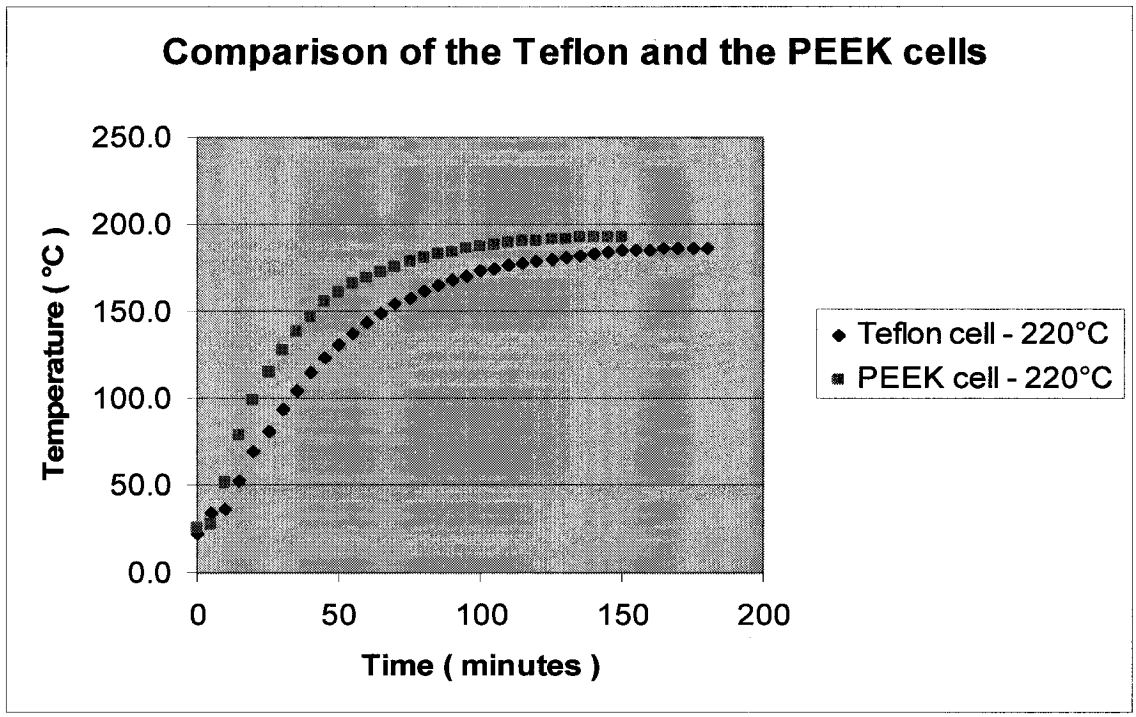


Figure 3-14: Comparison of PEEK and Teflon cells at 220°C.

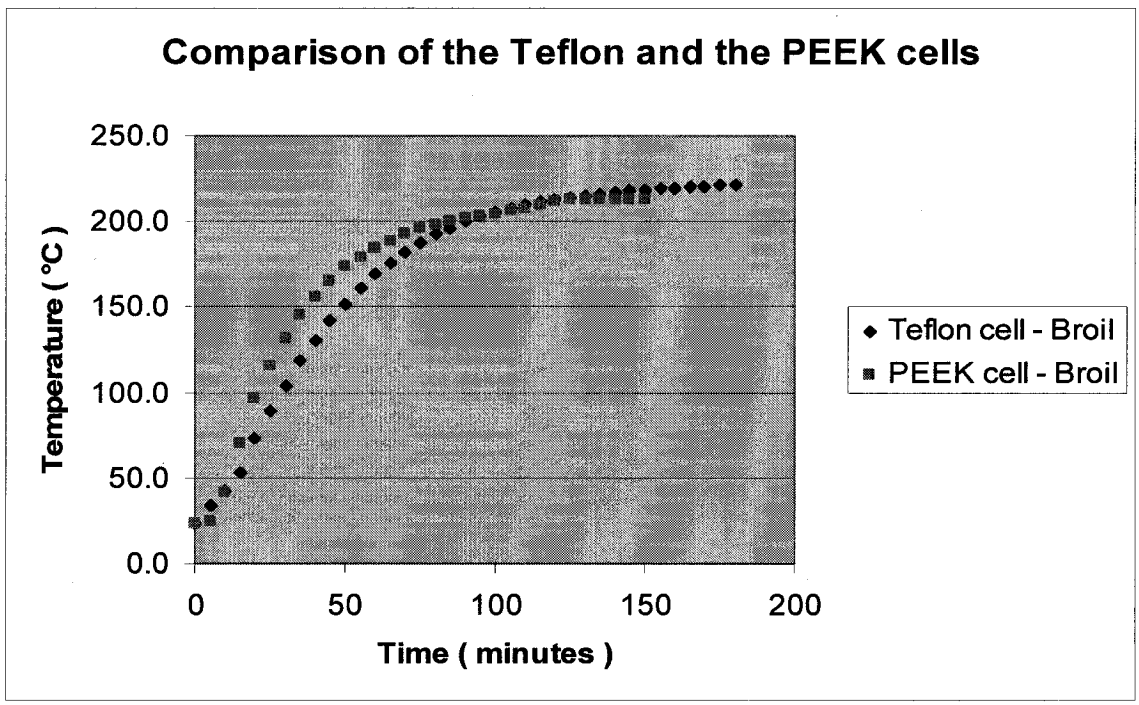


Figure 3-15: Comparison of PEEK and Teflon cells at "broil".

This new cell was also tested for leaks. The flow rate was set a 2.5 mL/minute and the high pressure alarm at 400 psi. The bottom frit was of porosity D and the top frit, porosity B. With every piece in place, the pump was started, and a leak was detected at the bottom of the cell holder through one of the 3 holes. The bottom and top parts of the cell were taken out of the holder and pressed against each other while the pump was started again. The holes under the bottom part of the cell were leaking. All pieces were assembled again to retry with the initial settings. One hole started leaking at the bottom of the cell holder after approximately 1 minute and 30 seconds, and after 5 minutes, it was the only hole leaking. It was believed that there was also a leak between the top part of the cell and the cell holder because the outside of the cell was wet on the top.

To see if it was always the same hole that was leaking, the holes of both the cell holder (1, 2, 3) and the bottom part (1, 2, 3) were numbered, with a pencil, and aligned. With the same initial settings, water was pumped through the cell from top to bottom for 10 minutes, and it did not leak. The pressure indicated on the display was 0 psi. All the parts, except, of course, the interior of the cell, were completely dry, even the inside of the cell holder and the outside of both the top and bottom parts of the cell. It is not known for sure why this attempt succeeded, but it might be because screw the cap was screwed as hard as possible to provide the tightest achievable seal. All the pieces were taken apart and put back together, with the holes aligned, and a second and a third attempts were made. It worked again, there was no leak detected for both attempts. Another attempt was made with an increased flow rate of 9.0 mL/minute instead of 2.5 mL/minute, and there was still no leak after 10 minutes of pumping water through the cell from top to bottom, and the pressure in the system was 0 psi.

Holding all these last parameters constant, the experiment was repeated by pumping water from the bottom to the top of the cell during 10 minutes. No leak was detected, everything inside the cell holder was dry, and the pressure inside the system was fluctuating between 220 and 280 psi, which was caused by the cell

being full of water. Now that the cell was known to work without leaking, it was time to test the system with water at higher temperatures to see how it behaved. The cell was filled completely with water, then the valves were closed and the oven temperature was set at 220°C. The temperature was monitored with the thermocouple placed around the cell holder in the oven. After several minutes, the cell was leaking again from the holes at the bottom of the holder. It was assumed it was because of the o-rings below the bottom part of the cell. When the cell was disassembled, they looked flattened, as if they had melted due to the heat. Therefore, these o-rings were changed as well as those on the spacer.

Water was run through the cell at room temperature to check for leaks after these o-ring changes, and everything worked fine. The cell was completely filled again with water through the bottom and then the bottom valves were closed to avoid water leaving the cell by gravity. The top valve was left open at the beginning of the experiment, but was then closed after 55 minutes of heating to avoid water leaving the cell by evaporation through the upper path. This same valve was re-opened and closed rapidly 10 minutes and 20 minutes later to vent the cell. Water vapor going out could be heard, which was a proof that the temperature inside the cell was at least 100°C, or that the pressure was high enough to bring water above its boiling point. After 1 hour and 30 minutes of heating, the oven was turned off and the cell left to cool. Valves were opened and the water was collected. No leak was detected during this experiment. Everything went pretty well and was finally working.

The next step was to try with a real soil sample and extraction fluid. The goal of the experiment was to put approximately 0.5g of sample inside the cell, fill it completely with the extraction fluid as above (closing the valves when the cell was full, meaning that the fluid was not circulated through the system during the extraction phase), and heat it for 3 hours at 220°C or BROIL (1 hour to reach the maximum temperature according to the temperature experiments plus 2 hours for the extraction).

The first time the above mentioned experiment was attempted (the day after the last experiment with water was done), the cell was leaking through all 3 holes one minute after the pump was started. The cap was tightened as hard as possible to see if it was the problem, but it was still leaking. The cell was emptied to check all the o-rings, but they looked fine. They did not look like the ones that were changed the day before, just before the last water experiment. The inside of the cell and the frits were cleaned, dried, and everything was assembled again. Extraction fluid was pumped through the cell, but it was still leaking. Everything was left as it was for 3 weeks.

Three weeks later, the pump was turned on and started to pump water through the cell, without touching the cell, the fittings, the valves, or the pump settings, and it was not leaking. Another week went by and by keeping again the same configuration, water was pumped from top to bottom and inversely, a few minutes in both directions. No leak was detected. The cell was disassembled and emptied of the water that was inside, and each piece was dried. It was then reassembled and water was run again in both directions, a few minutes each way, and there was no leak.

The cell was then heated again with water in it. It was filled completely through the bottom, the bottom path was closed so water could not get out of the cell by gravity, and the upper path was also closed to avoid water evaporating that way. The oven's temperature was set at 220°C and the cell was heated during 1 hour and 30 minutes. After 15 minutes of heating, the upper path valve was opened to vent the cell: nothing happened. It was probably because the inside of the cell was not hot enough yet. The inside of the oven was also examined and it appeared to have no leak. The cell was vented again after 30, 40, 50 and 60 minutes, and vapor went out. After 1 hour and 10 minutes, the valve was opened again to vent the cell: vapor went out, but the noise was much quieter than before, and after 1 hour and 20 minutes, nothing happened, probably because all the water that was inside was evaporated and escaped as vapor during the venting process.

The cell was left to cool and nothing was touched. The system had worked perfectly.

Four days later, water was run again through the cell without changing anything. It leaked again. The cell was disassembled to clean the pieces, but it was difficult to disassemble. Everything was stuck together. It was very difficult to separate each piece. A week later, it was reassembled to run water through it from both the top and the bottom and there was no leak. All the pieces were taken apart again to dry, and one had to pull very hard because it was tight. The bottom frit, porosity D, was broken. When the cell was reassembled, the bottom frit was replaced by a porosity C frit. Water was pumped both ways, and it was leaking. The cell was disassembled again (it was still hard) and dried, then put back together by switching the top and bottom frits. Water was pumped through the cell and it was still leaking.

Another attempt was made. Water was run through the cell, then, when it was completely filled, the metering valve was closed to raise the pressure to 110 psi. The high pressure limit of the pump was set at 110 psi so the pump would stop when it reached that value. By doing this, 110 psi would be maintained inside the cell. The oven's temperature was then set at 220°C. After approximately 40 minutes, according to the temperature experiments, the temperature inside the cell should have been around 150°C. The oven's temperature was then set to 150°C so the temperature inside the cell would be maintained. At that point, a check for leaks was done. According to the Handbook of Chemistry and Physics[2], water should not boil under these conditions of temperature and pressure. No leak was detected and everything seemed to work fine. Once the cell was back at room temperature and pressure, water was pumped through it and it was leaking a lot from the holes at the bottom of the cell holder, and also from the top part of the cell when the pressure inside was raised again.

After this experiment, the cell was given to the machinist because it was almost impossible to disassemble it. The expansion of the PEEK during the heating process is probably the cause. The machinist replaced the o-rings and believed that the problem may be that the cell was tightened down too hard. He also re-machined several parts.

3.5.3 Conclusion

For this PEEK cell prototype, see Figure 3-12, there were two major problems encountered: leaks through the bottom holes and the difficulty of taking pieces apart after they had been heated and cooled down to room temperature. These two problems seemed to be related since leaks were observed after a heating phase. In general, the first time the cell was heated with water inside, there was no leak and it was working perfectly, even if the pressure was increased a little bit. If heating was attempted a second time, then it would start leaking. It is believed that when the PEEK material was heated, it was expanding, making it difficult to dissassemble the different parts. Moreover, by expanding, it would change a little bit the shape of the pieces, thus generating leaks. Despite these problems, the PEEK design solved all the problems encountered with the Teflon design such as leaks at fittings connections and around the upper frit part of the cell. It was also possible to avoid breaking the bottom frit while pushing everything out of the cell by adding a spacer below the frit. Then, it was proven that this design could work without leaking and under pressure. The temperature experiments also showed that when the oven was set at "broil", a slightly lower temperature could be reached with the PEEK cell, but this temperature was reached more quickly than with the Teflon cell. The only thing that could be done would be to find the appropriate temperature that would not change or change minimally the shape of the pieces to prevent leaks.

3.6 References

1. G. Légère, *Capsule-Based Microwave Digestion*, **Ph.D thesis**, 12 and 44, (1995).
2. *Handbook of Chemistry and Physics*, 80th edition, D-160, 1999-2000, CRC Press LLC.

Chapter 4 : An Evaluation of EPA Method 1311: Toxicity Characteristic Leaching Procedure (TCLP)

4.1 Abstract

In this section, the EPA (Environmental Protection Agency) method 1311: Toxicity Characteristic Leaching Procedure was applied to various soil and sediment samples in order to get results that could eventually be compared to results that would be obtained with the flow-through apparatus. A first experiment was performed but it did not give reliable results. A second experiment was thus carried out. Extracts were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) using external standards, standard additions and internal standards calibration methods. It was concluded that both instruments gave similar performances, as well as the three calibration methods, and that the results could be kept for future reference.

4.2 Introduction

Factors affecting heavy metal retention by soils include: pH, soil type, cation exchange capacity (CEC), natural organic matter, age of contamination, and the presence of other inorganic contaminants. Metal mobility is also influenced by the organic fraction in the soil and clay and metal oxide content in the subsoils because these soil constituents have significant CECs. The initial metal concentration, the presence of inorganic compounds, and the age of contamination also influence metal mobility. Bearing this in mind, the EPA method 1311: Toxicity Characteristic Leaching Procedure was applied to certified reference material PACS-2, mine soil and OECD (Organization for Economic Cooperation and Development) soil samples in order to determine the amount of available metals that can be extracted. These experiments would then serve as a point of comparison when the same samples will be subjected to an extraction with the designed flow-through cell system.

4.3 Experimental

4.3.1 Mine Soil

The mine soil that was used for analysis was taken from near the Miramar Con Mine (N 62°25.781' W 114°24.652') located near Yellowknife and was passed through a 2-mm mesh sieve and mixed by shaking. Its properties are shown in Table 4-1 below, which was provided by Stephen Wong, a former student of Dr. Laurie Chan (McGill Professor at Macdonald Campus).

Table 4-1: Soil properties of the mine soil samples.

Soil Property	Mine Soil
Water Content (% ± SD)[a]	20.5 ± 0.9
Water Holding Capacity (% ± SD)[a]	71.1 ± 4.9
pH[a]	8.3 ± 0.1
Redox (mV ± SD)[b]	356.3 ± 0.8
Cation Exchange Capacity (cmol/mg ± SD)[a]	34.3 ± 0.5
Organic Matter Content (% ± SD)[a]	7.3 ± 0.3
Particle Size Distribution	24.8 % sand 16.3 % clay 58.9 % silt
Total Arsenic Content (mg/kg dry soil ± SD)[c]	2038.7 ± 149.2

[a] n = 3 replicates, [b] n = 2 replicates, [c] n = 4 replicates

4.3.2 OECD Soil

The artificial soil was provided by Dr. Laurie Chan's lab and was prepared according to the Organization for Economic Cooperation and Development (OECD) method and contained 70% (w/w) grade 4010 silica sand (Unimin Canada, Jérome, ON, Canada), 20% (w/w) colloidal kaolinite clay (CAS 1332-58-7) and 10% 2-mm screened Canadian sphagnum peat moss. Each ingredient was obtained from local suppliers. Calcium carbonate (1%, w/w) was used to adjust the pH of the wetted substrate to 6.0 ± 0.5. This artificial soil was used as a matrix reference for the extraction.

4.3.3 PACS-2: Marine Sediments Certified Reference Material

PACS-2 was collected in the harbour of Esquimalt, B.C. and was freeze dried, screened to pass a No. 120 (125 μm) screen, blended and bottled using the facilities of the Canada Center for Mineral and Energy Technology in Ottawa. After bottling, the sample was radiation sterilized with a minimum dose of 2.5 Mrad by Nordion International Inc. (Laval, QC, Canada) to minimize any effect from biological activity. Refer to Table 4-2 for the concentrations of metals that were under investigation.

Table 4-2: Total content of trace metals in PACS-2 used for analyses and for which certified values have been established.

Metal name	Amount in PACS-2 (mg/kg)
Arsenic	26.2 ± 2.6
Cadmium	2.11 ± 0.15
Chromium	90.7 ± 4.6
Copper	310 ± 12
Mercury	3.04 ± 0.20
Lead	183 ± 8
Tin	19.8 ± 2.5
Zinc	364 ± 23

4.3.4 First Experimental Procedure

The following represents the basic experiment that was reproduced during the project. It was done to match as much as possible the EPA method 1311: Toxicity characteristic leaching procedure[1], for the extraction of nonvolatile analytes.

The first step was to determine, based on the type of soil that would be used, which extraction fluid would be appropriate for the extraction. To do this, 5 grams of the mine soil were transferred to a 500 mL beaker and 96.5 mL of reagent water were added. The beaker was covered and its content stirred vigorously for 5 minutes using a magnetic stirrer. The pH was then measured and it was found to be 8.34. According to the EPA method, since the pH was higher than 5.0, 3.5 mL of 1N HCl (obtained by diluting 1 mL of 12N HCl with reagent water into a total of 12 mL) were added, the mixture was slurried briefly, covered again, heated to 50°C and the temperature was held for 10 minutes. The solution was cooled down to room temperature and the pH was measured again (pH = 4.47 at 23.5°C). Based on this result, extraction fluid #1 was to be used for the extraction since the pH was lower than 5.0. In order to prepare the extraction fluid #1, a 1N NaOH solution was first prepared by weighing 10.0742 g of sodium hydroxide pellets, ACS reagent (J.T Baker, lot number J24933), and dissolving it with reagent water in a 250 mL, acid washed, volumetric flask. Then, to prepare the extraction fluid #1 itself, approximately 500 mL of reagent water were added to a 1 L acid washed volumetric flask, and 5.75 mL of glacial acetic acid and 64.3 mL of the 1N sodium hydroxide solution were pipetted into the flask. The volume was completed with reagent water. The pH of the extraction fluid #1 was 4.76. It was adjusted to 4.93 at 19.6°C with drops of the 1N NaOH solution.

For this experiment, since the extraction vessels should be made of inert material which will not leak or absorb analytes, various sizes of Nalgene bottles were used. They were soaked at least 24 hours in ~ 25% trace metal nitric acid, and then rinsed three times with reagent water and left drying.

Approximately 5 grams of each sample were weighted in 250 mL Nalgene bottles (see Table 4-3 for the exact amount) and Teflon tape was put on each bottle's threads to seal properly. Also, 2 bottles filled with 100 mL of extraction fluid #1 only were prepared and submitted to the same extraction conditions as the samples to serve as blank solutions.

Table 4-3: Amount of sample used for the first round of extractions.

Sample name	Weight (g)
OECD soil	5.0590
PACS-2	5.0092
Mine soil 1	5.0144
Mine soil 2	5.0380
Mine soil 3	5.0302

According to the EPA method, the agitation apparatus that should be used must be capable of rotating the extraction vessel in an end-over-end fashion at 30 ± 2 rpm. Since such an instrument was not available, a Benchtop 80°C Incubator Orbital Shaker (model 420, Forma Scientific Inc., Marietta, Ohio, USA) was used.

The solid samples were to be extracted with an amount of extraction fluid determined by the following equation:

$$Weight\ of\ extraction\ fluid = \frac{20 \times percent\ solid \times weight\ of\ sample}{100} \quad (1)$$

So, with the help of a 100 mL volumetric flask, 100 mL of extraction fluid #1 was added to each bottle, which were then shaken manually in an end-over-end fashion 3 times to mix everything uniformly. The bottles were clamped on the Orbital Shaker and the rpm was set at 100 for a total extraction time of 20 hours. The ambient temperature at the start of the extraction was 25.9°C. After 15 minutes, 30 minutes and 1 hour of shaking, the extraction was stopped and the bottles opened and vented into a fume hood to relieve excess pressure that might have built up in the bottles.

After 1, 2, 3 and 4 hours, 1 mL of each sample was collected and centrifuged (Sorval MC 12C centrifuge, Fisher Scientific, USA) for 2 minutes. Then, 0.8 mL of the supernatant was pipetted into a 30 mL Nalgene bottle. Since the extracts were to be analyzed for metals, 1 mL of 1N nitric acid was added to acidify to pH < 2 to preserve the samples, and the volume was completed to a total of 10 mL with reagent water. All the collected extracts were stored at approximately 4°C until the analysis.

When the extraction was started, it was noticed that the samples formed a deposit at the bottom of the bottles and that it was not mixing very well, so for the last 45 minutes of the extraction, the shaking speed was increased to 250 rpm. At that speed, everything was mixed and shaken perfectly. The temperature stayed constant to ~ 26°C during the whole extraction process.

Once the extraction time was over, the samples were filtered through glass microfiber filters, GF series, grade GF/F, diameter 9.0 cm, pore size of 0.7 μm, part number 1825-090, from Fisher Scientific Company (Ottawa, Ontario, Canada), the pH of all the samples was recorded, and 1N nitric acid was added to each of them to lower their pH below 2. Refer to Table 4-4 for all the recorded values and quantities of nitric acid added.

Table 4-4: pH of extracts after 20 hours and after acidification.

Sample name	pH after 20 hours	HNO_3 added (mL)	pH after acidification
Extraction fluid #1	5.03	6.0	1.76
OECD soil	5.07	6.0	1.64
PACS-2	5.21	6.0	1.89
Mine soil 1	5.84	7.0	1.72
Mine soil 2	5.27	6.2	1.94
Mine soil 3	5.04	6.0	1.88

The analysis of the extracts was performed with an inductively coupled plasma – atomic emission spectroscopy instrument (ICP-AES), model IRIS 13283300, from Thermo Jarrell Ash Corporation (Franklin, Massachusetts, USA), using both external standards and standard additions calibrations. Standards of 1 µg/mL, 10 µg/mL and 100 µg/mL were prepared using a multi-element standard stock solution of 100 µg/mL in 5% nitric acid, lot SC2295912, a tin standard stock solution of 1000 µg/mL in 20% hydrochloric acid, lot SC1312548, and a mercury standard stock solution of 1000 µg/mL in 10% nitric acid, lot SC2050114, all from SCP Science (Baie d'Urfé, Québec, Canada).

The extracts were prepared for analysis according to the following procedure. For the six samples obtained after 20 hours, 8 grams of each were weighted accurately with an analytical balance, and 1 gram of reagent water was added. These samples were used as blanks. Then, another 8 grams of each were weighed to which 1 gram of the 10 µg/mL standard was added. These samples were analyzed right after their corresponding blanks. For the 24 samples obtained after 1, 2, 3, and 4 hours of extraction, 4 grams of each were weighed accurately with an analytical balance, and 1 gram of reagent water was added. These samples were used as blanks. Then, another 4 grams of each were weighed to which 1 gram of the 10 µg/mL standard was added. These samples were analyzed right after their corresponding blanks.

Lines that were used on the instrument for each element are presented in Table 4-5, and Table 4-6 lists the operating conditions for the instrument.

Table 4-5: ICP-AES lines used for analysis of extracts from the first extraction.

Element	Wavelength (nm)	Order
Arsenic	189.042	138
Arsenic	193.759	134
Arsenic	197.262	132
Cadmium	214.438	121
Cadmium	226.502	115
Cadmium	228.802	114
Chromium	267.716	97
Chromium	283.563	92
Copper	224.700	116
Copper	324.754	80
Copper	327.396	80
Mercury	184.950	140
Mercury	194.227	134
Mercury	253.652	103
Lead	220.353	118
Tin	189.989	137
Tin	242.949	107
Zinc	206.200	126
Zinc	213.856	122

Table 4-6: Plasma operating parameters.

Parameter	Setting
Plasma power	1150 W
Plasma gas flow	15 L/min
Auxiliary gas flow	0.5 L/min
Nebulizer gas flow	1.0 L/min
Pump rate	100 rpm
Sample uptake	1.5 mL/min
Number of readings	3 repeats / line
Flush time	30 s

Since it was observed that the samples were not mixed properly throughout the extraction process, it can be assumed that the results would not be appropriate to rely on. Therefore, these results will not be discussed, but they are available on CD and partly in Appendix A.

4.3.5 Second Experimental Procedure

Since it was observed during the first extraction experiment that the samples were not mixing very well on the shaker at the set speed, a second extraction experiment was performed by keeping all parameters of the first experiment except that the shaking speed of the Orbital Shaker was set at 200 rpm instead of 100 rpm. Also, the number of samples extracted was modified to have at least three replicates of PACS-2 marine sediment sample and only 1 bottle of extraction solution instead of 2. Refer to Table 4-7 for the exact amount of samples used. Finally, the total extraction time of 20 hours was changed to 48 hours in order to be able to detect more easily if a plateau was reached for the concentration of metals extracted. The ambient temperature at the start of the extraction was 26.7°C.

Table 4-7: Amount of sample used for the second round of extractions.

Sample name	Weight (g)
OECD soil	5.0002
PACS-2 #1	5.0009
PACS-2 #2	5.0129
PACS-2 #3	4.9981
Mine soil #1	5.1028
Mine soil #2	5.0296
Mine soil #3	5.0212

After 1, 2, 4, 8, 23, 27 and 31 hours, 1 mL of each sample was collected and centrifuged (Sorvall MC 12C centrifuge, Fisher Scientific, USA) for 3-4 minutes. Then, 0.8 mL of the supernatant was pipetted into a 30 mL Nalgene bottle. Since the extracts were to be analyzed for metals, 1 mL of 1N nitric acid was added to acidify to pH < 2 to preserve the sample, and the volume was completed to a total of 10 mL with 8.2 mL of reagent water. All the collected extracts were stored at approximately 4°C until the analysis.

Once the extraction time was over, the remaining samples were centrifuged (Sorvall RC 5C Plus centrifuge, Mandel Scientific Co. Ltd., Guelph, Ontario, Canada), instead of being filtered as in the first round of extraction, at 5000 rpm for 15 minutes. The supernatant was collected and the pH of all the samples was recorded, and 1N nitric acid was added to each of them to lower their pH below 2. Refer to Table 4-8 for all the recorded values and quantities of nitric acid added.

Table 4-8: pH of extracts after 48 hours and after acidification.

Sample name	pH after 48 hours	HNO_3 added (mL)	pH after acidification
Extraction fluid	4.96	7.0	1.79
OECD soil	4.93	2.1	1.87
PACS-2 #1	5.01	6.0	1.64
PACS-2 #2	5.03	5.0	1.67
PACS-2 #3	5.03	4.5	1.69
Mine soil #1	6.00	6.0	1.89
Mine soil #2	6.05	6.0	1.56
Mine soil #3	6.08	6.0	1.80

The analysis of the extracts was performed with an inductively coupled plasma – atomic emission spectroscopy instrument (ICP-AES), model IRIS 13283300, from Thermo Jarrell Ash Corporation (Franklin, Massachusetts, USA), using both external standards and standard additions calibrations. Standards of 0.1 µg/mL, 1 µg/mL, 5 µg/mL, 10 µg/mL and 15 µg/mL were prepared using a multi-element standard stock solution of 100 µg/mL in 5% nitric acid, lot SC2295912, a tin standard stock solution of 1000 µg/mL in 20% hydrochloric acid, lot SC1312548, and a mercury standard stock solution of 1000 µg/mL in 10% nitric acid, lot SC2050114, all from SCP Science (Baie d'Urfé, Québec, Canada).

The extracts were prepared for analysis according to the following procedure. For the eight samples obtained after 48 hours, 8 grams of each were weighed accurately with an analytical balance, and 1 gram of nitric acid 10% was added. These samples were used as blanks. Then, another 8 grams of each were weighed to which 1 gram of the 10 μg/mL standard was added. These samples were analyzed right after their corresponding blanks. For the 56 samples obtained after 1, 2, 4, 8, 23, 27 and 31 hours of extraction, 4 grams of each were weighed accurately with an analytical balance, and 1 gram of nitric acid 10% was added. These samples were used as blanks. Then, another 4 grams of each were weighed to which 1 gram of the 10 μg/mL standard was added. These samples were analyzed right after their corresponding blanks.

Lines that were used on the instrument for each element are presented in Table 4-9, and Table 4-10 lists the operating conditions for the instrument.

Table 4-9: ICP-AES lines used for analysis of extracts from the second extraction.

Element	Wavelength (nm)	Order
Arsenic	189.042	138
Arsenic	193.759	134
Arsenic	197.262	132
Cadmium	214.438	121
Cadmium	226.502	115
Cadmium	228.802	114
Chromium	267.716	97
Chromium	283.563	92
Copper	224.700	116
Copper	324.754	80
Copper	327.396	80
Mercury	253.652	103
Lead	182.203	143
Lead	220.353	118
Tin	189.989	137
Tin	242.949	107
Tin	242.949	108
Tin	283.999	92
Zinc	206.200	126
Zinc	213.856	122

Table 4-10: Plasma operating parameters.

Parameter	Setting
Plasma power	1150 W
Plasma gas flow	15 L/min
Auxiliary gas flow	0.5 L/min
Nebulizer gas flow	1.0 L/min
Pump rate	100 rpm
Sample uptake	1.5 mL/min
Number of readings	3 repeats / line (4 repeats / line for the 48h samples, blanks and standards)
Flush time	45 s
Purge time	90 s

The results for the concentrations obtained after 1, 2, 4, 8, 23, 27, 31 and 48 hours of extraction for each element analyzed in PACS-2 marine sediment sample #2 are presented in Figure 4-1, Figure 4-2, Figure 4-3, Figure 4-4, Figure 4-5, and Figure 4-6 . Mercury and lead results are not presented since it is suspected that the concentrations were below the detection limits.

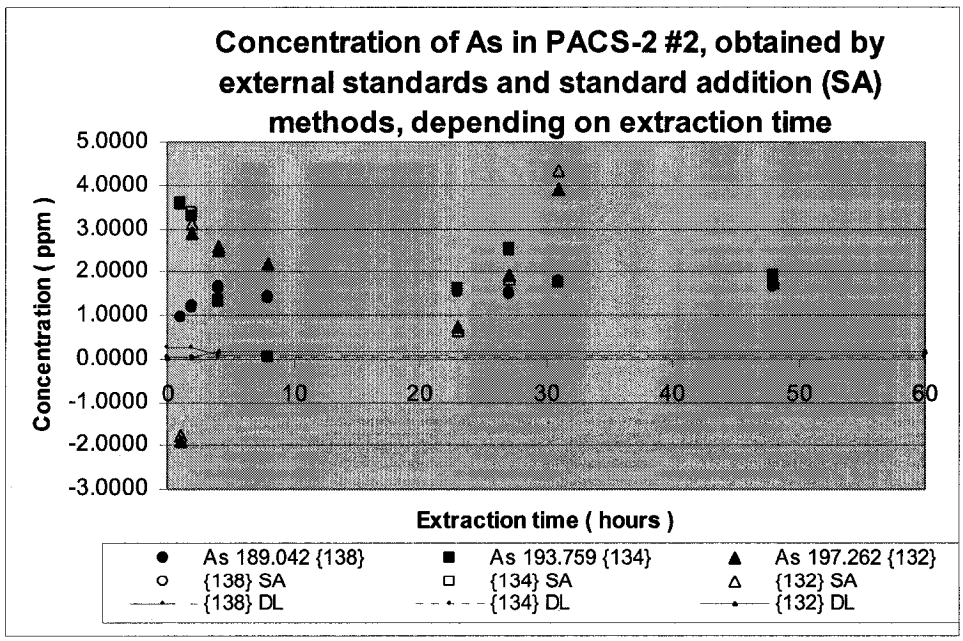


Figure 4-1: Concentrations of arsenic obtained after each timepoint with the ICP-AES instrument using external standards and standard additions methods. DL=detection limit.

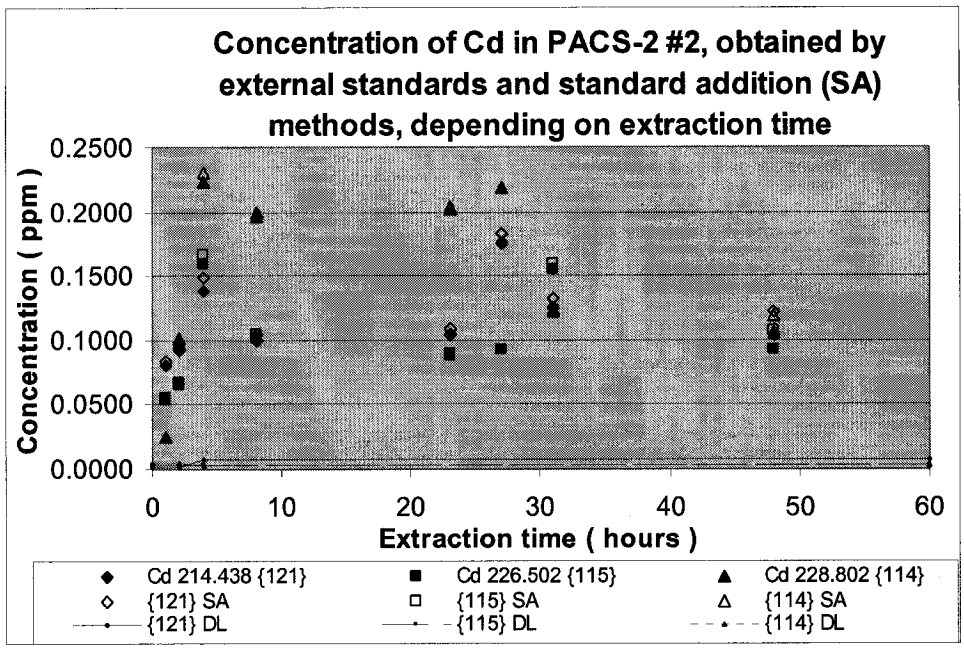


Figure 4-2: Concentrations of cadmium obtained after each timepoint with the ICP-AES instrument using external standards and standard additions methods. DL=detection limit.

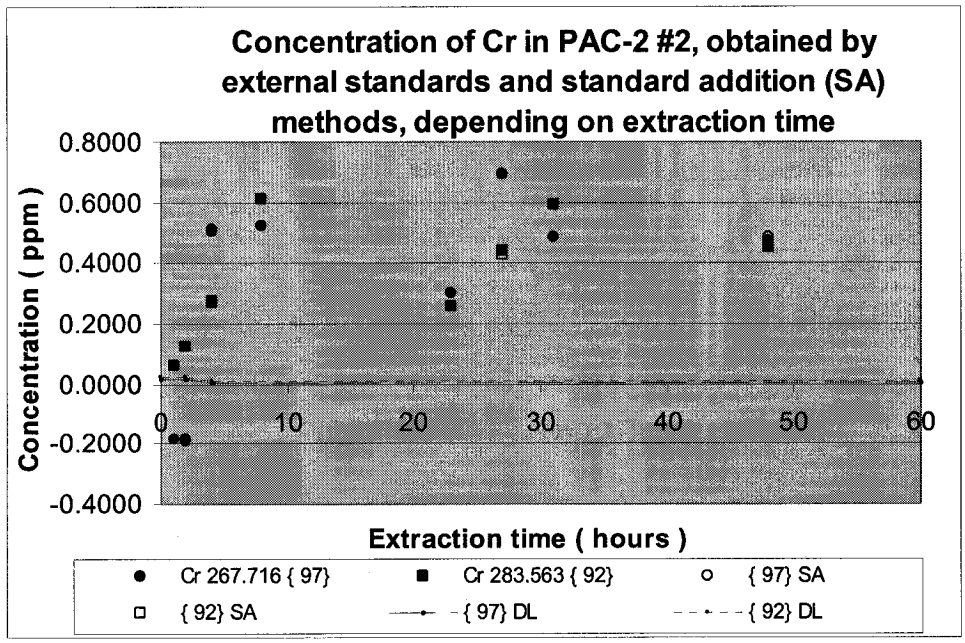


Figure 4-3: Concentrations of chromium obtained after each timepoint with the ICP-AES instrument using external standards and standard additions methods. DL=detection limit.

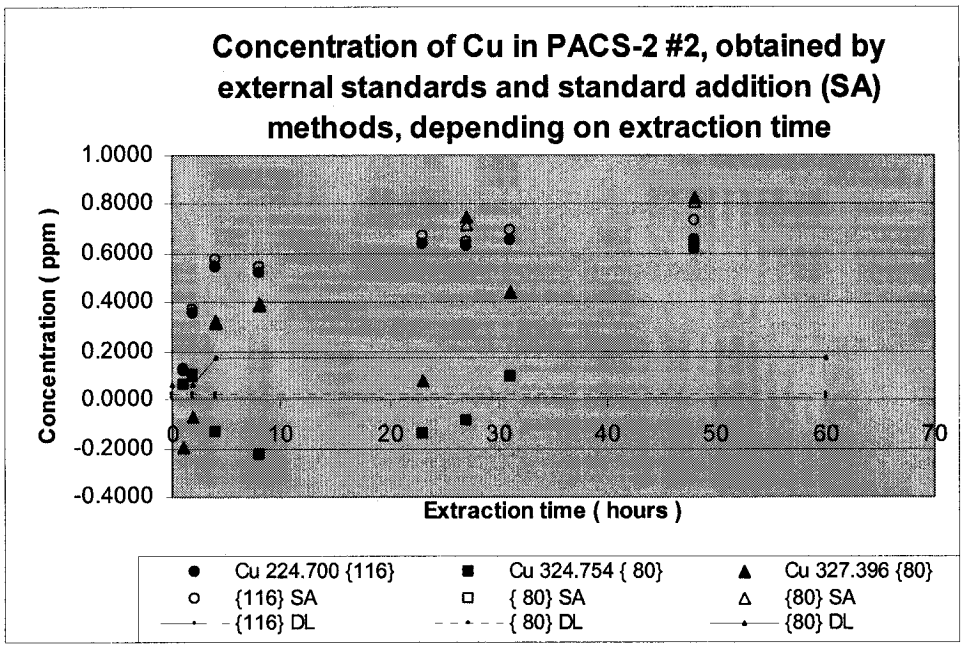


Figure 4-4: Concentrations of copper obtained after each timepoint with the ICP-AES instrument using external standards and standard additions methods. DL=detection limit.

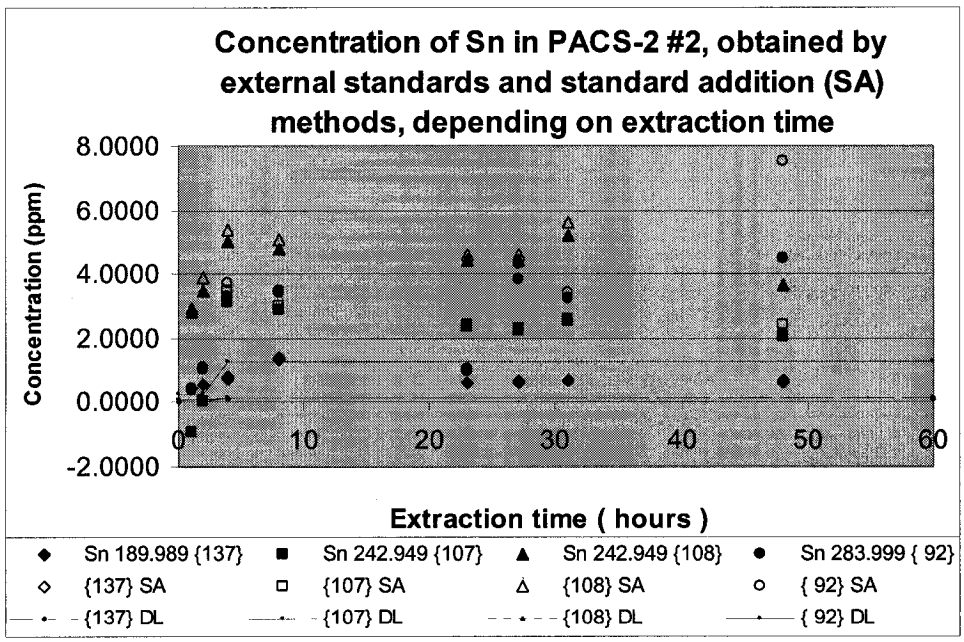


Figure 4-5: Concentrations of tin obtained after each timepoint with the ICP-AES instrument using external standards and standard additions methods. DL=detection limit.

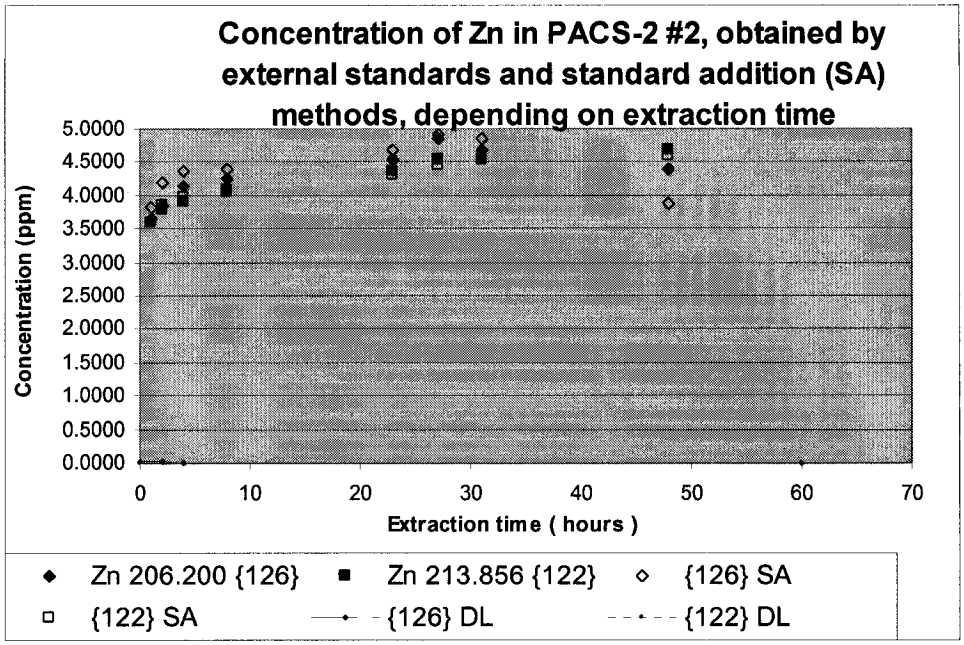


Figure 4-6: Concentrations of zinc obtained after each timepoint with the ICP-AES instrument using external standards and standard additions methods. DL=detection limit.

As can be seen for most of the graphs obtained, there is no clear trend, like a stabilization of the concentrations, that indicates that the extraction was completed. However, for certain elements, like zinc, cadmium (line 226.502 nm), copper (line 224.700 nm) and tin (line 283.999 nm), a clear logarithmic trend can be seen, sometimes by leaving 1 or 2 points out of the curve. If one takes into consideration the noise and the random error that could influence the concentrations, maybe this logarithmic trend could be seen in more graphs.

In general, the concentrations obtained by external standards and standard additions agree, with a slope of almost 1 (0.9155), as Figure 4-7 shows for the 48-hour extraction timepoint for the average PACS-2 samples (n=3). In the case of tin (Sn), the standard additions method gave a higher concentration, showing a possibility that for this element, some matrix effects were affecting the results and that these effects could possibly be overcome by the use of the standard additions method. Also, a statistical comparison (see Table 4-11), between the average results (n=3) obtained for the PACS-2 samples after 48 hours of extraction with external standards and standard additions methods, shows that statistically, the two methods agree most of the time except for cadmium and lead. The detailed calculation is presented on page 93 of this document. Based on Figure 4-7 and Table 4-11, it can be assumed the procedure applied on the samples gave reproducible results that could eventually be used as a reference to compare the extraction samples that would be obtained with the flow-through cell and analyzed by ICP-AES.

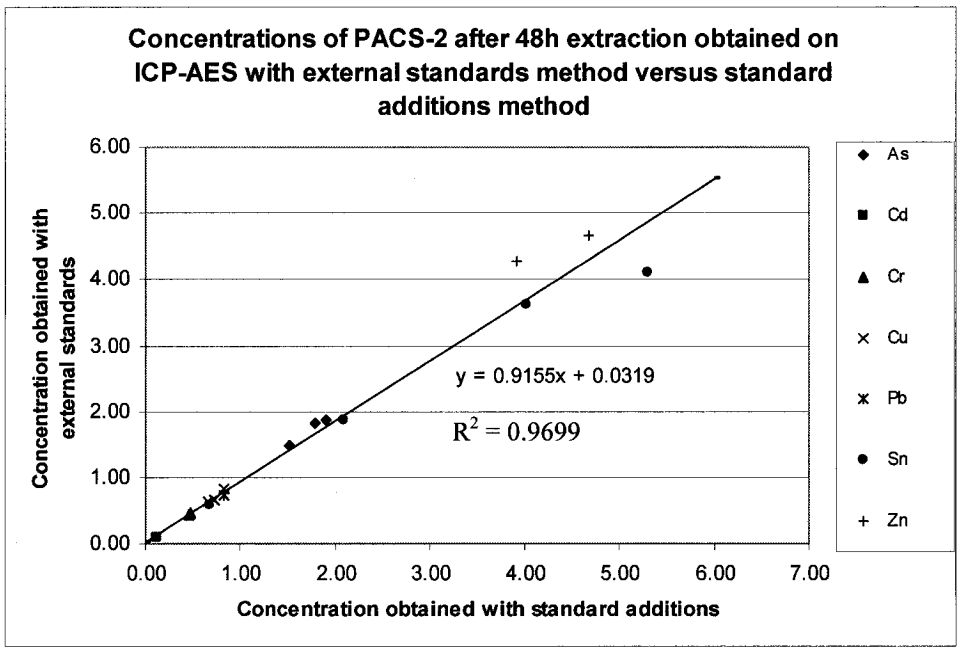


Figure 4-7: Correlation between concentrations obtained by external standards and standard additions methods.

Table 4-11: Statistical difference between average results obtained by external and internal standards methods for PACS-2 (n = 3) after 48 hours of extraction.

Average PACS-2 results at 48 hours		Ext. Std Mean	Ext. Std Std. Dev.	Std. Add Mean	Std. Add Std. Dev.	Pooled variance (S^2_{12})	Estimated Std. Dev. (S_D)	delta x	For N1+N2-2 degrees of freedom and at 95% CL tS_D	Is the difference significant ?
As	189.042 {138}	1.49	0.14	1.51	0.25	4.07E-02	0.14	0.02	0.28	NO
As	193.759 {134}	1.86	0.18	1.90	0.12	2.39E-02	0.11	0.03	0.21	NO
As	197.262 {132}	1.82	0.05	1.79	0.05	2.43E-03	0.03	0.04	0.07	NO
Cd	214.438 {121}	0.11	0.00	0.12	0.00	8.83E-06	0.00	0.02	0.00	YES
Cd	226.502 {115}	0.09	0.00	0.11	0.00	1.93E-05	0.00	0.02	0.01	YES
Cd	228.802 {114}	0.10	0.01	0.11	0.01	5.22E-05	0.01	0.01	0.01	YES
Cr	267.716 { 97}	0.46	0.02	0.48	0.02	4.04E-04	0.01	0.02	0.03	NO
Cr	283.563 { 92}	0.45	0.02	0.46	0.02	3.88E-04	0.01	0.01	0.03	NO
Cu	224.700 {116}	0.65	0.02	0.73	0.03	8.27E-04	0.02	0.08	0.04	YES
Cu	324.754 { 80}	0.63	0.03	0.66	0.04	1.06E-03	0.02	0.03	0.04	NO
Cu	327.396 { 80}	0.82	0.05	0.83	0.07	3.67E-03	0.04	0.00	0.08	NO
Hg	253.652 {103}	0.79	0.92	0.98	1.13	1.06E+00	0.73	0.19	1.41	NO
Pb	182.203 {143}	5.24	0.88	-19.06	40.02	8.01E+02	20.01	24.30	38.83	NO
Pb	220.353 {118}	0.73	0.05	0.83	0.07	3.99E-03	0.04	0.09	0.09	YES
Sn	189.989 {137}	0.59	0.02	0.68	0.03	7.28E-04	0.02	0.09	0.04	YES
Sn	242.949 {107}	1.86	0.16	2.10	0.33	6.66E-02	0.18	0.23	0.35	NO
Sn	242.949 {108}	3.63	0.03	4.01	0.33	5.41E-02	0.16	0.38	0.32	YES
Sn	283.999 { 92}	4.12	0.37	5.30	1.95	1.97E+00	0.99	1.18	1.92	NO
Zn	206.200 {126}	4.28	0.09	3.91	0.26	3.79E-02	0.14	0.37	0.27	YES
Zn	213.856 {122}	4.66	0.06	4.68	0.12	8.69E-03	0.07	0.02	0.13	NO

The analysis of the extracts was also performed with an inductively coupled plasma – mass spectrometry instrument (ICP-MS), model ELAN 6000 (serial number 4919804), from Perkin Elmer Sciex (Concord, Ontaria, Canada), using both external standards and internal standards calibrations. Standards of 5 ng/mL, 20 ng/mL, 100 ng/mL, 200 ng/mL and 1000 ng/mL containing 10 ng/mL of rhodium (Rh) and thallium (Tl) internal standards were prepared using a multi-element standard stock solution of 100 µg/mL in 5% nitric acid, lot SC2295912, a tin standard stock solution of 1000 µg/mL in 20% hydrochloric acid, lot SC1312548, a mercury standard stock solution of 1000 µg/mL in 10% nitric acid, lot SC2050114, a rhodium standard stock solution of 1000 µg/mL and a thallium standard stock solution of 1000 µg/mL, all from SCP Science (Baie d'Urfé, Québec, Canada). For rhodium and thallium, a stock solution of 0.4 µg/mL was

prepared and this solution was added to each standard and sample to give a concentration of 10 ng/mL. It was noticed afterwards that thallium should not have been used as an internal standard since it was present in the PACS-2 marine sediment and in the multi-element standard stock solution used to prepare the standards. Therefore, only rhodium will be used as an internal standard reference.

The extracts were prepared for analysis according to the following procedure. For all the samples obtained, 1 gram of each was weighed accurately with an analytical balance (except the PACS-2 samples obtained after 48 hours for which only 0.5 gram was weighed due to their higher concentration), 0.1 gram of the 0.4 μg/mL internal standard solution was added and the total volume completed with 3 grams of nitric acid 10%.

Isotopes that were used on the instrument for each element are presented in Table 4-14, and Table 4-12 and Table 4-13 list the operating conditions of the instrument.

Table 4-12: ICP-MS operating parameters.

Parameter	Setting
Plasma power	1100 W
Plasma gas flow	15 L/min
Auxiliary gas flow	1.2 L/min
Nebulizer gas flow	0.8 to 0.825 L/min
Sampling and skimmer cones	Nickel

Table 4-13: ICP-MS signal measuring parameters.

Parameter	Setting
Detector mode	Dual
Acquisition mode	Peak hopping
Sweeps per reading	5
Readings per replicate	1
MCA channels	1
Dwell time	100 ms

Table 4-14: ICP-MS isotopes used for analysis of extracts from the second extraction experiment.

Element	Isotope	Relative Abundance
Arsenic	75	100
Cadmium	110	12.49
Cadmium	111	12.80
Cadmium	113	12.22
Chromium	52	83.789
Chromium	53	9.501
Copper	63	69.17
Copper	65	30.83
Mercury	199	16.87
Mercury	200	23.10
Mercury	201	13.18
Mercury	202	29.86
Lead	206	24.1
Lead	207	22.1
Lead	208	52.4
Tin	117	7.68
Tin	118	24.23
Tin	119	8.59
Tin	120	32.59
Zinc	66	27.9
Zinc	67	4.1
Zinc	68	18.8

Even if the external standards calibration was done, the results, as can be seen in Figures 4-9 to 4-16, are questionnable, especially for zinc where the results obtained with internal standards are much higher. Therefore, it will be considered that the results obtained with the internal standard method are more reliable. The results for the concentrations obtained after 1, 2, 4, 8, 23, 27, 31 and 48 hours of extraction for each element analyzed in PACS-2 marine sediment sample #3 are presented in Figure 4-9, Figure 4-10, Figure 4-11, Figure 4-12, Figure 4-13, Figure 4-14, Figure 4-15, and Figure 4-16. The correlation coefficients of all the calibration curves obtained on November 19, 2003, for each element and each mass analyzed are presented in Table 4-15. An example of a graph representing the calibration curves obtained for tin on that same date is shown in Figure 4-8.

Table 4-15: Calibration curves from November 19, 2003 with Rh^{103} as internal standard.

Element	Mass	R^2
As	75	0.9982
Cd	110	0.9995
	111	0.9997
	113	0.9997
Cr	52	1.0000
	53	0.9999
Cu	63	0.9997
	65	0.9998
Hg	199	0.9965
	200	0.9974
	201	0.9974
	202	0.9972
Pb	206	0.9997
	207	0.9998
	208	0.9998
Sn	117	0.9998
	118	0.9996
	119	0.9999
	120	0.9997
Zn	66	0.9939
	67	0.9952
	68	0.9937

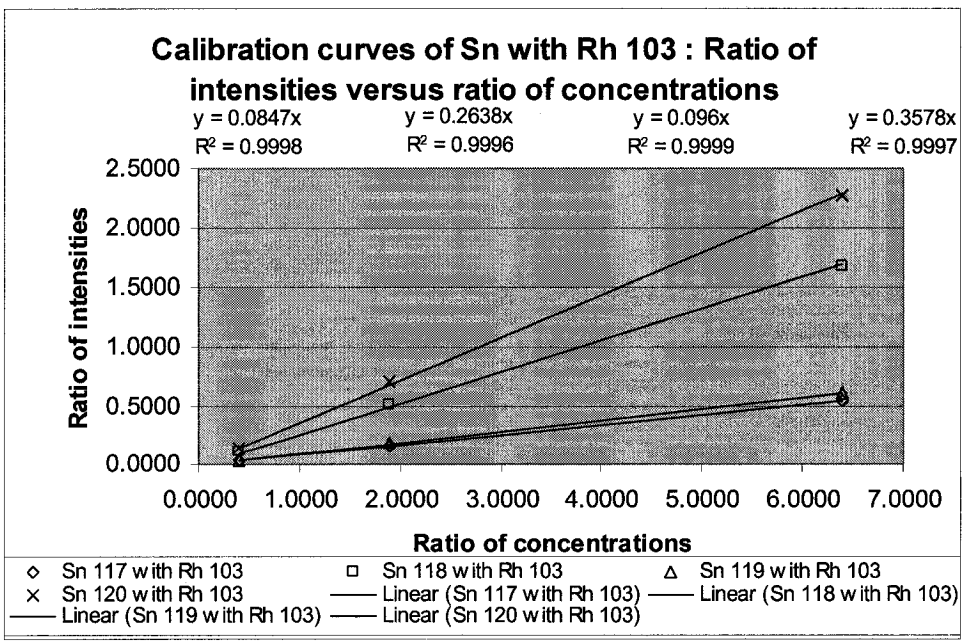


Figure 4-8: Calibration curves of tin (Sn) with Rh^{103} as internal standard.

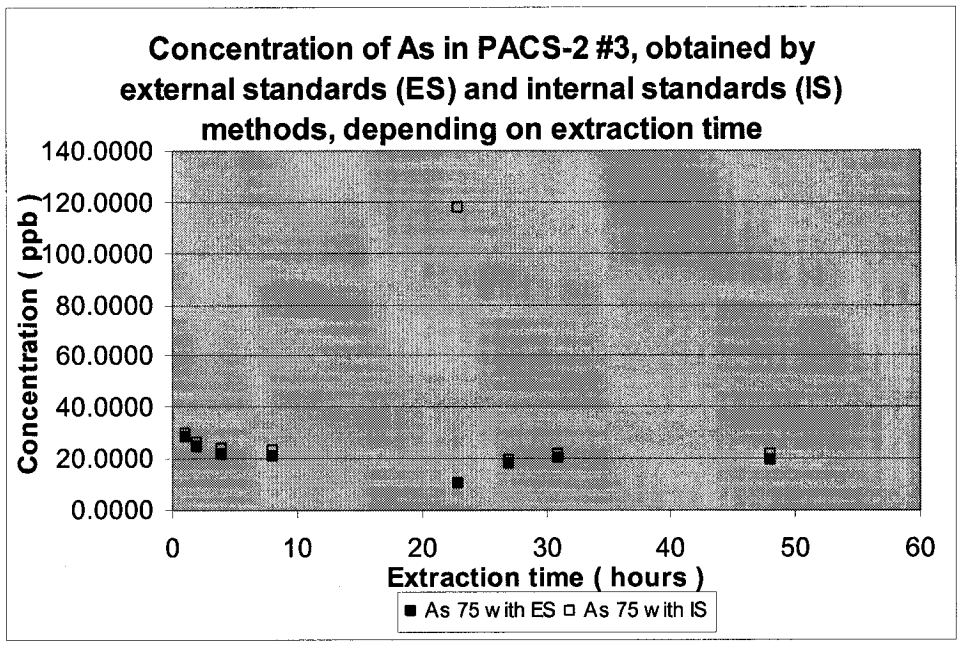


Figure 4-9: Concentrations of arsenic obtained after each timepoint with the ICP-MS instrument using external standards and internal standard methods.

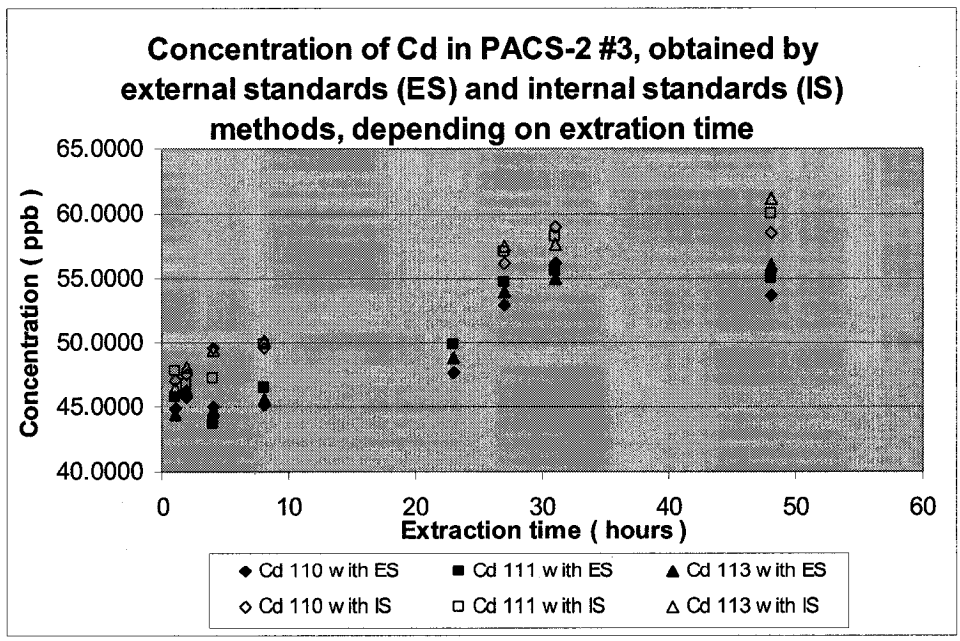


Figure 4-10: Concentrations of cadmium obtained after each timepoint with the ICP-MS instrument using external standards and internal standard methods.

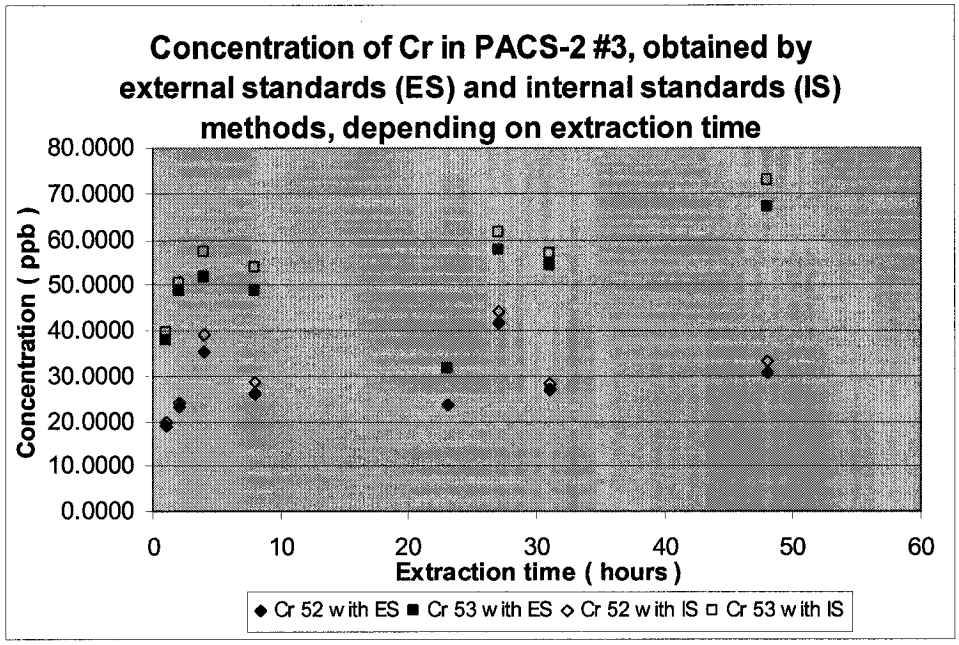


Figure 4-11: Concentrations of chromium obtained after each timepoint with the ICP-MS instrument using external standards and standard addition methods.

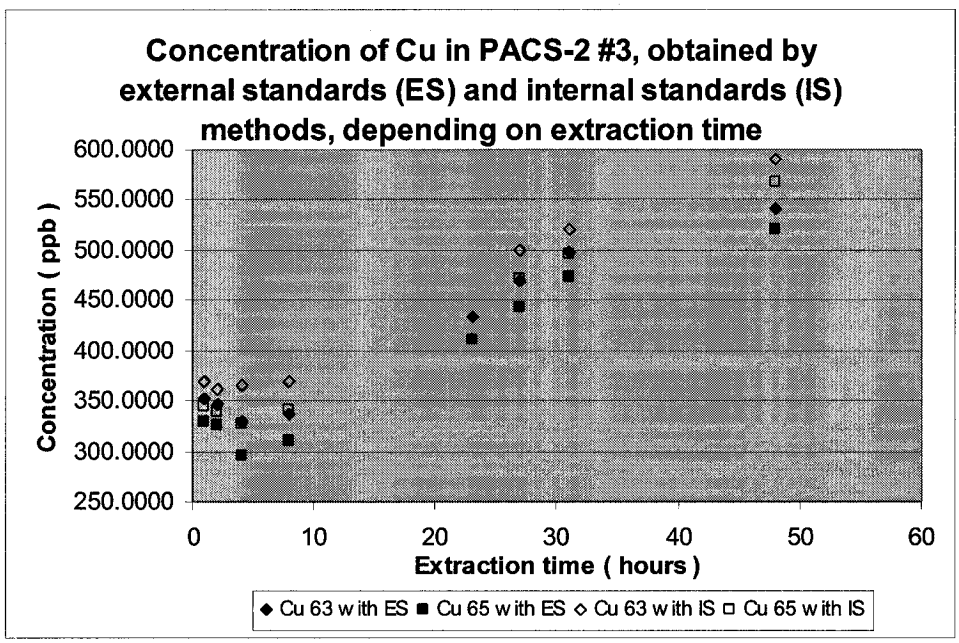


Figure 4-12: Concentrations of copper obtained after each timepoint with the ICP-MS instrument using external standards and internal standard methods.

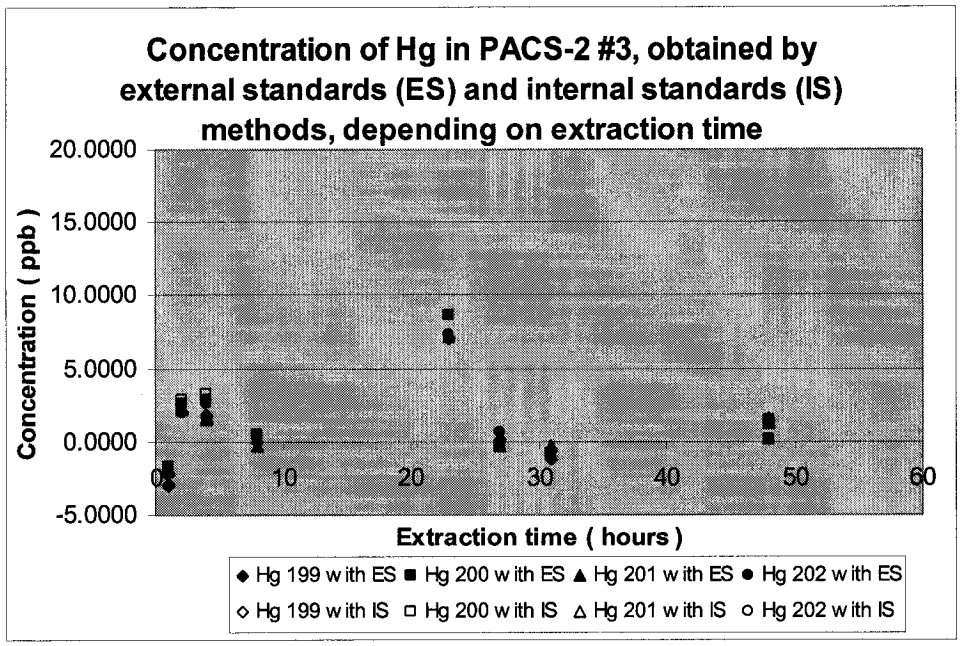


Figure 4-13: Concentrations of mercury obtained after each timepoint with the ICP-MS instrument using external standards and internal standard methods.

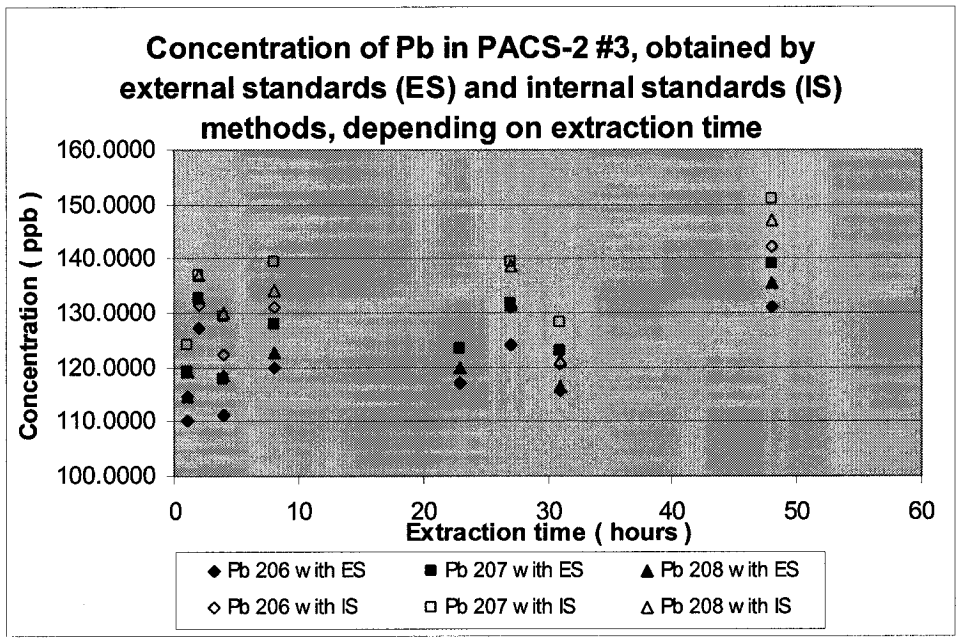


Figure 4-14: Concentrations of lead obtained after each timepoint with the ICP-MS instrument using external standards and internal standard methods.

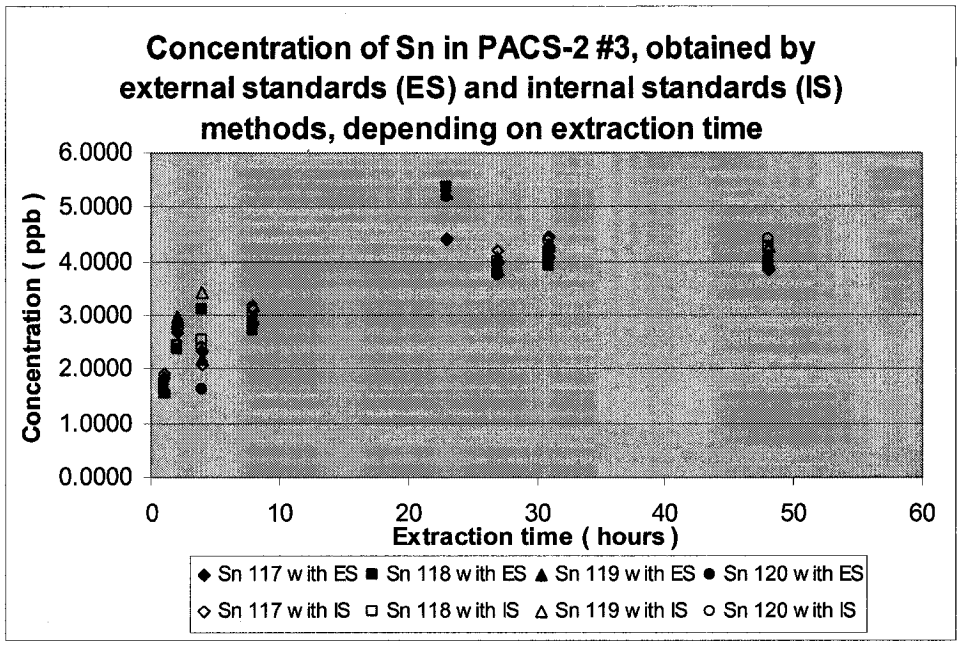


Figure 4-15: Concentrations of tin obtained after each timepoint with the ICP-MS instrument using external standards and internal standard methods.

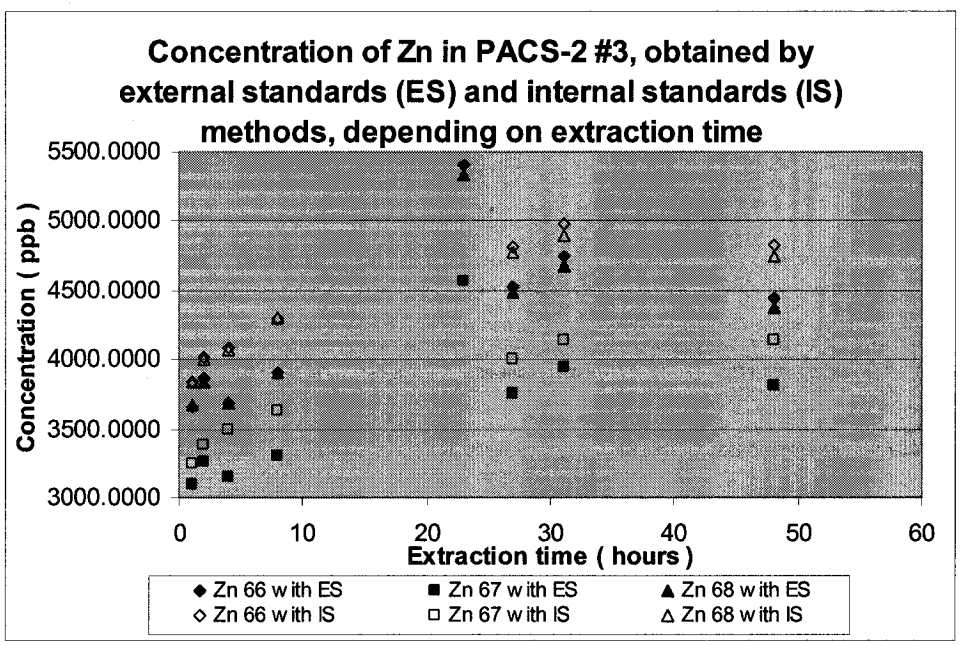


Figure 4-16: Concentrations of zinc obtained after each timepoint with the ICP-MS instrument using external standards and internal standard methods.

As can be seen for most of the graphs obtained, there is now a more defined trend than with the ICP-AES results. For most of the elements, an increase, sometimes ending with a plateau, is observed. This might be a proof that since the detection limits are lower with the ICP-MS, these results are more reliable. For arsenic and mercury though, a decrease in concentration is observed and everything seems to be extracted in less than 1 hour. Since they are volatile species, it could explain why the concentrations were decreasing and why there is no general trend observed. In general, if one looks at Table 4-16, the time to extract approximately 90% of the elements is lower than or equal to ~20 hours, so it is not necessary to run the procedure for a longer time, except for copper and cadmium. These two elements might be bound more strongly to the matrix or just be trapped deeper in the interstices of the matrix.

Table 4-16: Times to get ~50 and 90% of the elements extracted.

Element	Time ~50% extracted (hours)	Time ~90% extracted (hours)
As	< 1	< 1
Cd	~ 18	~ 30
Cr	~ 2	~ 5
Cu	~ 25	~ 48
Hg	< 1	< 1
Pb	~ 4	~ 8
Sn	~ 8	~ 20
Zn	~ 15	~ 22

Also, to prove the point mentioned earlier about the questionability of external standards results, a statistical comparison between both methods results was performed. First, the pooled variance of the two data sets was calculated to compare the means of the two series of measurements ($mean_1$ of N_1 observations and $mean_2$ of N_2 observations), using equation (2), S_1 and S_2 being the estimated standard deviations for the first and the second series of measurements, respectively.

$$S_{12}^2 = \frac{\{(N_1 - 1) S_1^2 + (N_2 - 1) S_2^2\}}{N_1 + N_2 - 2} \qquad (2)$$

Then, an estimated standard deviation in the difference between the two means, S_D, is calculated using equation (3).

$$S_D = S_{12} \sqrt{\frac{1}{N_1} + \frac{1}{N_2}} \qquad (3)$$

Finally, delta x (delta x = | $mean_1$ – $mean_2$ |) and tS_D at a 95% confidence level (the number of degrees of freedom being (N_1 + N_2 – 2) are calculated. For the number of degrees of freedom equal to 4 (3 + 3 – 2), the value obtained from the statistics tables is 2.78, while for the number of degrees of freedom equal to 2 (2 + 2 – 2), the value is 4.3. The value for tS_D is obtained by multiplying the appropriate value (2.78 or 4.3) by the estimated standard deviation (S_D). If delta x is higher than tS_D, then the difference between the two sets of measurements is significant. Results of this statistical comparison can be consulted in Table 4-17.

Table 4-17: Statistical difference between average results obtained by external and internal standards methods for PACS-2 (n = 3) after 48 hours of extraction.

	Ext. Std		Int. Std.		Pooled variance	Estimated Std. Dev.		For N1+N2-2 degree of freedom and at 95% CL	Is the difference significant?
	Average	Std. Dev.	Average	Std. Dev.	(S^2_{12})	(S_D)	delta x	tS_D	
As 75	17.95	1.90	19.82	1.97	3.76	1.58	1.87	4.40	NO
Cd 110	53.33	0.69	58.69	0.78	0.54	0.60	5.36	1.67	YES
Cd 111	54.55	0.72	60.01	0.73	0.52	0.59	5.46	1.64	YES
Cd 113	54.78	1.32	60.26	1.13	1.50	1.00	5.48	2.78	YES
Cr 52	28.07	2.96	30.80	3.09	9.13	2.47	2.73	6.86	NO
Cr 53	56.13	15.79	61.62	17.11	271.10	13.44	5.48	37.37	NO
Cu 63	535.50	9.03	588.39	7.38	67.98	6.73	52.89	18.71	YES
Cu 65	512.60	8.14	562.96	4.91	45.20	5.49	50.36	15.26	YES
Hg 199	1.52	0.60	1.68	0.67	0.40	0.52	0.16	1.44	NO
Hg 200	0.51	0.59	1.70	0.61	0.36	0.49	1.19	1.36	NO
Hg 201	1.44	0.42	1.59	0.48	0.20	0.37	0.15	1.02	NO
Hg 202	1.56	0.57	1.72	0.64	0.36	0.49	0.17	1.37	NO
Pb 206	120.74	9.62	132.15	9.70	93.33	7.89	11.41	21.93	NO
Pb 207	128.91	9.52	141.09	9.59	91.24	7.80	12.18	21.68	NO
Pb 208	124.85	10.12	136.65	10.31	104.41	8.34	11.80	23.19	NO
Sn 117	2.75	1.11	3.00	1.20	1.34	0.94	0.26	2.63	NO
Sn 118	2.77	1.65	3.01	1.77	2.92	1.71	0.24	7.35	NO
Sn 119	2.94	1.07	3.21	1.16	1.24	0.91	0.27	2.53	NO
Sn 120	2.86	1.20	3.12	1.29	1.55	1.02	0.26	2.82	NO
Zn 66	4489.33	43.66	4922.40	91.48	5136.87	58.52	433.07	162.69	YES
Zn 67	3821.51	28.91	4191.22	52.13	1776.57	34.41	369.72	95.67	YES
Zn 68	4419.73	44.22	4844.64	89.16	4952.66	57.46	424.91	159.74	YES

As per the previous table (Table 4-17), the difference between the results from external and internal standards methods is significant for cadmium, copper and zinc after 48 hours of extraction. It can also be seen in the concentration versus extraction time graphs where the concentrations obtained with internal standards are significantly above the ones obtained with external standards. But if we examine the statistical difference after each timepoint, see Table 4-18, overall, the two methods agree most of the time.

Table 4-18: Statistical difference between average results obtained by external and internal standards methods for PACS-2 (n = 3) after each timepoint of extraction.

Average of the 3 PACS-2 samples		Is the difference significant between external standards and internal standard results?							
		1h	2h	4h	8h	23h	27h	31h	48h
As	75	YES	NO	NO	YES	NO	NO	NO	NO
Cd	110	NO	NO	NO	NO	NO	NO	NO	YES
Cd	111	YES	NO	NO	NO	NO	NO	NO	YES
Cd	113	NO	NO	NO	NO	NO	YES	NO	YES
Cr	52	NO	NO	NO	NO	NO	NO	NO	NO
Cr	53	NO	NO	NO	NO	NO	NO	NO	NO
Cu	63	YES	NO	NO	NO	NO	NO	NO	YES
Cu	65	YES	NO	NO	NO	NO	NO	YES	YES
Hg	199	NO	NO	NO	NO	NO	NO	NO	NO
Hg	200	NO	NO	NO	NO	NO	NO	NO	NO
Hg	201	NO	NO	NO	NO	NO	NO	NO	NO
Hg	202	NO	NO	NO	NO	NO	NO	NO	NO
Pb	206	NO	NO	NO	YES	NO	NO	NO	NO
Pb	207	NO	NO	NO	YES	NO	NO	NO	NO
Pb	208	NO	NO	NO	YES	NO	NO	NO	NO
Sn	117	NO	NO	NO	NO	NO	NO	NO	NO
Sn	118	NO	NO	NO	NO	NO	NO	NO	NO
Sn	119	NO	NO	NO	NO	NO	NO	NO	NO
Sn	120	NO	NO	NO	NO	NO	NO	NO	NO
Zn	66	NO	NO	NO	NO	NO	NO	NO	YES
Zn	67	NO	NO	NO	NO	NO	NO	NO	YES
Zn	68	NO	NO	NO	NO	NO	NO	NO	YES

4.3.6 Comparison Between Results From ICP-AES and ICP-MS

After the first extraction experiments were done, another small experiment was performed with the extract of a PACS-2 sample obtained at the end of the extraction procedure (after 20 hours). This extract was analyzed again by ICP-AES and ICP-MS with both external standards and standard additions in order to be able to compare the performances of the two instruments. In general, the concentrations obtained, using standard additions method with both ICP-AES and ICP-MS, agree, with a slope of almost 1 (0.8896), as Figure 4-17 shows. In the case of arsenic (As) and cadmium (Cd), the two elements deviating the most, these deviations could be explained by the fact that the concentrations obtained by ICP-AES are approximately 3 times and 10 times higher than their detection

limits, respectively, thus introducing the possibility of having statistical uncertainty and noise.

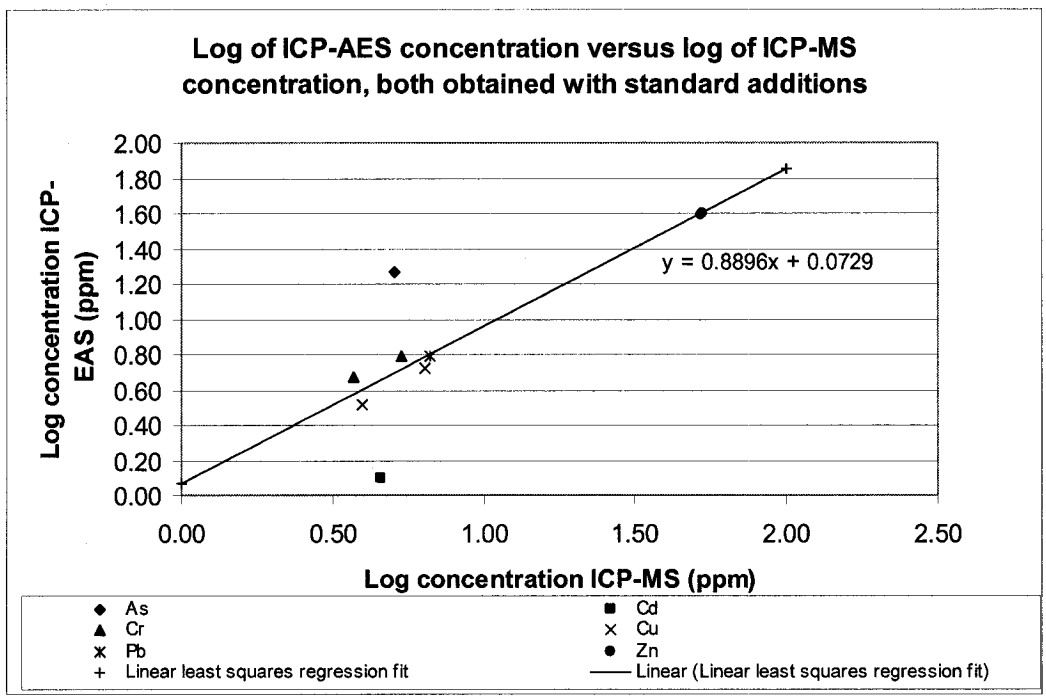


Figure 4-17: Comparison between both instruments results for standard additions.

4.4 Conclusion

For the first experimental procedure, since it was observed that the samples were not mixed properly throughout the extraction process, it can be assumed that the results would not be appropriate to rely on.

For the second experimental procedure, the results obtained by external standards and standard additions with ICP-AES did not show a clear logarithmic trend regarding the concentration versus extraction time, for most of the elements. Even if no clear trend was observed, the concentrations obtained by both methods seem to agree according to a statistical comparison and the slope obtained (almost 1) when comparing results from both methods. With ICP-MS, a logarithmic trend is observed for most of the elements, and a statistical comparison between the results obtained using external standards and those obtained using internal standards methods showed no significant difference. Even if for the second experimental procedure a 48-hour extraction was performed, there is no need of agitating more than ~20 hours, since for most of the elements monitored, a 90% extraction yield was achieved after this period.

When the performances of both instruments (ICP-AES and ICP-MS) are compared, a slope of almost 1 was obtained, which means that all the concentrations obtained agree more or less.

Overall, the results acquired can be kept to eventually be compared to results given by extracts obtained with the flow-through cell. If this experiment was to be repeated, it would be better to use ICP-AES coupled with external standards for elements with high concentrations, since the results would be less affected by matrix effects, and for low concentrations ICP-MS coupled with internal standards or standard additions would be best, since the detection limits are much lower than the ones obtained by ICP-AES.

4.5 References

1. EPA method 1311, *Toxicity Characteristic Leaching Procedure*, revision 0, July 1992.
2. "Isotopic Compositions of the Elements 1989" Pure Appl. Chem., Vol. 63, No. 7, pp. 991-1002, 1991. © 1991 IUPAC

Chapter 5 : Conclusions and Suggestions for Future Work

With the Teflon cell prototype, leaks were the main problem. Since the fittings were made out of PEEK, the Teflon of the cell was not able to compress the fittings enough to grasp the tubing, causing leaks. By building the second prototype out of PEEK, it solved all the problems encountered with the Teflon model. However, new problems came with that second cell. When the cell was brand new and a temperature experiment was done for the first time, the expansion or contraction of the PEEK caused the cell to seal up so it did not leak. As soon as the cell was cooled to room temperature and heated again a second time, it leaked through the bottom holes, meaning that there was a temperature stability problem of the material. Furthermore, after several cycles of heating and cooling of the cell, it was difficult disassemble all the pieces because of the expansion or contraction of the PEEK. This slight modification of the shape of the pieces generated a loss of the seal, thus causing leaks. Despite these problems, it was proven that this PEEK design could work at room temperature and under pressure, without leaking. It was unfortunate that this engineering problem could not be solved.

Another problem that was encountered was how to measure the temperature inside the cell. With the help of a thermocouple inserted inside the cell where the tubing should have been connected, it was possible to get an idea of how fast the interior of the cell would reach the desired temperature. Since these temperature measurements were done at ambient pressure and without any sample nor solution present in the cell, it did not reflect exactly what would happen during a real experiment. To solve this problem, one could try to embed a thermocouple directly inside the cell.

Regarding the experiments that were performed on real soil and sediment samples by applying the EPA method 1311 and by analyzing the extracts by ICP-AES and ICP-MS using external standards, standard additions and internal standards calibration methods, both instruments gave similar performances, as well as the three calibration methods. It was also observed on the concentration versus extraction time graphs that a 90% extraction yield was achieved for most of the elements after approximately 20 hours, so there was no need of continuing the extraction up to 48 hours. The results could thus be kept for future comparison with the extracts that would be obtained with the flow-through system.

At the beginning of this project, the microwave extraction was left aside because of certain problems, especially the one that metal could not be put inside a microwave, and also because it was difficult to measure the temperature inside a microwave since most of the temperature probes were made out of metal, thus causing sparks. It would still be an interesting concept to try though, since the cell that was built was metal-free. The major obstacle to this approach would be the slow heating since PEEK is an insulator, and the microwave would also have to be turned off to measure the temperature inside with a thermocouple. This would considerably slow down the experiment. Another possibility would be to step backwards and use a technique that was developed in Salin's laboratory by E. D. Salin and V. Karanassios[1], and further commercialized by CEM, which consisted of a coil incorporated in a microwave oven, in which a slurry could be introduced. All of these alternatives could be considered if one would want to carry-over this project.

5.1 References

1. V. Karanassios, F.H. Liu, B. Liu and E.D. Salin, *JAAS* **6(7)**, 527-533, (1991).

Appendix A

Results Obtained With ICP-AES For The First Experimental Procedure

All the results can be viewed on the CD in the Excel file "***Soil extraction data 100203.xls***". The tables and explanations presented below are samples of what can be found in this file.

First tab name: Conc. of samples & stds

All the samples and standards were prepared gravimetrically (by weighing them) instead of relying on volume measurements, so under this tab, all the weights were recorded: weight of bottles, multi-element or single element solutions added, water, spike, sample, and total weight. The different dilution factors and the exact concentration of each element in the standards were calculated.

Second tab name: Raw data

This tab contains the raw data that was obtained directly from the ICP-AES. Here is what it looks like.

[Sample Header]
Method=JA131202
SampleName=PACS-2 20h Blank
Operator=
Comment=
CustID=
CustSmpl=
LabID=
Run Time=12/13/2002 17:35
Sample Type=Unk
Mode=INT
CorrFactor=1.000000
Repeats=3

[Results]

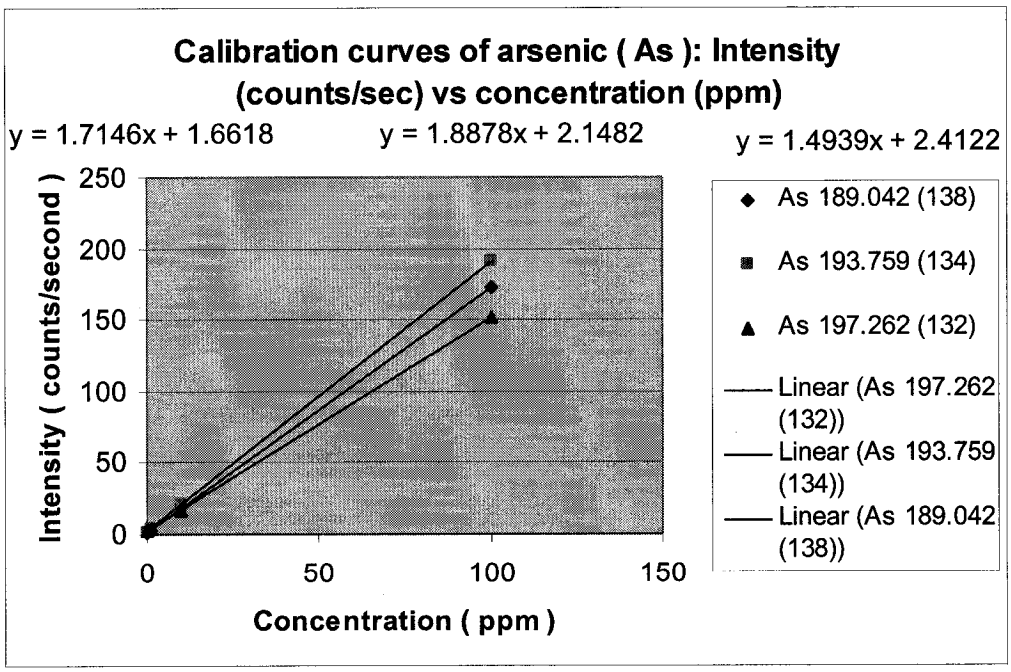
;Format=elem	wl	ISRef	inst	units	avg	stddev	%rsd	rep1..repn		
Elem0=As1890	189.042 {138}			Cts/S	3.011	0.2909	9.663	2.728	3.309	2.995
Elem1=As1937	193.759 {134}			Cts/S	4.411	0.0359	0.8144	4.442	4.372	4.42

The top part on the left indicates the method used, the name of the sample, the date and time the sample was analyzed, the type of sample (unknown), the number of readings (3 replicates). The first column lists the element, the second, the wavelength and order. The third and fourth columns were not used. The units are in counts/second, then the average of the 3 replicates (which are the last three columns) with its standard deviation and % relative standard deviation.

Third tab name: Calibration curves 12 dec.

This tab contains the calibration curves built for each element and each wavelength used on December 12, 2002. A table was filled with the instrument responses in counts per second and the curves were put into graphs. Here are a part of the table and an example of a graph for arsenic.

		milli-Q (cts/s)	1 ppm std (cts/s)	10 ppm std (cts/s)	100 ppm std (cts/s)
As	189.042 {138}	1.585	3.261	19.02	173.1
As	193.759 {134}	1.971	3.993	21.27	190.9



Fourth tab name: Calibration curves 13 dec.

This tab contains the calibration curves built for each element and each wavelength used on December 13, 2002. The data can be interpreted as in the third tab.

Fifth tab name: Detection limits

Here, the detection limits that were calculated using the calibration curves of December 13, 2002. The first column lists the element, wavelength and order. The second column is the average standard deviation of the extraction fluid blanks. The last column is the detection limit calculated as follows: three times the standard deviation of the blank divided by the slope of the calibration curve.

	Blank std	Slope of cal. curve	Detection limit (ppm)
As 189.042 {138}	0.01410	1.7773	0.0238
As 193.759 {134}	0.06184	1.9050	0.0974

Sixth tab name: External cal.

This tab contains the calculated concentrations for each element in the various samples and obtained using the external standards method. The tables found in this tab include the element's name and its wavelength, the name of the sample, the average signal (taken in the raw data tab), the concentration calculated by plugging the average signal in the calibration curve's equation, and then the average concentration for all the wavelength.

Element	Line {Intensity}	PACS-2, 1h Blank		
		Avg. (counts/s)	Conc. (ppm)	Avg. conc. (ppm)
As	189.042 {138}	1.546	-0.0099	
As	193.759 {134}	2.268	0.193491	0.1386219
As	197.262 {132}	2.65	0.232277	

Seventh tab name: Signal to noise on ext cal

Here, the signal to noise ratio was calculated for each element in all the samples analyzed with the external standards method. The average signal (counts/sec), standard deviation and % RSD were obtained directly from the raw data tab. The signal to noise was then calculated by dividing the average signal by the standard deviation.

Name of sample

		As 189.042 {138}	As 193.759 {134}
Milli-Q	Average (counts/sec)	1.437	1.834
	Std deviation	0.0266	0.3234
	% RSD	1.851	17.63
	S/N ratio	54.0226	5.6710

Eighth tab name: Std add.

This tab contains the calculated concentrations for each element in the various samples and obtained using the standard additions method. The tables found in this tab include the element's name and its wavelength, the name of the sample (spiked with standard [spiked] and spiked with water [blank], the average signal of each (taken in the raw data tab), the signal where the blank signal was subtracted (spiked-blank and sample-blank), the concentration of the spike, the slope obtained with the standard addition method and the concentration of the sample obtained by both external standards and standard additions methods.

Element	**Line**	**PACS-2, 1h Spiked**				
		Weight of sample (g) :		4.0017		
		Weight of sample+spike (g) :		5.0314		
	{Intensity}	Avg. signal (counts/s)	Spiked-blank (counts/s)	Conc. of the spike (ppm)	Slope (counts/s/ppm)	Conc. of sample (ppm)
As	189.042 {138}	5.008	4.4112		2.1506	0.0287
As	193.759 {134}	6.025	4.8523	2.0283	2.3356	0.0620
As	197.262 {132}	5.565	4.0866		1.8148	0.2811

Element	Line	PACS-2, 1h **Blank** Weight of sample (g) : Weight of sample+water (g) :		4.0273 5.0396
	{Intensity}	Avg. signal (counts/s)	Sample-blank (counts/s)	Conc. obtained with ext.cal. (ppm)
As	189.042 {138}	1.546	0.0492	-0.0099
As	193.759 {134}	2.268	0.1151	0.1935
As	197.262 {132}	2.65	0.4057	0.2323

The detailed formulas for the calculations are available by clicking on the desired cell in the Excel sheet on the CD.

Ninth tab name: Signal to noise on std add

Here, the signal to noise ratio was calculated for each element in all the samples analyzed with the standard additions method. The tables and calculations are the same as for the signal to noise on ext cal tab above.

Appendix B

Results Obtained For The ICP-AES and ICP-MS Comparison Experiment

All the results can be viewed on the CD in the Excel file "***Comparison AES-MS 080503.xls***". The explanations presented below give a summary of what can be found in this file. Since the tables are self-explanatory, none of them are shown.

First tab name: Concentrations

All the samples and standards were prepared gravimetrically (by weighing them) instead of relying on volume measurements, so under this tab, all the weights were recorded: weight of bottles, multi-element or single element solutions added, water, spike, sample, and total weight. The different dilution factors and the exact concentration of each element in the standards were calculated. One will also find the dilutions that were performed on the samples for analysis with the ICP-MS.

Second tab name: Comparisons

In this tab, all the sample concentrations obtained with the ICP-AES in December 2002 and May 2003, as well as the concentrations obtained with the same samples with the ICP-MS, are listed along with their detection limits.

Third tab name: Final results

All the results obtained by using external standards and standard additions methods with both instruments, ICP-AES and ICP-MS, are put next to each other along with their detection limits in order to be able to compare the results.

Appendix C

Results Obtained With ICP-AES For The Second Experimental Procedure

All the results can be viewed on the CD in the Excel file "***Soil extraction data nov07-03.xls***". The tables and explanations presented below are samples of what can be found in this file.

First tab name: Conc. of samples & stds

Same as in Appendix A.

Second tab name: Raw data

Same as in Appendix A.

Third tab name: Blanks

All the blanks average signals were grouped together so it was easier to spot the appropriate blank that was run nearest to a sample to do a blank subtraction to a specific sample.

Fourth tab name: Cal curves July-30

Same as in Appendix A.

Fifth tab name: Cal curves July-31

Same as in Appendix A.

Sixth tab name: Cal curves Aug-01

Same as in Appendix A.

Seventh tab name: Cal curves Sept-10

Same as in appendix A.

Eighth tab name: Cal curves Oct-15

Same as in Appendix A.

Ninth tab name: Cal curves Oct-17

Same as in Appendix A.

Tenth tab name: Detection limits

Same as in Appendix A.

Eleventh tab name: Ext. Cal.

This tab contains the calculated concentrations for each element in the various samples and obtained using the external standards method. The tables found in this tab include the element's name and its wavelength, the name of the sample, the weight of the sample and sample + spike (which is nitric acid) the average signal (taken in the raw data tab), the blank subtracted signal, the concentration calculated by plugging the average signal in the calibration curve's equation, and then the final concentration corrected with the appropriate dilution factor.

Element	Line {Intensity}	**PACS-2 #1, 1h ES**			
		Weight of sample (g) :			4.0089
		Weight of sample+HNO_3 (g) :			5.0015
		Avg. (counts/s)	Avg.-blank (counts/s)	Conc. (ppm)	Dil.fact. Correction (ppm)
As	189.042 {138}	1.096	0.1623	0.1150	1.7553
As	193.759 {134}	1.483	0.1300	0.0834	1.2728
As	197.262 {132}	1.705	0.0900	0.0729	1.1130

Twelveth tab name: Sig. to Noise on Ext. Cal.

Same as in Appendix A

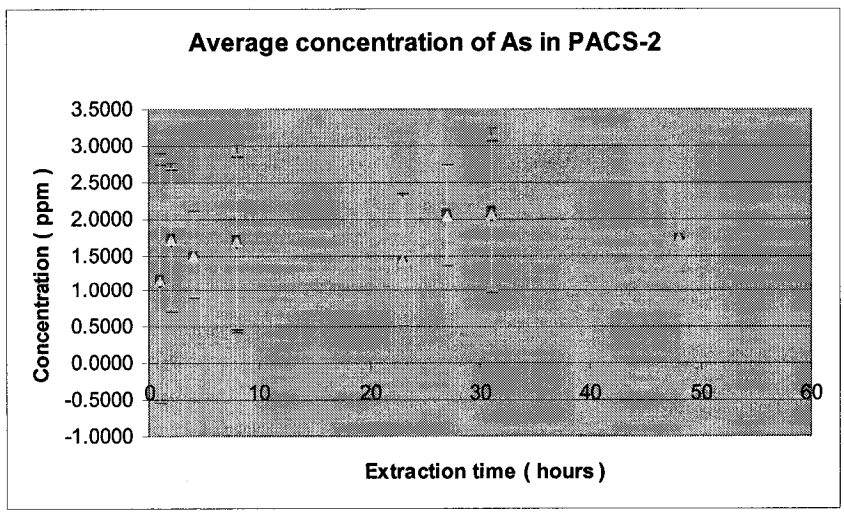
Thirteenth tab name: Graphs

Already explained and presented in Chapter 4 of the present document.

Fourteenth tab name: Avg. Sig.-Graphs

This tab contains tables in which, for example, the concentrations of the three replicates of PACS-2 samples obtained by external standards are averaged and the standard deviation calculated. The same calculation is done for the concentrations obtained by standard additions, and then, all of these concentrations are combined together to get global average and standard deviation. All these results are plotted with their respective standard deviations.

Element	Line	Avg. PACS-2, 1h					
		Ext. Std		Std. Add		Ext. Std. + Std. Add.	
	{Intensity}	Average	Std. Dev.	Average	Std. Dev.	Average	Std. Dev.
As	189.042 {138}	1.3517	0.5709	1.3913	0.6207	1.3715	0.4874
As	193.759 {134}	2.4259	1.6308	2.4436	1.5864	2.4348	1.3136
As	197.262 {132}	-0.4043	2.1458	-0.3162	2.0366	-0.3603	1.7088



Fifteenth tab name: Std. Add.

Same as in Appendix A, except that a column where a dilution factor correction is applied on the concentration was added as well as the concentrations obtained by external standards to have both concentrations next to each other.

Sixteenth tab name: Sig. to Noise on SA

Same as in Appendix A.

Seventeenth tab name: Comparison

All the concentrations obtained by both external standards and standard additions, for the three replicates of a sample, are put next to each other in one table.

		Soil #1 1h		Soil #2 1h		Soil #3 1h	
		Ext. Std.	**Std. Add.**	**Ext. Std.**	**Std. Add.**	**Ext. Std.**	**Std. Add.**
As	189.042 {138}	1.5315	1.5399	n/d	n/d	4.4960	4.5622
As	193.759 {134}	2.2640	2.3272	n/d	n/d	3.0902	3.0276
As	197.262 {132}	3.1581	2.9917	n/d	n/d	3.5968	3.4628

Eighteenth tab name: Statistics

The tables presented in this tab are explained in details in Chapter 4 of this document.

Appendix D

Results Obtained With ICP-MS For The Second Experimental Procedure

All the results can be viewed on the CD in the Excel file "***Soil extraction data MS feb-10-04.xls***". The tables and explanations presented below are samples of what can be found in this file.

First tab name: Conc. of stds

Same as in Appendix A.

Second tab name: Raw data nov12

Quantitative Analysis - Summary Report

Sample Date/Time:	Wednesday, November 12, 2003 16:48:42
Solution Type:	Sample
Blank File:	e:\elandata\Dataset\Julie Soils\Blank.028
Sample File:	e:\elandata\Sample\margaret.sam
Method File:	e:\elandata\Method\JAnov1203soils.mth
Sample ID:	PACS-2 #2 23h

Summary Intensities

Analyte	Mass	Meas. Intens. Mean	Meas. Intens. SD	Blank Intensity	Blank Intens. SD
Cu	63	56286.24	664.402	944.0407	42.6491
Pb	208	43165.56	782.9243	8849.8304	247.3021

Concentration Results

Analyte	Mass	Net Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD	Sample Unit
Cu	63	55342.2	5.0025	0.0963	1.9245	ppb
Pb	208	34315.73	3.2842	0.0419	1.2769	ppb

Third tab name: Raw data nov14

Same as second tab.

Fourth tab name: Raw data nov19

Same as second tab.

Fifth tab name: Cal.curves nov12

Same as in Appendix A.

Sixth tab name: Cal.curves nov14

Same as in Appendix A.

Seventh tab name: Cal.curves nov19

Same as in Appendix A.

Eighth tab name: Ext. Cal.

Same as in Appendix C.

Ninth tab name: Detection limits

Same as in Appendix A.

Tenth tab name: Int.Std.Cal.curves nov12

Same as in Appendix A, except that here, the ratios of one element's concentration and intensity relative to the internal standards were calculated. The graphs of the calibration curves are similar.

Eleventh tab name: Int.Std.Cal.curves nov14

Same as in Appendix A, except that here, the ratios of one element's concentration and intensity relative to the internal standards were calculated. The graphs of the calibration curves are similar.

Twelveth tab name: Int.Std.Cal.curves nov19

Same as in Appendix A, except that here, the ratios of one element's concentration and intensity relative to the internal standards were calculated. The graphs of the calibration curves are similar.

Thirteenth tab name: Int.Std.

Same table as for external standards, except that it is for the internal standards method.

Fourteenth tab name: Comparison

All the concentrations obtained by both internal standards and standard additions, for the three replicates of a sample, are put next to each other in one table. The results obtained by external standards and standard additions with the ICP-AES were also added to compare both instruments performances.

Fifteenth tab name: Graphs

Already explained and presented in Chapter 4 of the present document.

Sixteenth tab name: Statistics

The tables presented in this tab are explained in details in Chapter 4 of this document.