Studies of Leaching of Metals from Food Ceramics

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Abstract

In this study the leaching potential of food ceramic wares available in New Zealand has been done using ICP-MS analysis. A survey of ceramic wares purchased in New Zealand markets ranging from historical (antique) Victorian eras (Wilemen bone china and Chapman), mid - 20th century (Alfred Meakin), 1960-1980's New Zealand-made (Crown Lynn) and modern day ceramic wares manufactured in China, India and Thailand was carried out with respect to their elemental compositions, ceramic composition and leaching potential. All these ceramic wares were found to contain various amounts of heavy metals in their glazes used for imparting special colours, texture and smooth finishes.

Structural characterisation of these ceramic wares was carried out using different techniques such as solid state magic angle spinning NMR, Fourier transform infrared (FTIR), scanning electron microscopy (SEM) coupled to energy dispersive X-ray analysis (EDX), and X-ray fluorescence (XRF) to determine which elements were present in the bulk of ceramics clay sourced-body and in the glazes. The results of the XRF analysis informed the inductively coupled plasma mass spectroscopy (ICP-MS) studies by providing a list of elements to follow. In general XRF identified a number of heavy metals of interest in all the ceramic wares such as lead and cadmium in Victorian era Wileman and Chapman, mid-20th century Alfred Meakin and especially in the Crown Lynn wares. Barium was predominantly the heavy metal of interest in all modern ceramic wares that are predominantly used by many people in New Zealand. Cobalt, chromium, tin and zinc were present in all the ceramic wares. However, cadmium was significantly present in the red coloured modern ceramic wares.

These ceramic wares were subjected to leaching tests to detect whether various elements of relevance such as lead, cadmium, barium, cobalt and chromium migrated to any great extent into liquids exposed to these ceramic wares. Leaching studies were done following the ASTM 738 -94 standard test methods for specific metals leaching into 4% acetic acid solutions after a 24 hour exposure time. The lead leached from Victorian era Wileman bone chinaware studied with 4% acetic acid leaching solution was found to exceed the standard safe limits of lead as given by the FDA (3 µg/mL) and European Council Directive 84/500/EC

(4mg/L). The Victorian era Chapman and the New Zealand made Crown Lynn ceramic wares leached lead with 4% acetic acid leaching solution but was below the standard safe limit. However, the modern day ceramic wares manufactured in China, India and Thailand analysed in this research were found to leach extremely low levels of barium being well below the oral reference dose (RFD) for barium given by the US Environmental protection agency (EPA) as 0.07 mg/kg/day, i.e. 4 mg/person/day.

Ceramic teacups were exposed to other leachate solutions based on the normal domestic use and all the leachate solutions were analysed with ICP-MS. These leachate solutions which were exposed to the ceramic teacups for a ten minutes leaching test included: orange juice at room temperature, hot tea at 80 - 95 ^{o}C, hot water at 80 - 95 ^{o} C, cold water at 4 ^{o}C and Coca Cola at room temperature in which some of the Crown Lynn teacups studied were found to be continuously leaching lead in all the tested solutions at varying conditions i.e. pH of the leaching solutions, its temperature and duration of exposure to the leaching solution have influence in migrating the metals from these ceramic teacups tested. However, the level of lead leached from these ceramic teacups was well below the standard safe limits of lead leached from ceramic wares.

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Abbreviations

m/z	Mass to Charge Ratio
AAS	Atomic Adsorption Spectroscopy
ASTM	American Society for Testing and Materials
EDX	Energy Dispersive X-ray
FTIR	Fourier Transform Infra-red
GFAAS	Graphite Furnace Atomic Absorption Spectroscopy
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
ISO	International Organisation for Standardisation
LA-ICP-MS	Laser Ablation Inductively Coupled Plasma Mass Spectroscopy
NMR	Nuclear Magnetic resonance
ppb	Parts Per Billion
ppm	Parts Per Million
SSNMR	Solid State Nuclear Magnetic resonance
SEM	Scanning Electron Microscopy
XRF	X- ray Fluorescence
XRD	X-ray Diffraction

Glossary

Body	Clay part of the pot
Crazing	Very tiny cracks on the surface of the glaze
Flint	It is powdered form of silica which is the glass former in glazes
Flux	A melting agent added to reduce the melting temperature of glazes
Frit	It is previously fired and melted form of silica and flux, cooled and powdered for stabilizing solubility of toxic ingredients in glazes
Glaze	A thin glassy coating covering the clay body
Gloss	Shinny appearance
Matt	Dull appearance of the glazed surface
Slip	Creamy consistency of liquid clay
Quartz	Crystalline form of silica
Under glaze	Glaze usually applied on a low temperature fired clay body (bisque) and then covered with transparent glaze.
Vitrification	A stage during the firing process when the clay body becomes non porous before the application of glazes

Chapter 1: Introduction

1.1 Ceramics

The word "Ceramics" comes from Greek *Keramos*, which means "Burnt earth". Ceramics can be defined as heat resistant, non-metallic, inorganic solids that are made up of compounds formed from metallic and non-metallic elements. Ceramics are corrosion resistant, hard but brittle. Most ceramics are good insulators and withstand high temperature. They have well defined crystalline structures. The chemical bonds can be ionic or covalent depending on the chemical composition of the ceramics (Jones, 2013).

Traditional Ceramics

These include objects made from clay and cement that have been hardened at very high temperature. Porcelain is a hard tough ceramic that is less brittle than other ceramics. It is made from kaolin mixed with china stone and the mixture is heated to very high temperature (1300 ^{o}C or 2372 ^{o}C). Bone china has a composition similar to that of porcelain but it consists mostly of bone ash, kaolin and china stone. Bone china has very thin and translucent walls. Stoneware is dense, hard, grey or tan ceramics that is not as strong as bone china or porcelain and so is always made thicker and heavier than bone china or porcelain to improve its strength (Jones, 2013)

1.2 Clay

Clay consists of a large number of tiny flat plates that are stacked together with a thin layer of water separating each crosslinks. **Figure 1** shows the structure of natural clay mineral which has single layer of Al octahedra sandwiched between two layers of silicon octahedra. Alumina (Al_2O_3) and silica (SiO_2) combines with water and other elements in various proportions to form clay minerals.

Figure 1: Basic Layered Structure of Natural clay Mineral (Daulton, 2005)

Heating clay at high temperature withdraws this water resulting in the formation of bonds between the plates, holding them in place and forming a hard solid (Jones, 2013). Clay is one of the cheapest and most easily available raw materials. The difference in the texture, colour and quality of clay depends on how it was deposited and the type of mineral it collected during its formation (Flight and Lane, 1990)

Primary Clays and Secondary Clays

Primary clays are white or light coloured and are not eroded by movement through water. They are non-plastic and unstained by other minerals. Kaolin or china clay (see **Glossary**) is the most well-known and widely used of all clays. Kaolin is mostly used in clay bodies to contribute to its whiteness. Kaolin, a non - metallic material was discovered in China about 200 BC and has been widely used in ceramic industries. However, with the exploitation and increased utilization of kaolin resources, high quality kaolin had reduced increasingly; the newly built kaolin material base cannot meet the requirements of high - quality products. One of the poor quality kaolin used in the ceramic production is known as muscovite – type kaolin which turns red on high firing temperature due to the presence of Fe_2O_3 (haematite) (Yu et al., 2010). It is often mixed with other clays to improve its plasticity and lowers its maturing temperature in the kiln (Flight and Lane, 1990). The largest deposits of kaolin in New Zealand have been formed by hydrothermal alteration of volcanic rocks. Halloysite is known to be the words whitest clay and one of the main clay mineral deposits of Matauri bay in north land New Zealand. Chemically halloysite is similar to kaolinite

($2Al_2O_3.2SiO_2.2H_2O$) except it has four molecules of water instead of two. Around 15000 metric tonnes of kaolin are mined in New Zealand each year.

Secondary clays are transported by water or wind from the parent rocks. They have a fine particle size which gives them their plasticity. They are usually contaminated by iron oxide which makes the body of the ceramics made from such clays brown, yellow and red in colour. Ball clay is regarded as one of the finest secondary clays. It is light coloured clay which withstands very high temperature and is usually mixed with kaolin. It is used as a white slip for coating compatible dark bodies. Common clays and fire clays are also secondary clays which are used for building purposes such as the manufacture of fire bricks, furnaces and crucibles (Flight and Lane, 1990).

1.3 Evidence of the first pottery used in human history and its uses in food

The origin of pottery and its uses have been the subject of much research. The beginning of pottery production was associated with the evolutionary transition from hunter - gathers to agricultural fillers of the land (Shelah, 2012). Pottery was used for cooking, storing, processing, preserving, serving, transporting food as well as for ritual purposes. Pottery was first used as a prestige item rather than as for food storage and processing implements. One was the earliest pieces found pottery dates back about 20,000 years ago and was found in Xianrendong cave, Central China. Research shows that this pottery material was used for food preparation, storage and brewing alcohol. The raw materials used in that earliest type of pottery were crushed quartz and feldspar and they were fired at very low temperatures in open fires (Wu et al., 2012). The Citizen Newspaper, Ottawa, Canada in 24th July 1986 published an article which reported that the oldest pottery was found in a village in the Ganges valley, India and the literature from the anthropological survey reports that the pottery was used for burial rituals in India (The Press Trust of India, 1986).

1.4 Pottery industries, around the world

The British Industrial Revolution, technological advances and better education on pottery has led to the growth of various pottery industries with their own brand names and unique features. Different glazes, colours, clays were developed to meet customer requirements. The range of ceramics used in New Zealand since its colonisation varies from English made bone china through china supplied from a once thriving domestic industry to modern Chinese ceramics that flood the markets today (e.g. Crown Lynn)

Crown Lynn potteries (New Zealand)

Ceramics has only a short history in New Zealand as that of European colonisation. The greatest growth of the ceramic industry in Europe was noted in the 19th century. Crown Lynn china was made in New Zealand, in West Auckland. It was started in early the 1890s (Bell, 2012) with the production of ceramic drainpipes, bricks and acid resistant tiles, then in 1930 domestic china was made. The most famous Crown Lynn product from that early period was a special railways cup (see **Figure 2**).

Figure 2: New Zealand railway cup from 1940 and 1950s (Monk, 2006)

New Zealand made chinaware was called Ambricoware in the mid-1940s but had variable quality. The quality of the product was greatly improved in 1948 to meet competition from other English chinaware and this was the year it came to be known as Crown Lynn. Most of the decoration on the chinaware was done by hand. Some typical Crown Lynn ceramic wares and their back stamps are shown in (see **Figure 3** and **Figure 4**).

Figure 3: Hand painted designed tableware set named Fleurette which is most popular Crown Lynn product and its backstamp style (Monk, 2006)

From the mid-1970s cheaper imported Asian (Japanese+ Chinese) products became available in the New Zealand market which eventually forced Crown Lynn to cease production in 1989 (Monk, 2006). Although the company stopped its production Crown Lynn is still popular in New Zealand homes and is still widely available through second hand shops and charity shops and through online auction sites.

1960s ***1960s-1970s*** ***1964-1989***

Figure 4: Some of the styles backstamps used by Crown Lynn which identifies its maker (Monk, 2006)

British potteries, the Wileman and Co Longton, Staffordshire

Staffordshire is known historically as a potteries region and this region in Britain is famous for the pottery industry. Pottery has actually been manufactured at many sites in Britain since prehistoric times. Many potters came to Staffordshire because it had the kind of clay that could be made into ceramics and there was also an abundant supply of coal to fire the kilns for baking the pottery. In 1745, porous plaster of Paris molds were introduced which made the clay dry quickly and this speed up the production process and duplicates of the original forms were made at a much shorter period so that by 1800 Staffordshire became known as a national centre of ceramic industry. Also the English industrial revolution brought new techniques which introduced a variety of shapes, colours and motifs pottery to attract its customers (Hudgins, 2002) (see **Figure 5**). Among the numerous pottery industries Wileman &Co was one which began in 1872. It was known for its dainty white range pottery with its fluted panel and scalloped edges. They were produced in higher quality and were one of the successful shapes produced by this company.

a)

b)

c)

d)

Figure 5: a) Wileman china backstamp 1894-1910, b) Wileman Shelley aqua blue Cameo cup and saucer, 1901, c) Wileman china orange saucer and d) Wileman china showing backstamp pattern (Shelley and Wileman Backstamps, 2010)

The Wileman & Co used mother of pearl glaze for bringing up white backgrounds. The lustre decorated pieces were introduced in 1920, in which metallic oxides like copper and silver were used. It was renamed as Shelley china in 1925. The traditional type of shape and decoration of Shelley china was always popular in the U.S.A, Canada, New Zealand and Australia. Shelley Potteries Ltd changed its name to Shelley china in 1965. In 1966 Shelly potteries was taken over by the Allied English potteries and produced Royal Albert bone china and was taken over by Royal Doulton group in 1971(Watkins et al., 1980). The products are still available in New Zealand antique shops and also through the internet sites like eBay where they sell at very high prices.

Indian potteries

In India, the traditional method of pottery making is still followed by many potters families (Perryman, 2000). There is an earlier history of production of clay vessels dating back to 6,000 BC through discovered remains found on the western bank of the Indus river, India. The country tends to have more terracotta, earthenware and handcrafted clay culture (Perryman, 2000). Glazes were introduced during the 11th century via the invasion of Islam. Glazed pottery requires high temperature kilns which were not affordable to local potters and so they used low temperature fired clays. The decorative vessels made in Uttar Pradesh, India were backfired with silver inlay and supplied to the urban markets until now. The unfired vessels were produced in a state called Kutch in India (Perryman, 2000). Currently there are many manufactures of ceramics in India such as Tata ceramics a major producer and exporter of fine bone china crockery and tableware. Tata ceramics was incorporated in 1991 exportes to New Zealand, Australia, U.K, U.S, Ireland, Germany and many other countries (Agrawal, 2001). Another, Bengal pottery, started in 1925, is one of the biggest manufactures in India (Gupta, 1988). An India bone china tea cup is shown in **Figure 6.**

Figure 6: Fine bone china tea mug, India and b) its back stamp style (e-Bay, 2012)

Chinese potteries

The Chinese have a long history of ceramics dating back to the Neolithic period (Ong, 2005). Chinese potters have mastered the art of pottery making and each dynasty has contributed over to the different shape, glaze and clay for making potteries (Sheean, 1931). First glazed earthenware body was produced in Han dynasty (206 BC - 9 AD). Tricoloured pottery of Tang dynasty (618-907), monochrome glazed ceramic wares of Song dynasty (960 -1279) and purple clay pottery in Ming dynasty (1368- 1644) were well known Chinese made ceramic wares. Fine white wares of Sui and early Tang periods produced the earliest white porcelains. Blue and white wares of fourteenth century were exported to Asia and to Islamic countries. Chinese porcelain first reached Europe in 14th century. Jingdezhen in Jiangxi had been the leading producer of Chinese porcelain for thousands of years **Figure 7**. China is the leading producer and exporter of ceramic wares through the world (Kogel et al., 2006).

Figure 7: Chinese made teacup (blue and white) (Jingdezhen Porcelain Qing Hua teacup) (e-Bay 3, 2012)

1.5 Pottery making

The methods used to make pottery today is same as that used by the Egyptian potters about 4,000 years ago but with lot of research and improved machinery included to create a 'perfect' product. The process of pottery making can be explained in more simple way by a publication put out by Shelley potteries in 1937 which is the more basic process followed by most of the pottery industries but with the development of advanced techniques. Generally when pottery is made by hand on the potters wheel, the process is called throwing. A lump of clay is thrown on the wheel and is worked into a particular shape and it is polished inside by the turner who makes the surface even, smooth and of proper thickness.

If it is a cup the handler fixes the handles which are already made by the caster by pouring slip into plaster moulds. The end of the handle is dipped into a thick solution of slip and is fixed on to the cup. When it is fired in an oven the clay vitrifies and the cup and handle fuse together as one. The plates and saucer are made in a machine called a jigger. Then it is thrown onto a revolving wheel, pressed (see **Figure 8**) and then when the correct thickness is reached, it is dried and the edge is trimmed and sponged and fired.

Figure 8: The revolving wheel on which the clay takes the form under the pressure of the thrower's skilful fingers (Shelly, 1937)

Teapots, jugs, fancy shaped cups and all the irregularly shaped surfaces are made by the caster in plaster of Paris moulds. Bone china contracts or shrinks about one sixth when fired in the oven, so they are made of sufficient size to allow for this contraction. The placer places the clay in a Bisque oven. The grooved clay ring made by the thrower and turner keeps each cup safe without its going crooked during firing. The cups are placed in saggars and plates in settlers and then fired in an oven. The firing takes place till the temperature reaches about 1300 ^{o}C and after cooling, the manufacturers back stamp is applied. The next process is glazing which is done by the dipper by mixing raw materials like clay, flint, feldspar, lead oxide with water to a consistency of heavy cream. Hand dipping used to be widely practiced in large industrial plants and small potteries (see **Figure 9**).

Figure 9: The Dipper applying Glazes , The liquid glaze used is borax- flint –lead glass (Retrieved from (Lehman, 2002; Shelly, 1937)

The colours used on clay bodies are metallic oxides along with fluxes to reduce the melting points and to fuse them into the glaze when fired (Shelly, 1937).

The main fluxes used in low firing glazes are lead, soda and borax. In china manufacture the designer along with the engraver, printer, transferor, bander and gilder does the decoration on the pottery. The glazed pottery is then re-fired at about 800 ^{o}C and cooled down and is carefully examined and packed before distribution (Shelly, 1937). The Earthen ware bodies are fired at not more than 1000 ^{o}C are glazed and refired at about 1050 ^{o}C which is not too high for the vitrification to take place. The hard paste porcelain, on the other hand, is fired at 900 ^{o}C and re-fired at temperature between 1400^{o}C and 1600 ^{o}C which allows the body and glaze to fuse together (Sheets, 1998).

1.5 Chemistry behind pottery making

The main raw materials used in making the ceramic products as mentioned earlier are clay, feldspar and sand (Sharma, 1997). Crystallographic studies have shown that clay minerals are composed of tetrahedral sheet of SiO_2 and octahedral Al_2O_3 that is linked through bridging oxygen atoms. Some of the oxygen atoms are in the form of OH groups (Breuer, 2012).

The Feldspar is affected by the atmospheric carbon di oxide and water and undergoes decomposition with the formation of alkali carbonate, aluminium silicate and sand (Sharma, 1997) which is given by the equation **1-1**.

Conversion of feldspar into kaolinite

$$K_2O.Al_2O_36SiO_2 + CO_2 + 2H_2O \rightarrow K_2CO_3 + Al_2O_3.2SiO_2.2H_2O + 4SiO_2 \quad (1\text{-}1)$$

When the kaolinite is heated to about 600 ^oC it loses water forming an amorphous mixture of Si & Al. The weak hydrogen bonds are replaced by the stronger and shorter oxygen bridges which makes the clay shrink is given in equation **1-2** (Sharma, 1997).

Conversion of kaolinite into silica and alumina (amorphous)

$$Al_2O_3.2SiO_2.2H_2O \rightarrow Al_2O_3 + 2SiO_2 + 2H_2O \quad (1\text{-}2)$$

At about 940 ^oC amorphous alumina changes into a crystalline form of alumina with the liberation of a considerable amount of heat. Mullite is formed at about 1000 ^oC. At still higher temperatures the remaining silica is converted into crystalline crystobalite given in equation **1-3** (Sharma, 1997).

Conversion of amorphous alumina into crystalline form of alumina

$$3(Al_2O_3.2SiO_2.2H_2O) \rightarrow 3Al_2O_3.2SiO_2 + 4SiO_2 + 6H_2O \quad (1\text{-}3)$$

Earthenware pots are fired at about (1000 - 1150 ^oC) while the stoneware and porcelain are fired at temperature > 1200 ^oC. Most pots are glazed with three main components, silicon dioxide to provide the main body, aluminium oxide to increase the viscosity of the glaze by cross linking the Si networks and third one is fluxes which are added to melt glazes at specific temperatures (Breuer, 2012).

1.6 Glazes

A glaze may be defined as a glassy coating melted in place on a ceramic body, which may render the body smooth, nonporous, glossy, opaque and impart on it a desired colour. The earliest known ceramic glazes dates back to 2000 BC and were discovered by Egyptian and Chinese potters. During firing, the glaze melts and fuses with the surface through the formation of crystalline structure that unites it with the clay. Silica is the fundamental glaze material that occurs in nature as quartz facilitates the fusion of clay and the glaze material. Since the melting temperature of silica is relatively high, a flux is added to lower the melting point. Naturally occurring sodium, lead, magnesium, lithium and feldspar are commonly used in fluxes. Oxides of Pb, Na, K, Al, Zn, Ba, Li, Sr, Sb, Ti, Si are commonly used in glazes. When glazed ceramics comes in contact with acidic foods or liquids (Hight, 2001), leaching of added heavy metals can occur. This is due to the chemical attack on the glaze surface by the acid base reaction (Demont et al., 2012). The tendency to do so depends on the acid-resistance of the ceramic glazes (Hight, 2001).

Lead oxide is added as a flux to reduce firing temperature and to get a shiny glaze and is also valued for its rich, brilliant and deep colours that are possible with this element (Rhodes and Hopper, 2000). It has the ability to heal the manufacturing defects such as blisters and pinholes during processing. High toxicity is the main drawback of using lead in ceramic glazes especially the release of lead from ceramic food wares during normal household use. Raw lead compounds such as litharge (PbO) or red lead ($PbSO_4$) and white lead ($2PbCO_3$. Pb (OH_2)) used in the glazes lead to lead poisoning in the workers who handles it as well as affecting the general populations because of high solubility of these compounds in acidic environment (foods) during household use. But this problem was partially solved using lead in fritted form that is by chemically combining lead in a glassy matrix and then making it into powder form which makes lead compounds tightly bounded and reduces the solubility of lead (Lehman, 2002). Bristol glaze was developed in England to substitute for lead in which zinc was the principle flux. Insoluble form of zinc oxide gives a brilliant, smooth glaze to the ceramic wares (Peterson and Peterson, 2003).

Barium oxide is commonly used to provide matte surfaces along with vivid colours and especially with copper where a strong royal blue colour glaze is obtained. It is also used to replace lead in frits formulation for glazes. In combination with nickel, barium gives red, pink and purple. With chromium yellowish and green colours are possible. Barium oxide is introduced in glazes and clay bodies in the form of barium sulphate or which also has medicinal uses for medical imaging (Britt, 2007). Barium carbonate is also used in glaze recipe to introduce barium oxide which is highly toxic and is not recommended in ceramic wares for food use. But strontium oxide was used as a substitute for achieving the fluxing properties of barium carbonate and to get the blue shades of barium carbonate (Jernegan, 2009).

Chromium oxide imparts a strong green and strong black colour in glazes while in combination with tin oxide chromium oxide encourages a pink colouration and with zinc it gives a brown colour. Cadmium sulphide imparts yellow colour to pottery glazes. It gives orange to brilliant red with selenium. It is very important for potters for the wide range of colours they offer (World Health Organisation, 1976). Copper and zinc gives turquoise green. Cobalt oxide or cobalt carbonate is used to produce medium to deep blue shades in glazes. When combined with copper and iron it produces a black colour. Iron oxide is added to glazes to produce yellow, brown and orange shades in oxidation firing. A small amount of iron oxide produces celadon blue and in higher percentages produces a deep orange colour. Iron oxide in combination with lead produces deep earthy tones or yellow and brown shades (Burleson, 2003). Iron is usually added in the glazes in the form of Hematite (Patwardhan, 2005). Manganese dioxide is added to glazes to produce purple or brown colours. It gives a purple shade with lead and a brown colour at very high temperatures (Rhodes and Hopper, 2000). Oxides of lead, cadmium, manganese, chromium, iron, cobalt and various other elements were used for imparting special colours, providing a wide temperature ranges for obtaining unique colours bringing food safe surfaces for ceramic wares, for increasing the durability of pottery used routinely.

1.7 Background studies done on leaching of heavy metals from ceramic glaze

Over glaze decorated ceramic wares can release toxic metal into food substances and constitute health hazards (Omolaoye et al., 2010). A large number of poisoning cases had been reported in 1970s. Hence the European union decided to monitor the dinnerware's for lead and cadmium leaching and set a Directive 84/500/EC which had a standard limit for the migration of lead and cadmium (see **Table 1**) from ceramic wares used for food (Demont et al., 2012).

Table 1: Standard limit for lead and cadmium release according to European council Directive 84/500/EC

Category	Lead (Pb)	Cadmium (Cd)
Articles which cannot be filled, articles which can be filled, the internal depth of which is measured from lowest point to the horizontal plane passing through the upper rim which cannot exceed 25mm.	0.8 mg/dm^2	0.07 mg/dm^2
All other articles which can be filled	4.0 mg/L	0.3 mg/L
Cooking ware, packaging and storage vessel having a capacity of more than 3L.	1.5 mg/L	0.1 mg/L

According to the United States Food and Drug Administration the maximum allowable concentration of leachable lead ranges from 0.5 - 3 µg/mL for the dinnerware used in food consumption. In the USA, State of California a more strict regulation for lead leaching from dinnerwares. The limits range between 0.1 and 0.23 µg/mL and labels are required on all dinnerware sold that expose users to lead (Belgaied, 2003). The International Organisation for Standardisation (ISO) also has limits for lead and cadmium release from glazed ceramic food wares (Reilly, 2008). All these limits were obtained from 24 hour leaching test with 4% acetic acid.

Heavy metal leaching has been studied intensively through many investigations in relation to various factors including temperature, pH and duration of contact of the ceramic glazes with food (Belgaied, 2003).

pH influence on lead leaching

In Mexico there has been a long tradition of using lead glazed low fired ceramic wares manufactured by small family businesses. Research has shown that children living in such areas supplied by such pottery business suffered from elevated lead levels in their blood mainly associated with consuming food in lead glazed ceramic wares. Different pH foods like canned tomatoes (pH=4.1), canned black bean (pH=6.0) and canned yellow hominy (pH=6.3) were tested for lead (Pb) by cooking for about 5 minutes in locally purchased ceramic dishes with a closed lid to prevent evaporation. Cooked food had then been homogenised in a blender and digested with concentrated HNO_3 in a laboratory microwave for analysis. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) had been used to analyse leached food with a detection limit of 0.020 mg/l. Leached lead level below the detection limit of ICP–AES has been subjected to graphite furnace atomic absorption spectroscopy (GFAAS) (Lynch et al., 2008). Lead was found to leach from most of the ceramic wares cooked with highly acidic foods.

Similar tests were conducted in Hidalgo, Mexico with acidic foods materials stored in the vessel for 24 hours at 4 ^{o}C and then digested with hydrogen peroxide and concentrated HNO_3 in a Teflon TFM vessel at 280 ^{o}C for 35 minutes and later filtered with whatman filter paper and analysed by inductively coupled plasma mass spectrometer. It was found that as acidity increased the leaching of lead increased. Also the graph (see **Figure 10**) below shows concentration of lead leached in the wares tested increased with the number of extractions (Valadez-Vega et al., 2011).

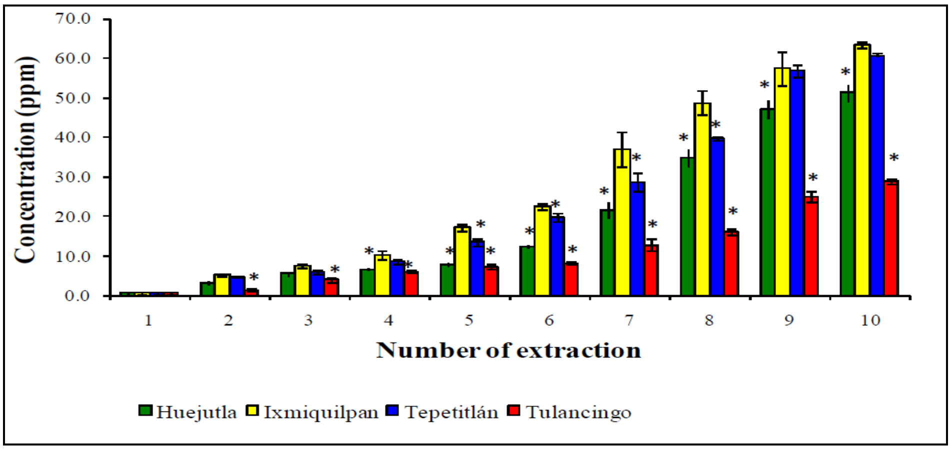


Figure 10: Amount of lead leached from the ceramic wares during a 24 hours leaching test with tomato puree at 4^{o}C (Valadez-Vega et al., 2011).

4% Acetic acid leach test

In Malaysia, imported ceramic containers and cutleries from China had been tested for lead leaching following an ASTM 738.81, 1982 and a modified British standard procedure. The products were washed with distilled water and dried. Then 4% acetic acid solution prepared freshly were added to the ceramic containers and left in them for about 24 hours at room temperature to observe the leachabilty of lead from inside the glazed surfaces that comes in contact with food. Cutlery has also tested for lead leaching by completely soaking it in 4% acetic acid solution for 24 hours at room temperature. The leached solution in these studies was analysed using Atomic absorption spectroscopy (AAS). Ceramic cutlery and sauce plates with highly coloured designs leached lead that exceeded the FDA (Food and Drug Administration) safe standard limit of lead leached from ceramicwares. The amount of lead leached decreased with successive leaching of the ceramic wares used in this study (Mohamed et al., 1995).

Arsenic leaching has been reported in Turkey from poorly glazed and non- glazed potteries using 4% acetic acid and 1% citric acid solution as leaching agent using atomic adsorption spectroscopy (AAS) (Henden et al., 2011). The poorly glazed pottery released high amount of arsenic during the leaching test which indicates that the glazes has to be fired at significant temperature where it melts and forms a glassy coating with the clay body making it insoluble which reduces the risk of metal release during these ceramicwares.

In India, tea cups from various pottery units were leached with different leaching solutions i.e. 4% acetic acid (room temperature), orange juice (room temperature) and hot tea (80 ^{o}C) using AAS. The test results shows that the total concentration of heavy metals leached from these tea cups exceeded the maximum permissible limit passed by the Indian council of medical research 1975 for drinking water which for Cr – 0.05 mg/L, Cu - 3.0 mg/L, Fe - 1.0 mg/L, Pb - 0.1 mg/L, Mn - 0.5 mg/L, Zn - 15.0 mg/L (Mohamed et al., 1995).

1.8 General aims of this thesis

The aim of this project is to characterise various chinaware used in New Zealand in terms of what elements are present and to study its leaching potential using different techniques. The range of ceramics used in New Zealand since its colonisation has varied from British to locally manufacture to predominantly Chinese ceramics wares. Not many studies have apparently been done in this subject in New Zealand. So the result of each section is mostly compared with the previous studies done in leaching studies of ceramic food wares from other countries.

The initial objective of this research was to characterize the various ceramics ware available in New Zealand markets from various eras ranging from Victorian era to present days.

1. Collect for survey samples from various sources which represent the type of chinaware used in New Zealand over the ages and is still used to either a minor or major extent.
2. Characterise the elements present in the body of the chinaware and glazes. Samples to be characterised using scanning electron microscopy linked to energy dispersive X –ray spectrometer and Fournier transform infra-red spectrometer. The results of these studies will be used to identify elements of interest for the leaching studies. Raw materials used for different chinaware will also be studied using MAS - solid state NMR.

The main aim of this research is to investigate if the collected chinawares are food safe with no trace of heavy elements leaching from the vessels under different testing conditions.

- To proceed with the investigation the concentration of various heavy elements in different coloured food wares collected need to be studied. For this X-ray fluorescence technique will be used to determine the concentration of elements and their oxides used in the chinawares. Also the durability of the heavy metals in the glazes will be tested with different leaching solutions at varying temperature, duration and pH. The leaching solutions will be chosen whose pH matches with the food served in this chinawares. The duration of the test will be selected to correlate with the realistic conditions for normal use of the chinaware. The leachate solution will be tested with ICP-MS technique in contrast with previous studies where AAS was mostly used. The heavy elements leached out are to be compared with the standard limits for metal release from ceramic wares regulated by various government and nongovernment agencies which are outlined in this study. No studies have been done in this subject in New Zealand concerning the common available. This study aims to assess the constituents of these ceramicwares and to determine the relative leachability of metals from the glazes.

Chapter 2: Theory of experimental techniques and their background studies

This chapter provides some background information on instruments that have been used for studying ceramic wares in past investigation and which have been used in the present investigation. The elemental characterisation of ceramic pottery has been previously carried out using scanning electron microscopy (SEM) coupled with EDX (Energy Dispersive X-ray) analysis X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infra-red spectroscopy (FTIR), solid state NMR and laser ablation-inductively coupled plasma-mass spectroscopy (LA-ICP-MS). Metal leaching from ceramic ceramicwares has been studied recently using ICP techniques combined with mass spectroscopy (ICP-MS).

2.1 Scanning electron microscopy (SEM)

The SEM was first constructed in the 1930s by Manfred Von Ardenne. Many advances have been made since the first commercial instrument was developed by the Cambridge instrument Company in 1965 (Khursheed, 2010). SEM uses electrons for imaging of the sample surface and it gives highly magnified images compared to what is possible with a light microscope. All modern SEM instruments are equipped with energy dispersive X-ray spectrometers (EDX) for providing qualitative and quantitative elemental information on the material being analysed. In the SEM technique, a beam of electrons generated in the electron gun is attracted to the anode, where it is condensed by the condenser lens (first magnetic lens) and then focussed to a very fine point on the sample by the objective lens (second magnetic lens) (see **Figure 11)**. When the electrons hit the sample secondary and back - scattered electrons are produced from this interaction. The intensity of the electrons emitted is displayed as brightness on a cathode ray tube which represents the morphology of the surface area scanned by the electron beam. The electrons collected by the secondary and back - scatter detector (which is located on the specimen side of the second magnetic lens) are converted to voltage and amplified (Khursheed, 2010).

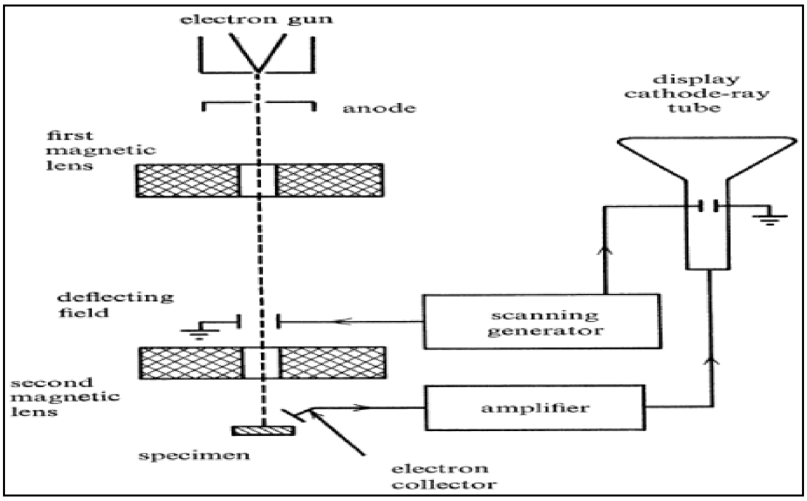


Figure 11: Basic schematic representation of scanning electron microscope (Nixon, 1971)

SEM/EDX techniques generally give information about the major (bulk) elements in the raw materials used for making chinaware conditions and the elements present in their surface decorations (Froh, 2004). For instance, black gloss pottery produced between the 1st and 4th centuries BC in the western part of the Mediterranean basin, were studied with SEM/EDX. SEM images were acquired with either secondary or backscattered electrons and EDX analyses was used to collect information about the slip (see **Glossary**) composition through spot analysis; by focussing the electron beam on a 5 µm diameter area (Mirti and Davit, 2001). Elemental composition of the archaeological pottery pigments were successfully studied with SEM/EDX. The elements corresponding to various colours of the glaze pigments were able to be studied in low vacuum conditions without any charging effects (Mazzocchin et al., 2003).

2.2 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is an important and versatile analytical technique based on the vibrations of the bonds between atoms in a molecule. The first commercial FTIR was introduced in 1969 by BioRad. Infrared radiation is passed through an interferometer with a beam splitter; a fixed mirror and a moving mirror (see **Figure 12**). It is then passed through a sample, where a part of radiation is absorbed and the remaining radiation reaches the detector. The detected interferogram (spectrum of intensity versus time) over a range of IR wavelengths is converted by a mathematical function known as the Fourier transform into an IR spectrum (spectrum of intensity versus frequency) (Davis and Mauer, 2010). The energy at which any peak appears in an absorption spectrum depends on the frequency of a vibration from the sample (Macedo et al., 2012).

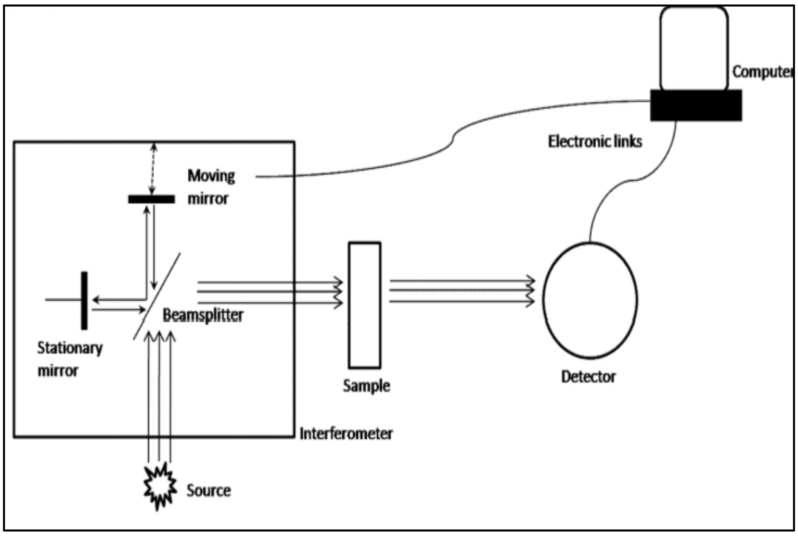


Figure 12: Basic components of a Fourier transform-infrared spectrometer (Davis and Mauer, 2010)

FTIR can be used to assist in deducing possible mineral compositions of a ceramic material (Shoval and Beck, 2005). For instance, archaeologically sourced potteries samples were studied using FTIR to distinguish the history and origin of different pieces of pottery. FTIR was mainly used for identifying the type of clay and mineral transformation of minerals at different firings (Shoval and Beck, 2005). The archaeology department of Tamilnadu, - India, for example conducted an FTIR study of grey pottery collected from an Alagunkulam archaeological site to identify different components of ceramic body and its crystalline phases (Velraj and Janaki, 2011). This study provides information related to the minerals in the fired potteries which can be used as reference for further studies.

2.3 X- ray fluorescence spectroscopy (XRF)

X-ray fluorescence spectroscopy is one of the simplest, most accurate and widely used non-destructive analytical techniques (Lobo and Bonilla, 2003) for the determination of the chemical composition of solids, liquids and powdered products (Craig et al., 2007). The basic components of an XRF spectrometer are shown in **Figure 13**; consisting of an X-ray source to irradiate the sample, a detector connected to the spectrometer and a computer. XRF results are based on the energy of the photon emitted (fluorescence) by individual atoms when they are excited by an external energy source (primary X-ray beam) (James, 2012).

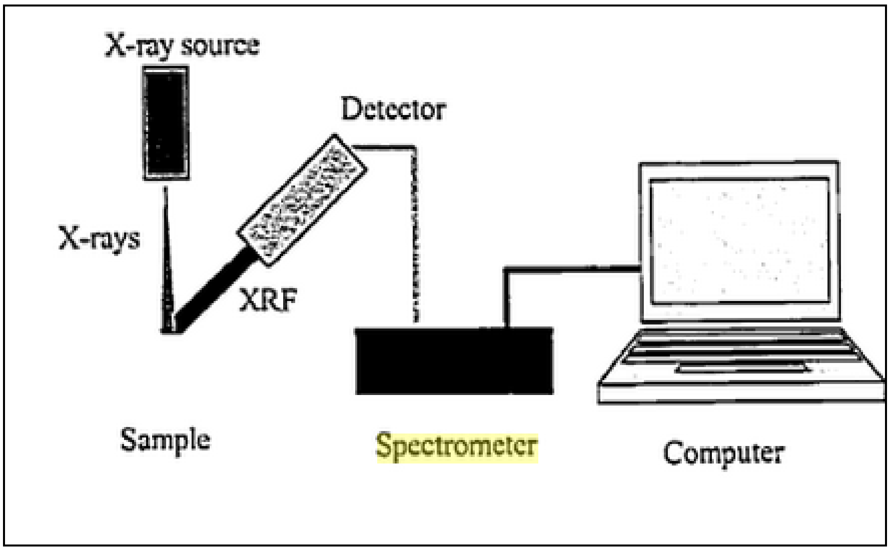


Figure 13: Basic components of an XRF spectrometer (Horiba Scientific, 2013)

XRF has been used to routinely determine quantitatively and qualitatively most elements of interest in ceramic materials (Sanchez-Ramos et al., 2000). Portable XRF is used to measure the pigments in archaeological paintings and pottery (Ferrero et al., 1999). XRF can also identify the elements present in ceramic glazes as well as the concentration of each element in the analyte. It is normally made into a pellet or glass form according to the analytical element of interest (Kelloway and Birmingham, 2010).

2.4 Solid state NMR

NMR spectroscopy is the study of molecular structure through measurement of the interaction of an oscillating radiofrequency electromagnetic field with a collection of nucleus immersed in a strong external magnetic field. These nuclei are parts of atoms that are assembled into molecules. So NMR spectroscopy gives detailed information about the structure and dynamics of research materials NMR spectroscopy gives detailed information about the structure and dynamics of research materials (Macomber, 1998). Nuclear magnetic resonance is based on the magnetic properties of the atomic nuclei (Balci, 2005). Resonance in an NMR experiment is achieved by either varying the frequency at a fixed magnetic field strength called the frequency sweep method or through field sweep method in which the magnetic felid strength is varied keeping the oscillatory frequency constant(Anonymous, 2005). NMR spectroscopy is used successfully for both solution and solid states (Apperley et al., 2012).

Solid state NMR spectroscopy, discovered in 1945 (Klinowski, 2005), is a spectroscopic technique which provide structural information and the dynamics of the process that occurs within the studied materials. Solid state NMR spectroscopy gives information about the co-ordination and atomic environments of various elements of interest to the ceramic scientist. High resolution solid state spectra can be obtained by minimising or eliminating the broadening effects due to internal interaction in solids, by spinning the sample (filled into a rotor) very rapidly at about 20,000 revolutions s^{-1} at an angle 54.74 ^{o} to the magnetic field axis, which is known as magic angle spinning (MAS). The cross polarisation technique was used in solid state NMR for enhancing low intensity signals and has been combined with MAS to obtain high sensitivity, high resolution solid state NMR signals. Nuclei including ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P, ^{29}Si, ^{27} Al, ^{79}Se and ^{119}Sn are NMR active (Balci, 2005) and a number of these are relevant to ceramic materials. For instance ^{27}Al MAS NMR spectra give details about the co-ordination number of Al and the nature of atoms surrounding the Al (MacKenzie and Smith, 2002). ^{27}Al NMR spectroscopy has also been used to gather information about the distribution of Al atoms in tetrahedral and octahedral sheets of clay minerals (Eisazadeh et al., 2012). Thermal transformations of kaolinite, a raw material in the manufacture of ceramic ware were studied by ^{27}Al and ^{29}Si MAS NMR at a spinning frequency of 3 and 4 kHz in tetra methyl silane (TMS) with $Al(H_2O)_6^{3+}$ as a reference material (Balci, 2005; Watanabe et al., 1987). ^{31}P has 100% natural abundance and high resonance frequency(MacKenzie and Smith, 2002) so it is particularly useful for probing bone china which contains bone ash (Hydroxyapatite + Tri-calcium phosphates) one of the main raw material.

2.5 Inductively coupled plasma mass spectroscopy (ICP-MS)

Inductively coupled plasma mass spectroscopy was first used in 1983 (Becker and Dietze, 2000). ICP-MS is an efficient and sensitive analytical mass spectrometric technique used widely for multi element determination to trace and ultra-trace concentration levels for digested solid samples such as ceramics and aqueous solution such as leachates (Becker and Dietze, 2000). Sample introduction is mostly in liquid form at 1mL/min through a nebulizer where it gets converted into a fine aerosol by argon gas flowing at 1L/min. This fine aerosol only represents 1-2% of the sample as it gets separated from large droplets at the spray chamber and enters the plasma torch via a sample injector. It is progressively dried, vaporised, atomised and ionised as it travels through heating zones of the plasma torch and finally reaches the analytical zone of the plasma where the temperature ranges from 6000- 7000 K. Only ground state atoms and ions which represent the elemental composition of the sample are detected at this point (Thomas, 2003). The resulting ions pass through a series of different cones into a high vacuum mass analyser (see **Figure 14)**. A mass to charge ratio (m/z) is used to detect the isotopes of elements. The amount of the element can be calculated from the intensity of a specific peak of that element in a mass spectrum (Casavant, 2008). It is the generation, transportation and detection of number of positively charged ions that gives ICP-MS its characteristic ultra- trace detection capacity (Thomas, 2003).

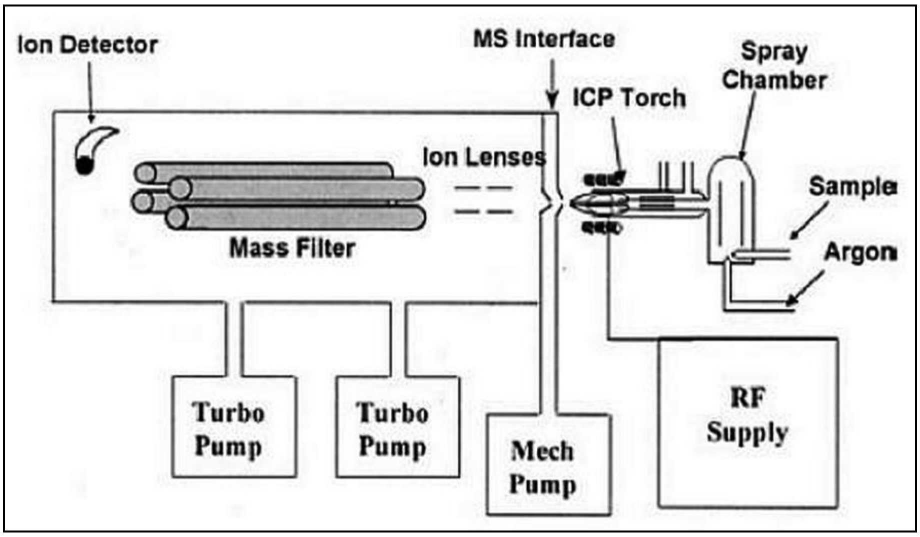


Figure 14: Basic instrumental components of ICP-MS (Thomas, 2003)

Tunstall et al. in 2002 measured the concentration of lead leachate from ceramic glazes using ICP-MS. ^{206}Pb, ^{207}Pb and ^{208}Pb isotope ratios can also be accurately measured this way (Tunstall and Amarasiriwardena, 2002).

Compared with other analytical techniques ICP-MS is better for trace element determination of the leachate from the ceramic glazes due to its low detection limits. Trace element composition of ancient glazed chinaware from various Chinese manufacturers was studied with ICP-MS using the 24 hours standard leach test as explained in Section 1.9.2 (Li et al., 2003).

The limitation of ICP-MS lies in the sample preparation time taken for the acid digestion of the solid products before analysis. To overcome the long procedures and to avoid destruction of the ancient collected products, the technic of development of laser ablation - inductively coupled plasma mass spectroscopy (LA-ICP-MS) was developed. LA-ICP-MS has been widely used in the chemical characterisation of ceramic pigments for archaeological studies. In the LA- ICP-MS technique, a laser beam is focussed on the surface of the material being analysed within an ablation chamber as shown in **Figure 15**. With this interaction, a portion of the material gets ablated and is transferred by gas flow (argon or helium) through polymer tubing into the ICP. The ions from the plasma reach the mass analyser which separates the ions according to their mass to charge ratio.

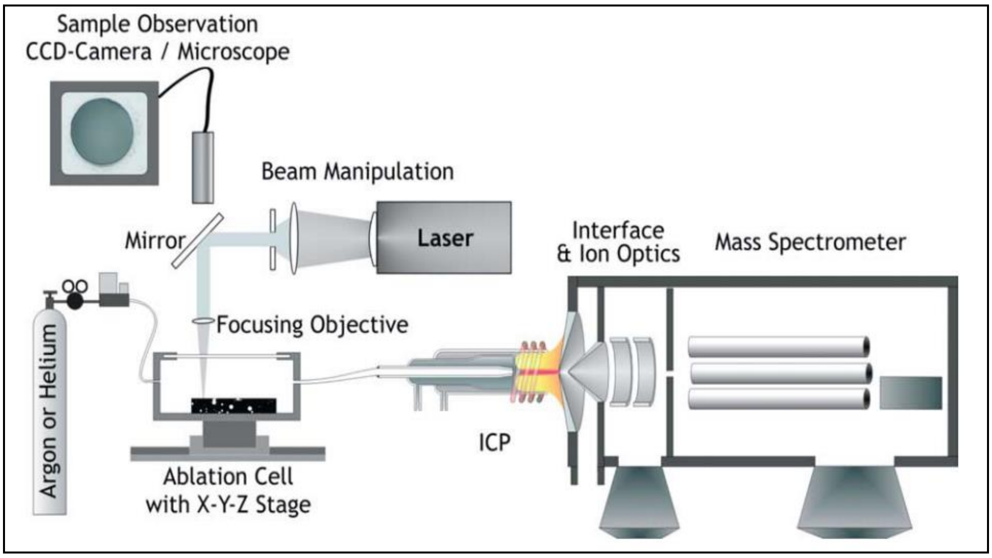


Figure 15: Schematic set up of laser ablation- inductively coupled plasma mass spectroscopy (Gunther and Hattendorf, 2005).

LA-ICP-MS is a more suitable technique for characterising ceramic pigments than XRF and SEM because of its sensitivity and ability to measure a wide range of trace elements at once and due to the fact that the pigments can be studied in situ (Speakman and Neff, 2005).

Specific locations on a piece of pottery can be studied using laser ablation directly which is not possible when characterising the sample by the acid digestion process (Jakes et al., 2002). A new and powerful spot testing technique, which is a combination of laser ablation and inductively coupled plasma with time of flight mass spectroscopy (LA-ICP-TOF-MS) has been used to study the slips and paints used in red wares from east central Arizona, New Mexico (Duwe and Neff, 2007; e-Bay; e-Bay). However precision and accuracy of LA-ICP-MS are affected by the non-stoichiometric effects in the transient signals by heterogeneous chemical and textural compositions, different sample characteristics and vaporisation characteristics. It requires matrix matched calibration standards and internal standardisation using elements present in the material being analysed (Gunther and Hattendorf, 2005).

In terms of ICP-MS as analytical technic, the main advantage is its higher sensitivity and wide dynamic range. Also the detection limit is the most important consideration in choosing a suitable analytical technique for a given application problem. ICP- MS has lower detection limits compared to flame atomic absorption spectroscopy (FAAS) (see **Figure 16**) which was used for testing heavy metal leaching especially lead and cadmium (Hight, 2001). FAAS is an older single element technique which uses a flame to generate ground state atoms from materials analysed. The ground state atom absorbs light of particular wavelength which can be used to determine the concentration of certain element in parts per million (ppm) detection limits (Thomas, 2003).

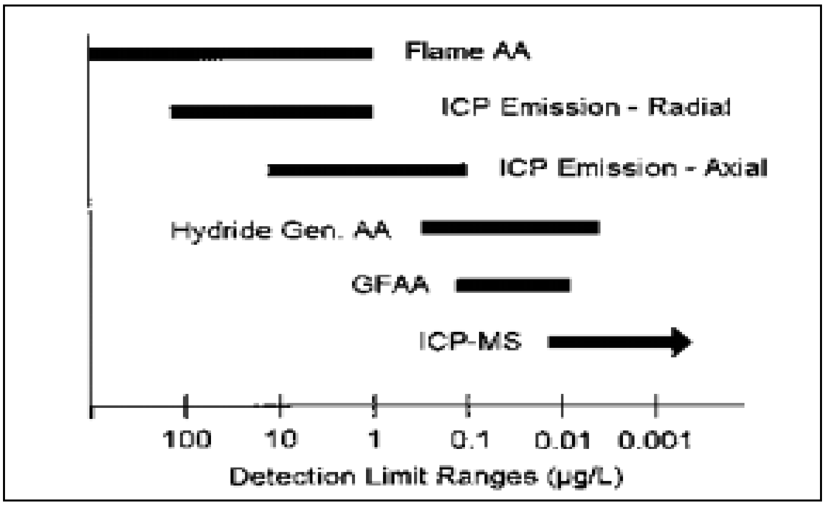


Figure 16: Detection Limit range for some of the major atomic spectroscopy techniques (Thomas, 2003)

When interpreting data from ICP-MS, it is important to note that the technic and suffer from three significant interferences, i.e.; spectral, matrix and physical based interferences. Spectral overlaps are most the serious type of interferences that occur due to the presence of isobars, doubly charged ions or a molecular ion with same mass as the nuclide of interest. These interferences are overcome by using double focused sector field mass spectrometer instead of quadruple filter. A Double focused sector field separates analyte ion signals from the interfering ions which reduces the spectral interference. Blank corrections and mathematical correction help to resolve this problem (covered in **Chapter 4**). Also modern instrumentation and good software combined with optimized analytical methodologies has reduced the negative impact of these interferences on the trace element determination in ICP-MS

In the current study, ICP-MS is used in leaching investigations of the trace elements leaching from the ceramic wares of various eras. It was used because the leachate elements were anticipated to be at very low concentrations. SEM and XRF techniques were also used for bulk glaze characterisation to get an overview of the actual elements present in the sample and to confirm what leached elements to analyse in ICP- MS. It was also to confirm that elements were actually from the sample itself and not from other sources.

Chapter 3: Materials and Methods

3.1 Ceramic materials for the investigation

Ceramic food wares including bowls, plates, tea cups, saucers and dinner or bread plates made by various manufacturers, both local and international and different eras (1890- present), were obtained from different sources within New Zealand (**Table 2**). All the modern Chinese ceramic wares and one Indian bone china tea cup analysed were purchased from the Warehouse in Hillcrest, Hamilton, New Zealand. The traditional New Zealand made Crown Lynn and English made ceramic wares were purchased from antique shops, or were sourced from online purchases which had arrived broken in the post.

Table 2: List of samples used in this research with their sample code, picture and manufactures details

Serial No	Sample type	Sample code	Sample picture	Manufacturers details and colour
1	Bowl	A1		Made: China Source:The Warehouse Colour: Black
2	Bowl	A2		Made: China Source: The Warehouse Colour: Blue

3	Tea cup	A3		Made: China Source: The Warehouse Colour: Red Brand: Nova
4	Sauce dish	A4		Made: China Source: The Warehouse Colour: White Brand: Harrison &Lane
5	Bowl	A5		Made: China Source: The Warehouse Colours: Yellow, red, black and blue
6	Plate	A6		Made: China Source: The Warehouse Colour: Red Brand: Harrison & Lane
7	Tea cup	A7		Made: India Source: The Warehouse Colour: White Brand : Home Concepts

8	Bowl	A8		Made: China Source: The Warehouse Colours: Blue and white
9	Tea cup	A9		Made: China Source: The Warehouse Colour: Blue Brand : Nova
10	Tea cup	A10 (c9)		Made: China Source: Farmers , Hamilton New Zealand Colours: Green, white and yellow Brand : Haven
11	Tea Cup	A11 (B3)		Made: Thailand Source: The Warehouse Colours: Bluish green and yellow
12	Bowl	B1		Made: England Source: Broken online purchase from eBay, UK Colours: White, blue, green, gold and brown

13	Plate	B2		Made: England Source: Broken online purchase from Trade me Colours: Blue and white Brand: Wileman & Co Longton Staffordshire 1892-1911
14	Small plate	B3		Made: England Source: Broken online purchase from eBay, UK Colours: Red and white Brand: Wileman & Co Longton Staffordshire 1892-1911
15	Bowl	B5(C4)	 	Made: England Source: Antique shop, Hamilton Colours: Blue and white Brand : Bleu De Roi Alfred Meakin
16	Tea cup	B6 (MM)		Made: England Source: Personal collection of M. Mucalo Colours: Cream, pink and green Brand : Meakin

17	Tea Cup	C1		Made: New Zealand Source: Antique shop, Hamilton Colour: Grey Brand : Crown Lynn
18	Tea Cup	C2		Made: New Zealand Source: Antique shop, Hamilton Colour: Blue Brand : Crown Lynn
20	Saucer	C3		Made: New Zealand Source: Antique shop, Hamilton Colour: Pink Brand : Crown Lynn
21	Small plate	C4(B6)		Made: New Zealand Source: Antique shop, Hamilton Colour: Brown and green Brand : Roydon Tam O Shanter, (Crown Lynn)
22	Plate	C5		Made: New Zealand Source: Antique shop, Hamilton Colour: Purple, green, brown red and white Brand : Crown Lynn

23	Small plate	C6 (B7)		Made: New Zealand Source: Antique shop, Hamilton Colour: Dark brown Brand : Crown Lynn
24	Plate	C7 (B8)		Made: New Zealand Source: Antique shop, Hamilton Colour: Yellow Brand : Kelston ceramics (Crown Lynn)
25	Tea Cup	C8 (c6)	 (Monk, 2006)	Made: New Zealand Source: Antique shop, Hamilton Colour: Honey colour Brand : Crown Lynn

3.2 Materials used for analytical methods

Type 1 water (distilled and deionised) (G =18$\pm$.2 μs) was used throughout the experiment obtained from a Barnstead system.

3.3 Methods

Ceramic samples collected from various sources were washed using dishwashing liquid with a soft cotton cloth to prevent scratching the surface and rinsed with lukewarm tap water three times and then rinsed three times again with Type 1 water and air dried in a clean atmosphere.

3.4 Scanning electron microscopy

All the images and micrograph were obtained from Hitachi S-4700 SEM linked with EDX at 20 kV to review the elemental composition of ceramic wares.

The aim was to separate the glaze from the clay body for SEM analysis of the elements in the ceramic glazes. Removing glazes from ceramics using sandpaper and glass grinders did not give enough samples large enough for analysis and instead it posed a risk of contamination of the collected glaze powder by particulate matter associated with the sandpapers. Therefore separation of the glazes and the clay body was not achieved and thus bulk sample pieces were selected instead for SEM analysis.

Air dried ceramic wares were broken into small pieces using an iron hammer. This was carried out inside a fume hood to avoid the possible inhalation of dust from ceramic glazes while cracking. Mask and gloves were worn for safety.

Small broken ceramic pieces of samples A1, A7, A11, B2, C6, C7 and C6 were selected for SEM analysis. Samples were mounted on an aluminium stub with a conductive double-sided carbon tape. The samples were sputter coated with platinum in an E-1030 Hitachi ion sputter for about 80 seconds under argon atmosphere. Platinum coating and carbon tape prevents charging and loss of resolution by providing a conduction pathway for electrons.

3.5 Fourier transform infra-red spectroscopy

FTIR analysis was performed using a Perkin Elmer Precisely Spectrum 100 FTIR spectrometer. Ceramic wares were manually ground with a mortar and pestle into a fine powder. The powdered sample was then gently mixed with analytical grade KBr at 1:10 ratio using an agate mortar and pestle, pressed into transparent disks using a hydraulic press at 110 V and the disk obtained was mounted in a sample holder. The spectra were recorded in the 4000 cm^{-1} - 400 cm^{-1} range at 4 cm^{-1} resolution over 50 scans.

3.6 Solid state NMR spectroscopy

^{29}Si, ^{27}Al and ^{31}P MAS NMR spectra of various ceramic wares (A1, A2, A3, A4, A7, A10, B2, B5, C5, C4 and C7) were obtained using direct polarisation in a Brunker MAS 11 Avance 300 mHz solid state NMR spectrometer. Solid state NMR was used for the characterisation of different clay at various firing conditions. Bulk ceramic sample powders were prepared by finely grinding the ceramic ware with a mortar and pestle for about 10 to 20 minutes. These were then packed into a Zirconium rotor with a KEL-F cap and inserted into a MAS probe in which was spun at 5000 - 100000 Hz at the magic angle of 54.74 ^{o}. Cross polarisation spectra were not able to be acquired on these samples due to lack of signal since no protons were associated with the nuclei of interest. Spectra acquired with solid state NMR used the parameters outlined in **Table 3.**

Table 3: Various parameters used during acquisition of spectra in solid state NMR spectrometer

Isotope	Relaxation delay (s)	Pulse length (μs)	Power level dB	Acquisition time (s)	Frequency used (mHz)	Number of scans
^{29}Si	8	3.5	2.0	0.043	59.69	5000
^{27}Al	1	1.0	0.50	0.0346	78.2	2000
^{31}P	2	4.0	3.0	0.021	121.5	2000

^{29}Si MAS NMR measurements were calibrated with 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt as a standard reference for ^{29}Si, the peak occurs at 0 ppm. Yittrium aluminium oxide, which is expected to give a peak at +0.7 ppm, was used for ^{27}Al and ammonium dihydrogen orthophosphate with a peak at 0.81 ppm was used for ^{31}P.

3.7 X- ray fluorescence spectroscopy (XRF)

The XRF instrument used was a Spectro X- Lab 200 X- ray spectrometer housed in the Department of Earth and Ocean Sciences at Waikato University. Sample powders were prepared by grinding with a mortar and pestle. Pressed pellets of the samples were made using 5 g of the ground powder. The powder was weighed into a paper cup, then mixed with 10 - 13 drops of PVA binder using a wooden spatula and filled into a pre-weighed Al cup. The Al cup was placed on the raised metal base with a cylinder over it and a plunger was inserted against the sample. The entire base with the sample, cylinder and plunger was placed in a hydraulic press and gently pressed at 90 bars pressure. The pressed pellet was kept in an oven at 70 ^{o}C for about 2 hours to evaporate off the binder. After cooling, the sample was weighed again to record the exact sample weight. The pressed pellet was then inserted into the XRF carousel in the instrument. Blank samples used were analytical grade aluminium oxide prepared in the form of a pressed pellet to test for any method contamination. Calibration standards were Geostandard BX-N (Bauxite) for major and trace elements (refer to **Appendix** for detail) similar to elements present in the research samples.

3.8 *Inductively coupled plasma mass spectroscopy (ICP-MS)*

ICP-MS used for these leaching studies was Perkin Elmer ICP-MS spectrometer with ELAN DRC 11 Axial field technology.

Materials required

Polypropylene beakers and volumetric flask, para-film sealing film and aluminium foil were used. Sartorius Stadium Biotech Minisart single use filters (0.45 µm), Greiner Bio-one Ultra-tip pipette tips (1 mL, 5 mL, 10 mL), Greiner falcon tubes (15 mL, 50 mL) were all purchased from the science store of the University of Waikato. Calibrated auto pipettes (1 mL, 5 mL and 10 mL) were used for pipetting out sample solution for ICP-MS analysis.

Testing solution

Glacial acetic acid (CH_3COOH) 60.05% was the main chemical reagent purchased from Ajax Finechem Pty Ltd, Batch No: 1002295.

The ceramic wares were tested with locally available food products such as Premium Keri orange juice (2.4 L) Batch No: 2220, Coco Cola and Lipton tea (black tea and lemon tea).

Acid digestion

Some of the samples required acid digestion prior to analysis by ICP-MS. Concentrated nitric acid (65%) from Merck and analytical grade hydrogen peroxide (30%) purchased from Ajax Finechem Pty Ltd was used.

Elements for analysis by ICP-MS

^{10}B, ^{23}Na, ^{24}Mg, ^{27}Al, ^{39}K, ^{43}Ca, ^{51}V, ^{53}Cr, ^{54}Fe, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{75}As, ^{82}Se, ^{85}Rb, ^{109}Ag, ^{111}Cd, ^{118}Sn, ^{137}Ba, ^{205}Ti, ^{207}Pb, ^{238}U were the elements analysed by ICP- MS. In Chapter 4 (results and discussion) only the elements that pose health hazards to consumers are explained.

Standards used for ICP-MS calibration

ICPMS calibration standards were used in the range of concentrations that may exist in samples based on results of other studies. Inorganic Ventures multi element (Ag, Al, As, Ba, Cd, Co, Cu, Cr, K, Mg, Mn, Na, Ni, Pb, Rb, S, Se, Sn, Sr, Ti, U, V and Zn) calibration standard 1V –ICP-MS 71A 50ppb + 3% HNO_3 (v/v), Merck IV 50ppb + 2% HNO_3 (Ag, Al, B, Ba, Cd, Co, Cu, Fe, Mg, Mn, Na, Ni, Pb, Rb, S, Se, Sr, Ti U, V and Zn) and Merck ICP - multi element (similar elements mentioned under calibration standard along with Na, K, Ca and Fe) standard solution IV 5000 ppb in dilute HNO_3 were the standards used. The reference standard used throughout the entire ICP-MS experiment was Ottawa River water, Canada SLRS-5. The quality control standards used were Inorganic Ventures multi element calibration standard 1V–ICP-MS, Merck IV 50 ppb Merck IV 1000 ppb and Plasma CAL tin (Sn) and zirconium (Zr) standards were used.

4% Acetic acid leach test

Acetic acid 4% was the main test solution used for leaching samples in this study. The standard test method followed was an American Society for Testing and Materials (ASTM) C738-94 protocol. C738-94 was used to determine the leaching of heavy metals extracted by 4% acetic acid from the glazed ceramic surfaces. The acetic acid used in this study was always freshly prepared as required before each leach test. About 40 mL of glacial acetic acid was pipetted out using a 10 mL Eppendorf calibrated auto pipette and made up to 1L (v/v) with Type 1 water in a volumetric flask. Its pH was noted using pHM240, pH/ ION Meter, Metler Lab; which was calibrated with pH 4.01 and pH 7.00 buffer solutions. Ceramic food wares for testing were rinsed three times with Type 1 water then air dried and placed in a clean atmosphere to avoid contamination. The weight of each ceramic ware was recorded before the test. Each test item was filled with the testing solution (i.e. 4 % acetic acid) up to the rim until it started overflowing with test solution. All the ceramic wares tested were covered with para-film and topped with aluminium foil to prevent evaporation and to avoid reaction of certain heavy metals (e.g. Cd) in the presence of light. Care was taken to avoid contact between the Al foil and testing solution. A polypropylene beaker, which is highly resistant to acid attack, was used for blank sample preparation. Samples were left undisturbed for 24 hours at room temperature (22 ^{o}C to 24 ^{o}C). After stirring, a 5 mL aliquot of the testing solution was taken into a clean 15 mL falcon tube and then diluted with 5 mL (v/v) Type1 water. The solution was mixed well by inverting the tube upside down with a closed lid at least three times. Duplicates were taken for all samples analysed. Tests were repeated two or three times with the same leaching conditions (room temperature and 24 hours exposure time) for the same ceramic dishes with freshly prepared 4% acetic acid to determine the varying level of leaching metal during each repeated test at different days.

Orange juice leaching test

Orange juice brought from a local supermarket was used under room temperature conditions for the leaching test. Teacups (coded as A_{3}, A_{7}, A_{9}, A_{10}, A_{11}, B_{6}, C_{1}, C_{2}, C_{8} (see **Section 3.1**) for pictures of teacups) were chosen for this test, because often consumers do use ceramic cups for drinking juices and this could potentially result in heavy metal leaching and unwitting intake by consumer. Procedures such as washing, drying, weighing and pH testing were performed as followed for the acetic acid leach test. All ceramic cups were filled with the orange juice (100 to 250 mL) to the rim, then sealed with para film and Al foil. The leaching time

(time of exposure) was set as 10 minutes to provide a realistic measure in comparison with normal use of a cup. The sample was mixed thoroughly and 10 mL of solution was transferred to a 15 mL falcon tube for centrifuging to separate the solid matter from the liquid. The liquid (colloidal appearance) solution was filtered using a 0.45 µm filter and then a 1 mL aliquot was diluted with 9 mL of Type 1 water for ICP-MS analysis in a 15 mL falcon tube. The solid extract on the other hand was transferred to a clean petri dish and dried in an oven at 30 ^{o}C. To about 0.1 g of the dried solid extract 3 mL of HNO_3: H_2O_2 (2:1) was added. The sample was left overnight to digest before heating it on a heating block at 75^{o}C for 90 minutes. The digested sample from the solid extract was diluted 200 times to match it to 2% HNO_3 for ICP-MS analysis. Two sample analyses (liquid and solid) per piece of ceramic ware were performed. Duplicate analyses were performed for every sample analysed.

Leaching in hot water and cold water

Hot Type 1 water (boiled in 2 L conical flask using a Bunsen burner and brought to boiling before using for leach test) at 100 ^{o}C and cold Type 1 water at about 2 ^{o}C was added to teacups (coded as A_3, A_7, A_9, A_{10}, A_{11}, B_6, C_1, C_2, C_8 (see **Section 3.1)** for pictures of teacups) at different times after following the same procedure for washing, drying, weighing and sealing as followed for 4% acetic acid leach test. After 10 minutes the weight was recorded and then a 10 mL aliquot of test solution was pipetted into a 15 mL falcon tube. Type 1 water was stored in a 2 L polypropylene volumetric flask in the refrigerator and temperature reduced to 2 ^{o}C before the leaching test. Method blanks were sampled from a polypropylene beaker for hot and cold water. Duplicates were tested for all samples.

Leaching into black tea and lemon tea

About 2 L of Type 1 water was boiled in a conical flask using a Bunsen burner and 8 tea bags (approximately 2 g each) soaked in the boiling water until the tea extracts were completely absorbed by the boiling water. 0.5 L of milk was added and after thorough mixing with a wooden spatula, cups were filled up to the rim, the weights were recorded and then the cups were sealed with aluminium foil without touching the surface of the tea solution. A method blank was also prepared by filling tea solution into a polypropylene beaker. A hot water blank test was also carried out to check for contamination from the conical flask. After 10 minutes all samples were mixed thoroughly and 1 mL aliquot was taken from each test solution before filtering through 0.45 µm filter and diluted to 10 mL (v/v) with Type1 water. Lemon tea was also sampled following the same procedure for black tea but without milk added. pH measurement of both the leaching tea samples were noted.

Coca Cola leaching test

Cups were filled with Coca Cola up to the rim just before overflowing and the mouth of the cup covered with para - film and then aluminium foil on top to avoid direct contact of Al foil with the testing solution. A blank sample solution was prepared following the same principle in a polypropylene beaker. Before sealing the weight of the test sample was recorded. After 10 minutes of leaching test the solution was mixed well and a 1mL aliquot was taken from each sample tested then mixed with 9 mL (v/v) of Type 1 water in a falcon tube and well mixed by inverting upside down three times.

Interferences were overcome using drift corrections through recalibrating the instruments every 24 samples by running a flush blank followed by quality control standards and calibration standards previously mentioned in **Section 3.8**.

Chapter 4: Results and Discussion

This Chapter will cover the results for characterisation done on ceramic wares available in New Zealand markets from various eras ranging from Victorian era to New Zealand Crown Lynn potteries to the modern Chinese, Indian and Thailand ceramic wares using FTIR, Solid state NMR, SEM/EDX and XRF along with the visual survey results of the above mentioned samples. The visual survey results features the pictures of the studied ceramic wares. A detailed description of all the samples investigated is presented in **Table 2.** The main results section for the ICP-MS is presented as a separate topic with subheading for Victorian, Crown Lynn and modern ceramic wares (Chinese, Indian and Thailand) and subheadings for different leachate solutions used for testing the durability of the elements added to the glazes to produce those colourful ceramic wares.

4.1 Visual survey results

British Victorian era and mid-20th century samples

Table 4: Pictures of the Victorian era samples with their sample codes

			
B1- Chapman	B2-Wileman	B5- Alfred Meakin	B6- Alfred Meakin

The British Victorian era samples (Wileman and Chapman) and mid-20th century (Alfred Meakin) chosen for the leaching studies are illustrated in **Table 4** for reference in this chapter. The Chapman sample (B1) was a high gloss white glazed bowl with much of the decorated designs on the outer surface of the rim.

The Wileman bone china plate (B1) used in this study had highly decorated blue coloured designs on the surface of the plate which would have been exposed to food or liquids and plain white on the back with the manufactures stamp in it. It had gold gilt on the rim.

The Alfred Meakin bowl (B5) studied had a plain shiny white surface and dark blue colouration only in the rim area which would not ordinarily come into contact with the food served on these bowl. Another Alfred Meakin teacup (B6) had a cream coloured glaze body with a pink coloured design both inside and outside the cup. It also had the gold coloured design on the outside of the tea mug. The teacup was also highly crazed due to routine usage.

Crown Lynn samples

All Crown Lynn samples used in this investigation are shown in **Table 5**.

Table 5: Pictures of the Crown Lynn samples with their sample codes

 ***C1***	 ***C2***	 ***C3***	 ***C4***
 ***C5***	 ***C6***	 ***C7***	 ***C8***

Crown Lynn samples were not all brightly coloured. About 8 Crown Lynn samples were chosen for these leaching studies. Sample C1 is a used teacup with highly glossed grey colouration throughout the surface. While C2 is also a used teacup which had grey colour inside and blue glaze outside the teacup. Some crazing of the glazed surface was noted on long term use of this teacup. Sample C8 was a tea cup with dark brown coloured design throughout and no crazing was observed inside or outside. Crown Lynn teacups did not have the highly coloured decorated over glaze design in them as seen in the Alfred Meakin teacup (B6)

All the Crown Lynn plates bought from antique shops are used. Sample C3 is a small plate with a worn - out pink coloured surface which would be exposed to foods. Sample C4 is a cream coloured plate with brown and green stripes on the surface. Sample C5 has highly decorated coloured surface on the plate that would be exposed to foods. Sample C6 is a small plate with dark brown and yellow colour design on the surface of the plate and plain brown on the outside of the plate. Sample C7 is a yellow glazed plate with a brown colour decorated design under the glaze.

Modern ceramic wares made in China, India and Thailand

All modern ceramic wares used in this study were new unused ones as bought from the local store shown in **Table 6**.

Table 6: Pictures of the modern ceramic samples (manufactured in China, India and Thailand) with their sample codes

 ***A1***	 ***A2***	 ***A3***	 ***A4***
 ***A5***	 ***A6***	 **A7- Indian**	 **A8**
 **A9**	 ***A10***	 ***A11-Thailand***	

When compared to the ceramic wares from British Victorian era, mid- 20^{th} century and Crown Lynn, modern Chinese ceramic wares used in this study were brightly coloured (black, blue, red, yellow, orange, green and bluish green). Out of four teacups two of them A3 and A9 had bright colours both inside and outside while the inside was more shiny than the outside glazed surface. Sample A10 had green, yellow and brown coloured decorative glaze outside and a plain white glaze inside the cup very different from the other Chinese teacups.

All the bowls (A1, A2, A5 and A8) had dark coloured inner surfaces that would come in contact with the food. A small square white plate (A4) did not have any decorative colours in it. While sample A6 was a shiny, bright red plate throughout and sample A5 had colours like red, blue, yellow, black and orange coloured designs on the plate that would be exposed to food served in it as seen in the picture.

One of the Indian bone china teacup (A7) used had white glazed surface with a bright pink and green coloured flower design outside and a plain white glazed surface inside the cup. Another teacup made in Thailand had bluish green, yellow and brown coloured glazed outer surface and an off white coloured glazed inner surface.

4.2 Characterisation of ceramic wares used in this investigation

Characterisation studies using SEM/EDX and XRF were mainly performed to get an idea of what elements were present in the ceramic wares so these could be followed by ICP-MS leaching studies technique. The SEM/EDX technique was initially attempted as a trial to obtain useful elemental information related to the glazes as these are highly exposed to liquids and foods. But the EDX spectra only gave the basic details of the raw materials used for making the clay and not informative about the elements present in the glazes. However XRF was used as an alternative technique and it gave lot more reliable quantitative and qualitative information than EDX.

The structural characterisation using FTIR and solid state NMR gave details about the bulk mineralogical composition and various phases of the feeds stock materials used.

4.3 Solid state NMR results

SSNMR results for British Victorian era (Wileman) and mid-20th century (Alfred Meakin) ceramicwares

The structure of the raw materials present in the bulk Wileman (B2) and the Alfred Meakin samples (B5) were studied using chemical shift resonances of ^{29}Si, ^{27}Al and ^{31}P with solid state NMR spectroscopy. The chemical shift obtained for each sample is given in the **Table 7**. Solid state NMR spectra (^{29} Si, ^{27}Al and ^{31} P) of Wileman bone china (B2) is shown in **Figure 17**, **Figure 18** and **Figure 19** for Alfred Meakin sample (B5) given in **Appendix -1**.

Table 7: Solid state NMR chemical shifts resonances of 29Si, 27Al and 31P of British Victorian eras (B2) and Alfred Meakin (B5) samples

Sample Code	^{29}Si shift ppm 5 kHz	^{27}Al shift ppm 10 kHz	^{31}P shift ppm 10kHz
Wilemen (B2)	-90.5 and -102.2	41.7 and -20.2	0.5
Alfred Meakin (B5)	-101.5	39.0 and -20.8	1.1

Tectosilicates (tetrahedral silicates linked in extensive three dimensional networks) have shifts in the range -83 to 114 ppm. Two ^{29}Si shifts were observed in Wileman sample (B2) at -90.5 and -102.3 ppm (see **Figure 19)** and one at -101.5 ppm for Alfred Meakin sample (B2). They are due to tetrahedral silicates. The chemical shift between 30- 40 ppm is due to the 5- coordinated Al in well-defined crystalline compounds. The negative chemical shifts up to 25 ppm in phosphate containing Wileman bone china was due to the aluminophosphates which is expected in a bone china ware. Chemical shift at 0.5 ppm for ^{31}P of Wilemen sample in **Figure 18** and 1.1 ppm for Alfred Meakin sample shown in **Appendix -1** might be due to PO_4 from the added bone ash (HAP (hydroxyapatite) + TCP (Tri calcium phosphate)) in all the bone chinawares (MacKenzie and Smith, 2002). Two side bands are seen in the ^{31}P spectra for the Wileman bone china and Alfred Meakin sample.

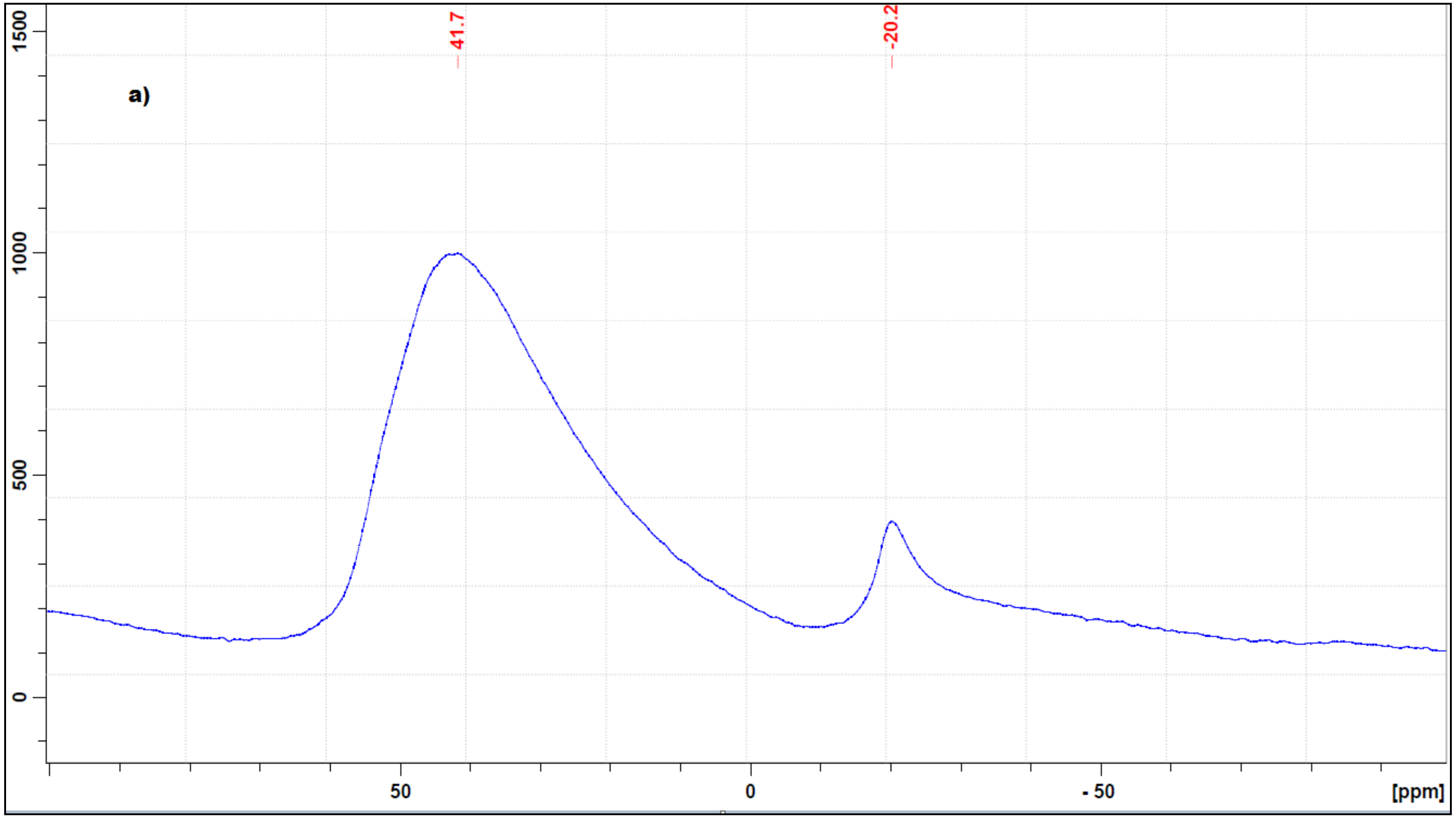


Figure 17: MAS Solid state NMR of Wileman bulk bone china powder (B2) for 27 Al with direct polarization method.

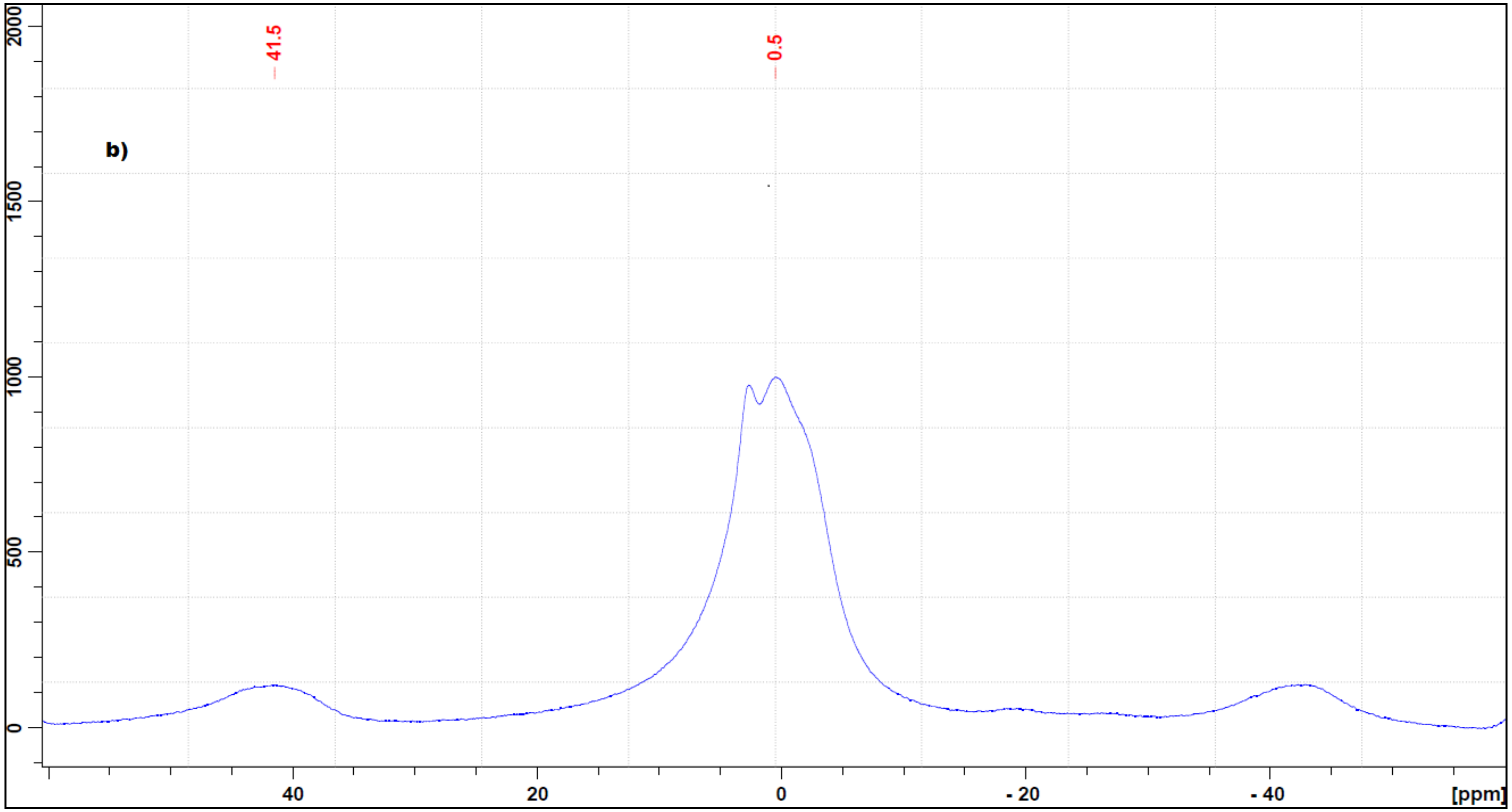


Figure 18: MAS solid state NMR of Wileman bulk bone china powder (B2) for 31P with direct polarization method

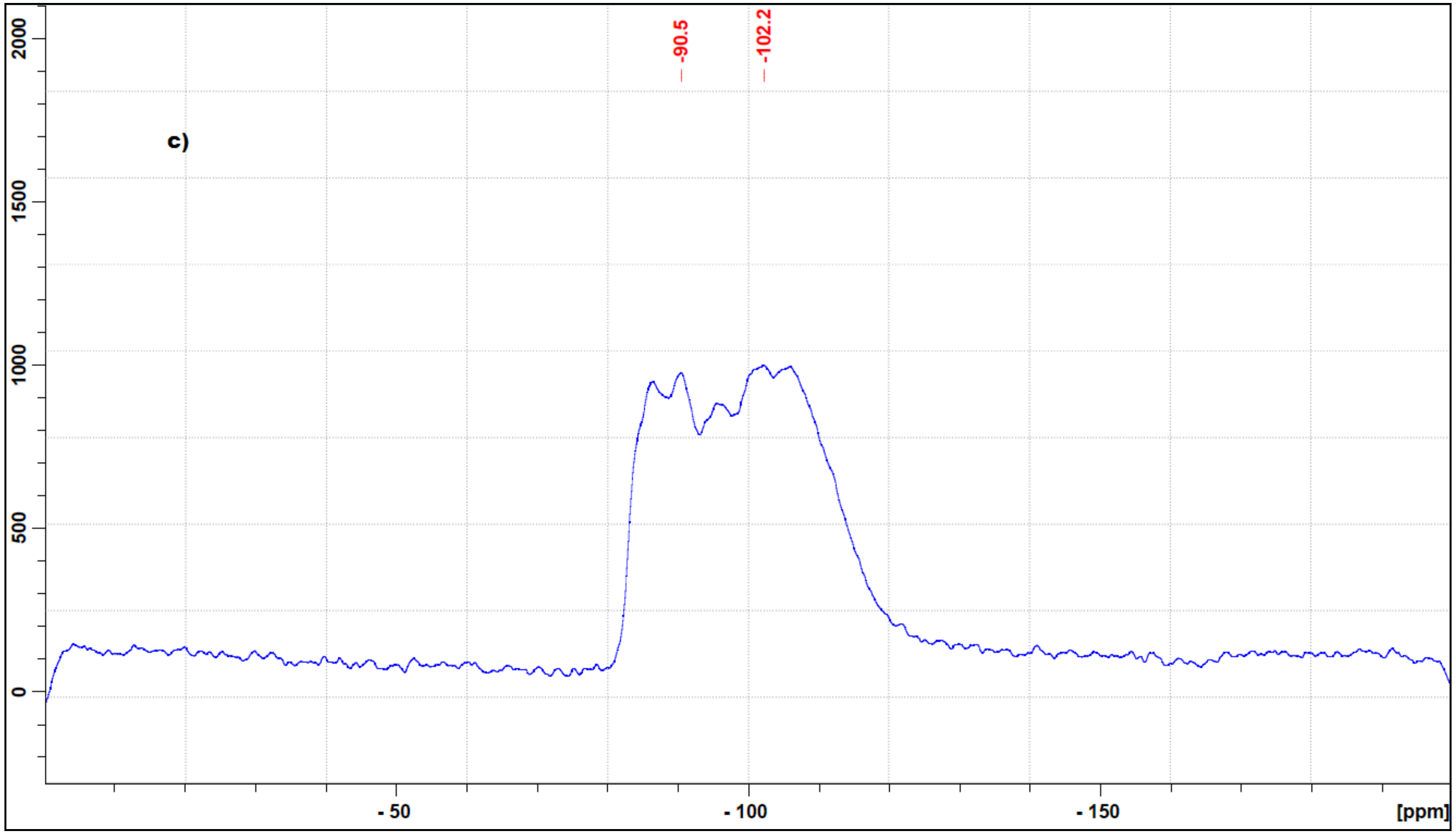


Figure 19: MAS solid state NMR of Wileman bone china powder (B2) for 29 Si with direct polarization method

SSNMR results for Crown Lynn samples

The solid state NMR chemical shifts obtained for ^{29}Si, ^{31}P and ^{27}Al for the Crown Lynn ceramic wares are shown in **Table 8**. All the spectra corresponding to the chemical shifts obtained were given in the **Appendix 1**.

Table 8: Solid state NMR chemical shifts resonances of 29 Si, 27Al and 31 P of Crown Lynn samples

Sample Code	^{29}Si shift ppm 5 kHz	^{27}Al shift ppm 10 kHz	^{31}P shift ppm 10kHz
C4	-106.0	36.9	No peak detected
C5	-109.4	39.8	No peak detected
C7	-109.4	35.7	No peak detected

The ^{29} Si shift of tetrahedral silica with no bonded aluminium atoms occurs in the range -102 to-116 ppm and tetrahedral silica with one aluminium atoms show ^{29}Si chemical shift at -97 to -107 ppm. Tectosilicates like cristobalite have ^{29}Si chemical shift resonance at -109 ppm (MacKenzie and Smith, 2002). Cristobalite had been found in New Zealand clays that were used for pottery making in Crown Lynn potteries (Christie, 2012). ^{29}Si at -106 ppm was due to coesite. It is a high pressure polymorph of SiO_2 and is transformed into quartz at a temperature of 1100 to 1350 ^{o}C (Encyclopaedia, 2012). ^{29}Si chemical shifts for quartz may occur at -107 ppm. The Chemical shift ranges of ^{29}Si in Wileman and Alfred Meakin samples were slightly different from the Crown Lynn wares but they are all tectosilicates mineral peaks (MacKenzie and Smith, 2002).

^{27}Al NMR chemical shifts in the range 30 to 40 ppm could be due to well defined crystalline compounds. Firing temperatures plays an important role in the production of ceramic materials and very different minerals occur at different temperature ranges. At 550 ^{o}C, when kaolinite loses its structural water to form amorphous meta- kaolinite two new peaks occurs at 66 ppm and 34- 39 ppm (MacKenzie and Smith, 2002). Only one peak was found in 34-39 ppm was observed in this experiment which might be due to meta-kaolinite. Meta-kaolinite was also observed in the FTIR spectra of Crown Lynn wares. No ^{31}P chemical shifts were detected for any of the Crown Lynn ceramic wares.

SSNMR results for modern ceramic wares

Solid state NMR chemical shifts for ^{29}Si, ^{27}Al and ^{31}P of modern ceramic wares are detailed in **Table 9**. Solid state NMR spectra of analysed samples are shown in **Appendix-1.**

Table 9: Solid state NMR chemical shifts resonances of 29 Si, 27Al and 31 P of modern ceramic wares made in China and India

Sample Code	^{29}Si shift ppm 5 kHz	^{27}Al shift ppm 10 kHz	^{31}P shift ppm 10kHz
A1	-110.6	37.8	No peaks detected
A2	-103.7	0.7 and 37.7	No peaks detected
A4	-107.6 and -88.6	35.1 and -11.0	No peaks detected
A7	-101.1 and -90.1	-20.3 and 52.3	0.5
A10	-106.2	37.0	No peaks detected

The identified ^{29}Si chemical shift resonances signals at -110.6, -103, -107.6, -88.6, -101.1, -90.1, 106.2 ppm were due to the tectosilicate mineral (MacKenzie and Smith, 2002) similar to that observed in Crown Lynn and Victorian era samples. The ^{21}Al chemical shift resonance at 35.2, 37.2, 37.0 and 52.3 ppm were due to the well characterised five coordinated aluminium compounds (MacKenzie and Smith, 2002). The two most common aluminium compounds in ceramics are tectoaluminosilicates and aluminosilicates and their chemical shifts occur in the range 55-68 ppm and the layered aluminosilicates. The chemical shifts resonance signal at 70 to 80 ppm. Signals in these ranges of chemical shifts were not detected in any of the analysed ceramic wares (MacKenzie and Smith, 2002).

Indian bone china A7 showed chemical shift resonance for ^{31}P at 0.5 ppm and it might be due to PO_4 from the added bone ash (HAP (hydroxyapatite) + TCP (tri calcium phosphate)) and two spinning side bands for ^{31}P were also observed in Indian bone china similar to Wileman bone china (B2) Broad ^{29}Si peaks were observed for A7 different from other modern ceramic wares where more narrow peaks were observed. Broad ^{29}Si of Indian bone china peaks was similar to the ^{29}Si of Wileman bone china.

4.4 FTIR results

FTIR spectroscopy was found to be useful for detecting the minerals present in the clay through their characteristic vibrational frequencies.

FTIR results for British Victorian era ceramic wares

The FTIR spectra of the Victorian era Wilemen bone china are illustrated in **Figure 20** with their frequencies and tentative assignments given in **Table 10**. FTIR has numerous advantages of chemical analysis of calcium phosphate containing products, here we use bone china ceramic wares which contains (TCP) as the main ingredient from the bone ash as mentioned in **Chapter 1**. FTIR spectra provide useful information about the location of the peaks, their intensity in a particular wave number range (Berzina-Cimdina and Borodajenko, 2012). The broad peak at 3464 cm^{-1} is due to moisture within the KBr blank and can be discounted.

Table 10: Observed infra- red frequencies of Victorian ceramic wares with tentative vibrational assignments and references.

B2 /cm^{-1}	**Tentative vibrational Assignments**	**References**
1043	P-O stretching and bending vibrations of the PO_4^{3-} groups Si-O vibrations of kaolinite	(Berzina-Cimdina and Borodajenko, 2012; Laird, 2010; Prabakaran et al., 2010)
948, 602 and 558	P-O stretching and bending vibrations of the PO_4^{3} groups	(Berzina-Cimdina and Borodajenko, 2012; Laird, 2010)

The peaks at 1043, 948, 602 and 558 cm^{-1} were assigned to the different modes of P-O stretching and bending vibrations of the PO_4^{3-} moiety. The strong and broad band at 1043 cm^{-1} shows Si-O vibrations of kaolinite which might be present in small amount in the feed stocks of bone china sample. However there is also a contribution from the P-O stretch of phosphate groups (Laird, 2010).

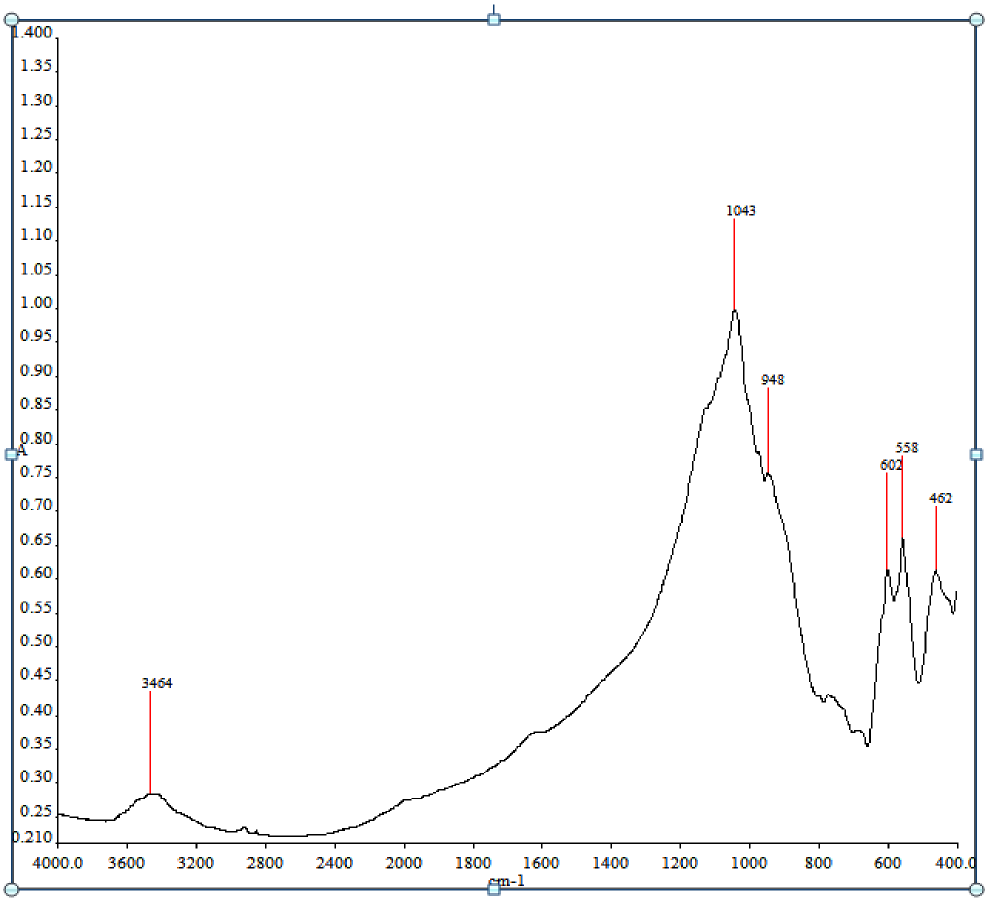


Figure 20: FTIR spectra of Wileman bone china (B2)

FTIR results for Crown Lynn samples

The FTIR results for Crown Lynn samples are given in **Table 11** with their frequencies and tentative assignments. The figures showing the FTIR spectra of ceramic wares were given in the **Appendix 2**. Peaks in the range 1080 to 1090 cm^{-1} were assigned to the Si-O stretching band of quartz. Si-O stretching band of kaolinite occurs in the range 1031 to 1038 cm^{-1}. No peaks were obtained in the range 1031 to 1038 cm^{-1} for any of the Crown Lynn wares as expected due to the fact that these were not bone china so had no phosphate. The additional peaks around 795 and 778 cm^{-1} were seen in all the Crown Lynn wares expect C5 where the 778 cm^{-1} peak was missing. These observed bands were the stretching vibrations of quartz. Bending vibrations of quartz were observed at peaks 693, 559, 558 and 567 cm^{-1}. Solid state NMR detected no phosphate peaks for Crown Lynn ceramic wares and this can be seen from the absorption bands obtained for Wileman bone china where the main peaks were due to the PO_4 groups as opposed to Crown Lynn samples where the main stretching band is due to quartz and kaolinite.

Table 11: Observed infra- red frequencies of Crown Lynn ceramic wares with tentative vibrational assignments and references.

C3	C4	C5	C6	Tentative vibrational Assignments	References
cm^{-1}					
3459	3475	3448	3475	O-H stretching of adsorbed moisture	(Shoval et al., 2011)
1091	1087	1090	1083	Si-O stretching band of meta-kaolinite and quartz	(Shoval et al., 2011)
796	795	795	795	Si-O symmetrical stretching vibrations of quartz	(Saikia et al., 2008)
778	778	-	778	Si-O symmetrical stretching vibration of quartz	{Saikia, 2010 #163}
693	693	694	693	Si-O bending vibration of quartz	(Saikia et al., 2008)
458	459	467	459	Si-O symmetrical bending vibration of quartz, Si-O-Si bending.	(Prabakaran et al., 2010; Saikia et al., 2008)

FTIR results for the modern ceramic wares

The FTIR vibrational frequencies of some of the modern ceramic wares are given in the **Table 12.** Si-O stretching vibrations of quartz as observed for Crown Lynn wares were also detected in modern Chinese ceramic wares (A1, A2, A3, A5, A9 and A10) between 1076 and 1082 cm^{-1}, around 795 and 778 cm^{-1}. A weak band at 693 cm^{-1} can be attributed to the Si-O bending of quartz for all the modern

Chinese samples (Palanivel and Velraj, 2007; Saikia and Parthasarathy, 2010; Saikia et al., 2008; Shoval et al., 2011).

Si-O stretching modes and P-O stretching modes at 1043 cm^{-1} for Indian bone china (A7) were assigned to kaolinite and the added bone ash as was done for the Wileman bone china (B2). All stretching and bending vibrational frequencies of the quartz (798, 778, 693 and 459 cm^{-1}) were observed also in modern (Indian) bone china (A7) which was not observed in Victorian era (Wileman) bone china (B2) (Berzina-Cimdina and Borodajenko, 2012; Laird, 2010; Prabakaran et al., 2010).

Table 12: Observed infra- red frequencies of modern ceramic wares with tentative vibrational assignments and references.

A1	A2	A3	A5	A7	A9	A10	Tentative vibrational Assignments
3471	3468	3452	3456	3449	3452	3450	O-H stretching of adsorbed water
1080	1076	1079	1082	-	1082	1082	Si-O stretching of quartz
-	-	-	-	1043	-	-	P-O stretching modes of PO_4^{3-} and Si-O stretching mode of kaolinite
795	796	796	798	796	796	798	Si-O symmetrical stretching vibrations of quartz
778	-	778	776	778	778	-	Si-O symmetrical stretching vibration of quartz
693	693	693	693	693	693	-	Si-O bending vibration of quartz
456	459	459	451	459	459	467	Si-O symmetrical bending vibration of quartz, Si-O-Si bending.

4.5 SEM/EDX results

The SEM/EDX analysis results gave information about the expected feed stocks in the clay that is used for making ceramic wares. The SEM images were collected for all different ceramic wares from different periods which gave basic information on the firing temperature conditions of the clay bodies making up the china. EDX spectra were able to provide only the basic bulk elemental composition of the raw materials for all ceramics wares. However it was less reliable in terms of identifying elements expected in some samples, e.g. glaze components. However, the main interest of this research is the elements present in the glazes which are the parts of the china exposed to food and from which heavy metals may enter foods and liquids.

SEM results for Victorian era and mid-20th century samples

SEM image of the Victorian era Chapman sample (B1) is given in the **Appendix 3.** It shows a highly porous surface. SEM image of Wileman bone china (B2) is given in **Figure 21**.

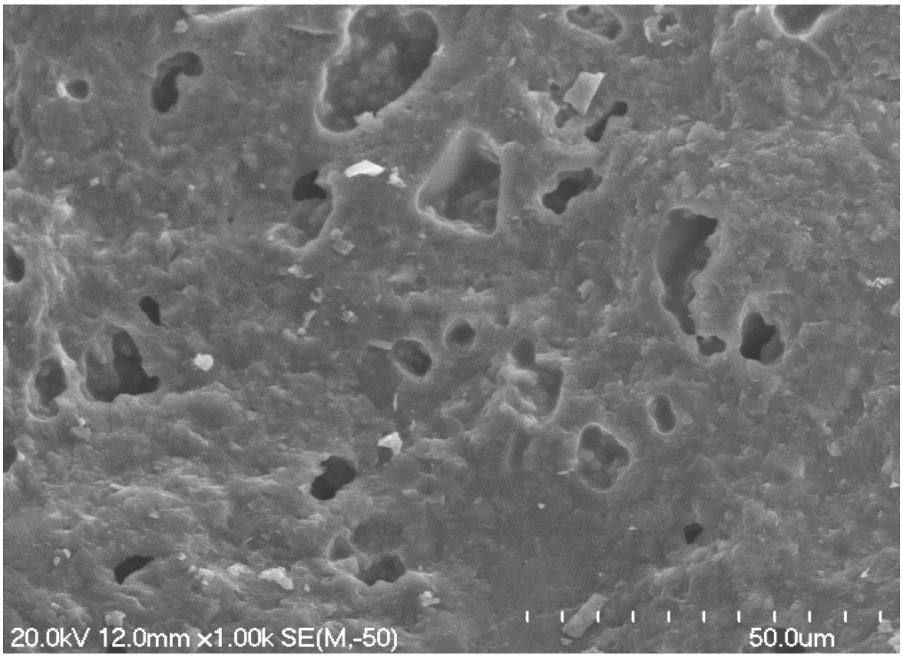


Figure 21: SEM image of the Victorian Era - Wileman bone china (Sample B2)

The Wileman bone china (B2) shows a highly vitreous surface with a few large sized pores. At high firing temperatures (1050^{o}C to 1250^{o}C) a smooth glass surface appears with a smaller number of pores (Kitouni and Harabi, 2011). The bone china was obviously fired at very high temperature for the body to become vitrified and relatively non- porous (Jones, 2000) which can be confirmed from the obtained SEM micro image of Wileman bone china (B2).

The EDX spectra for B1 sample is given in **Appendix -3**. B1 shows strong peaks for aluminium, silica, oxygen, sodium and potassium. The texture of clay body was very similar to the Wileman bone china so is calcium and phosphate peaks were expected, but no peaks for calcium and phosphates were detected. However, it does not show any Pb peaks which might be expected from this era of chinaware.

The EDX spectra of Wileman bone china (B2) is shown in **Figure 22**. The basic ingredients of the bone china are kaolin $(Al_2\,O_3.\,2SiO_2.\,H_2O)$, feldspar and bone ash $Ca_3(PO_4)_2$ (Hamer and Hamer, 2004). The EDX spectra shows the peaks for calcium and phosphorous which may be from the bone ash and the aluminium, silica, and oxygen peaks from the kaolin. Feldspar contains alkali (sodium and potassium) along with silica and aluminium oxide. So the peaks for sodium and potassium in the Wileman sample were due to the feldspar. All the EDX peaks obtained for Wileman bone china are as expected for bone china wares but unfortunately are inconsistent in terms of the Pb peak which is expected from the glaze. **Figure 22** below is of a piece of Wileman bone china with glaze that had been as received but it clearly shows no Pb peak. However when sanding was done on the surface of the B2 sample, a Pb peak was observed in cross sectional analysis of the broken end between the glaze and the clay body. The EDX spectra of Wilman bone china (B2) showing the peak for Pb is given in the **Appendix 3.**

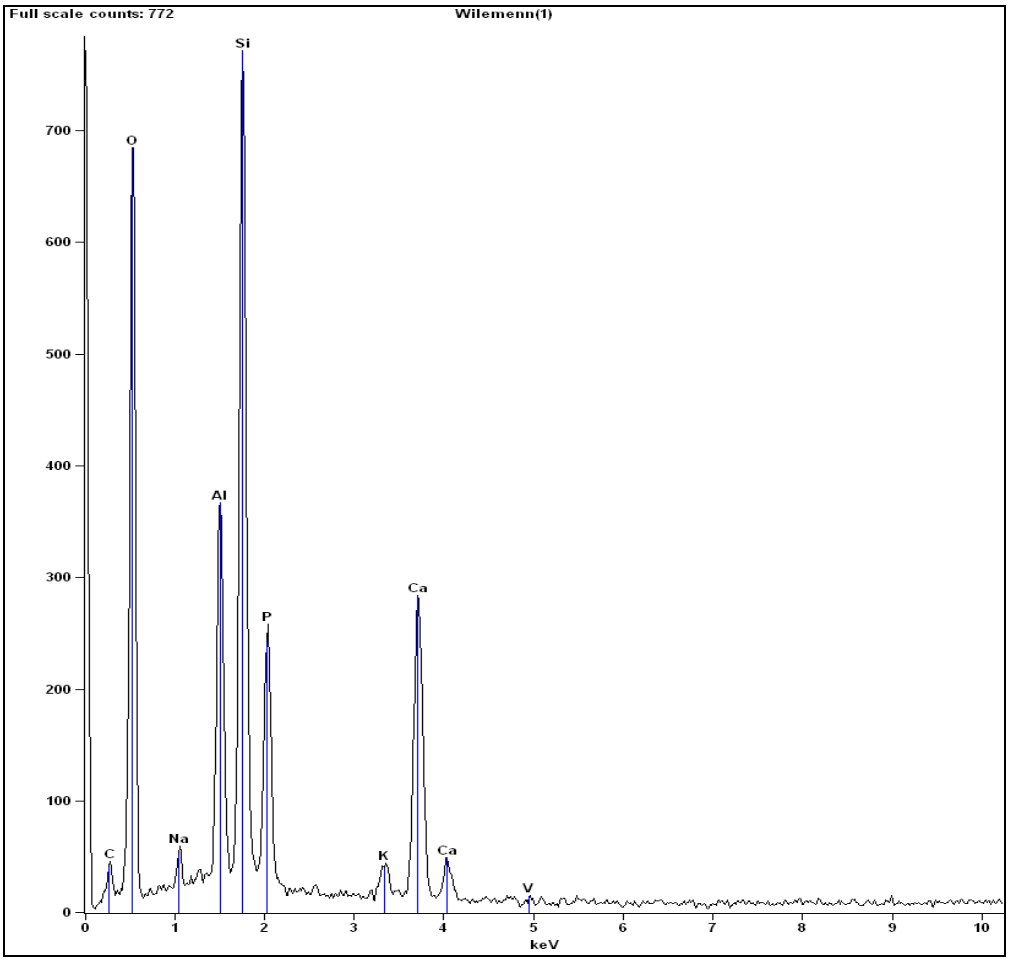


Figure 22: EDX spectra of Victorian Era -Wileman bone china (B2)

SEM/ EDX results for Crown Lynn wares

The SEM image of the sample C4 shown in **Appendix 3** has a partly vitreous surface with a number of misshapen pores. The partial vitreous surface suggests that the firing temperature conditions achieved were less than that of the Wileman bone china (B2) with highly vitrified body.

The SEM image of the Crown Lynn sample C7 shown the **Figure 23**. It shows a surface with uneven particle size in it with a small pore size very different from the micrograph of the Victorian era sample Chapman sample (B1) and Wileman bone china (B2).

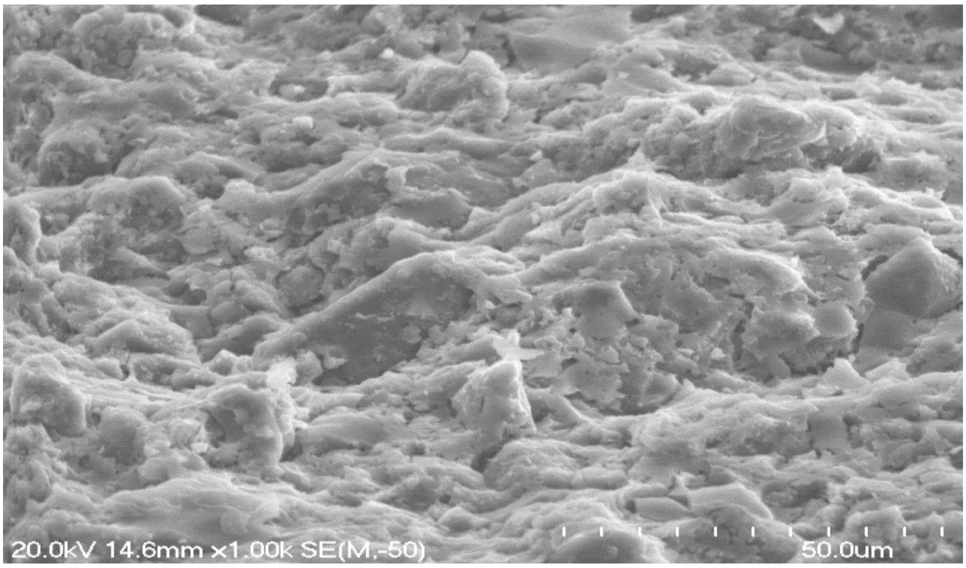


Figure 23: SEM image of Crown Lynn sample (C7)

The EDX spectra for sample C4 is given in the **Appendix-3**. The EDX spectra C7 is shown in **Figure 24**. It show silica, aluminium and oxygen peaks and this can be assigned to kaolinite and quartz while the sodium and potassium peaks were showing the presence of small amount of feldspar as seen in the Wileman sample (B2).

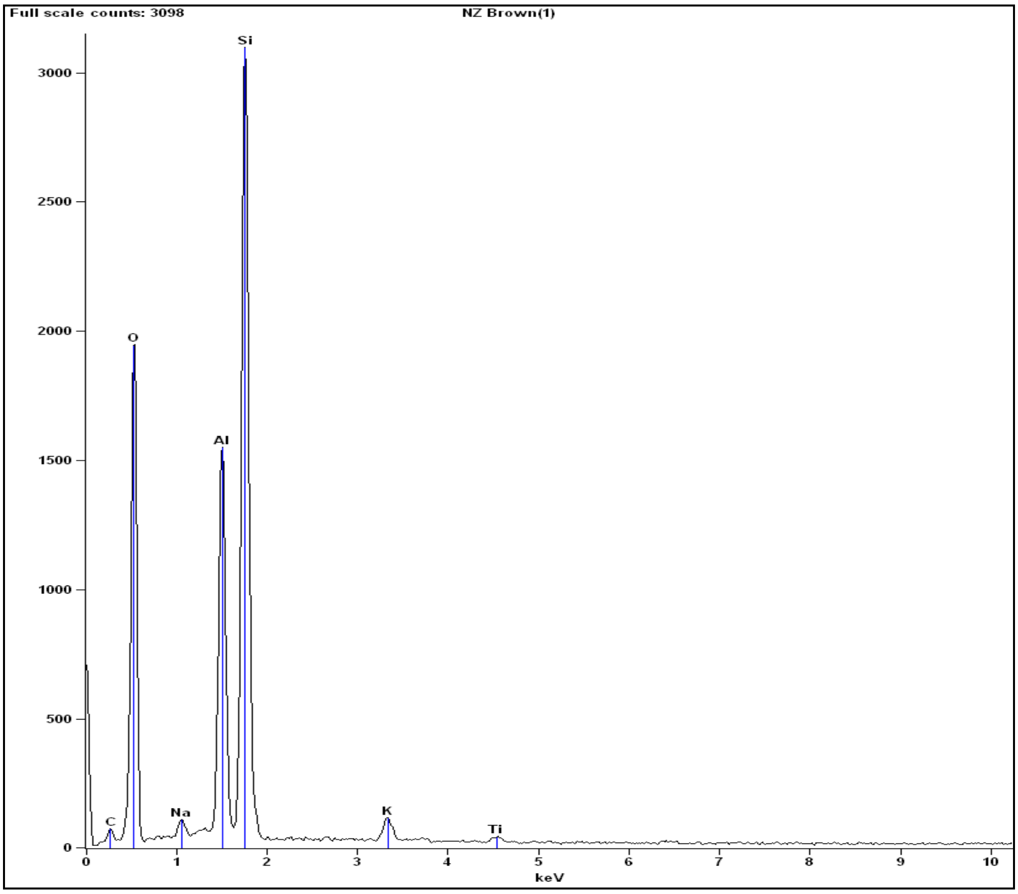


Figure 24: EDX spectra of Crown Lynn sample (C7)

Although SEM/EDX was known to be used successfully for studying ceramic glazes (Perez-Arantegui et al., 2004) for many years, the results obtained from the SEM/EDX spectra for Crown Lynn wares only gave information about the main feed stocks of the ceramics and no peaks were obtained for any added metals present in the glazes. Removing the top layer of the glaze through sanding using sandpaper was only tried in one of the Wileman sample due to the concern about any contamination. It is highly time consuming and very hard to separate the top layer of the glazed surface.

SEM/EDX results for modern ceramic wares

The SEM image of the modern Chinese ceramic ware (A1) is shown in **Figure 25**.

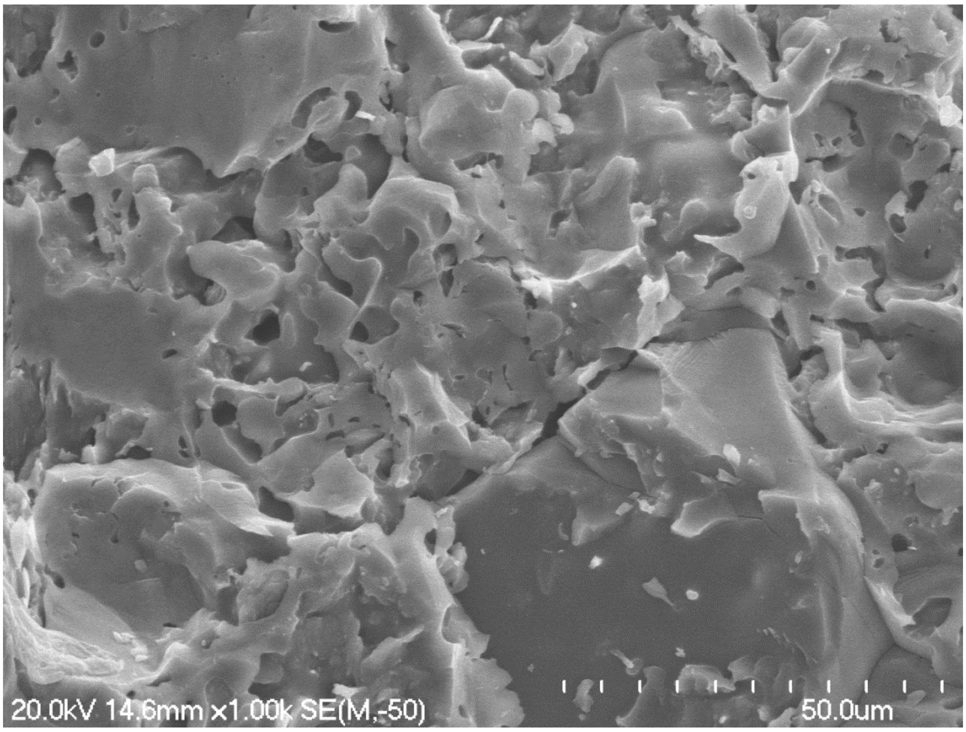


Figure 25: SEM image of the modern Chinese ceramic sample (A1)

SEM image of sample A1 shows vitrified body but it is not a continuous vitrified surface as seen in Wileman bone china (B2). It is showing a more irregular surface with few small pores. The firing temperature conditions might be higher than that followed for the studied Crown Lynn wares (C4 and C7)

The Indian bone china (A7) had similar SEM image (see **Appendix 3)** of the observed for Wilemen bone china (B2) with continues vitrified surface and small pores joined together into large rounded pores. The continuous vitrified body of the sample A7 shows that it might be fired at a temperature around 1050^{o}C for bone china wares.

The SEM image of the Thailand teacup (A11) shows large numbers of irregularly shaped pores and a moderately vitrified ceramic body with small grains on the surface (see **Appendix 3**).

The EDX spectra of the modern Chinese ceramic ware (A1) (see **Figure 26**)shows intense peaks for silica, aluminium and oxygen as seen in Crown Lynn and Victorian era samples which indicates the presence of kaolinite. Weak peaks were observed for magnesium, sodium and potassium in all EDX spectra of Chinese ceramic wares. The week peak observed for sodium and potassium might be due to feldspar content. Feldspar is an alumino-silicate mineral added as a flux to the ceramic wares (Sivasankar, 2008). No results regarding the elements present in the glazes of the modern ceramic wares were obtained.

The Indian bone china (A7) showed two extra peaks for calcium and phosphorous which can be assigned to bone ash (HAP +TCP) as was seen in Wileman bone china (see **Appendix 3**). The results obtained with SEM/EDX about the major elements (silica, alumina, oxygen, calcium and phosphorous) and firing conditions were mainly of the clay body and not for the glazes.

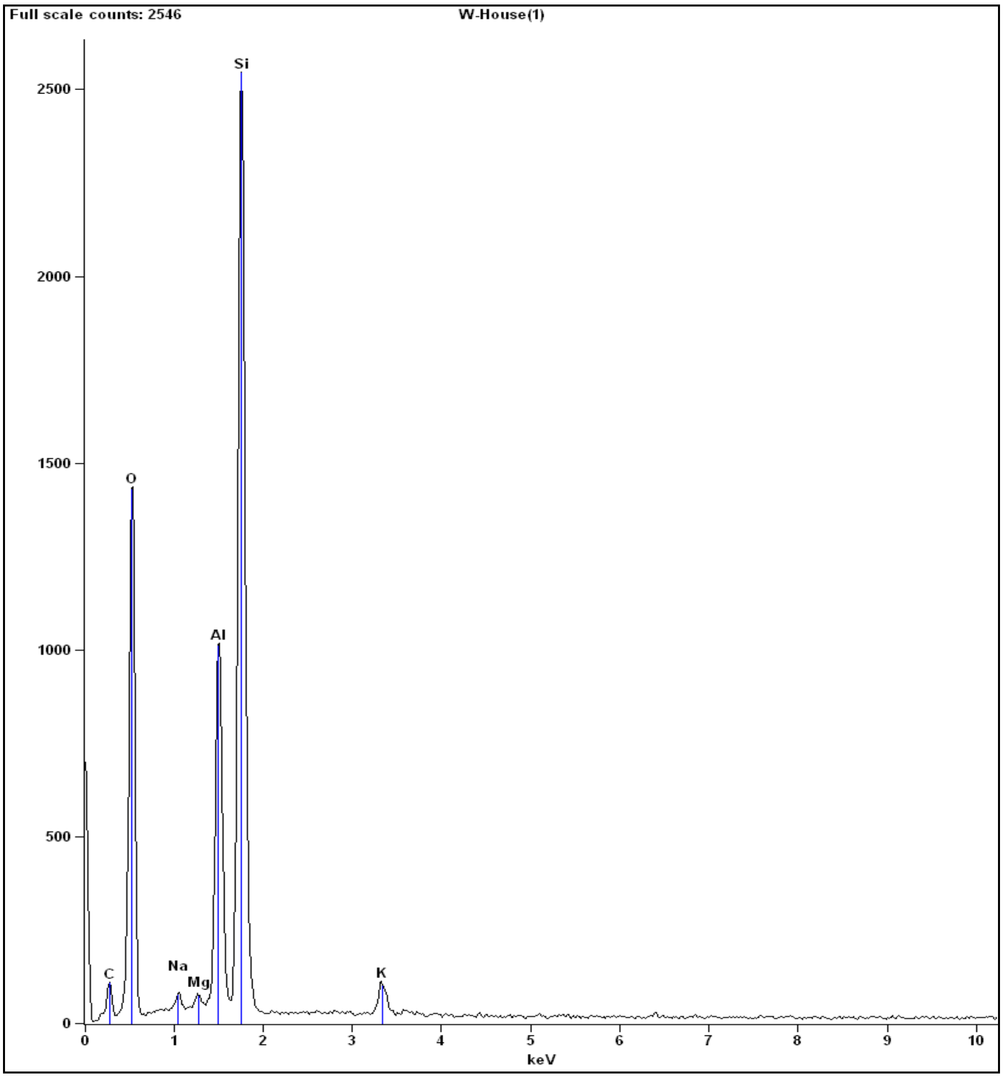


Figure 26: EDX spectra for modern Chinese ceramic bowl (A1)

4.6 XRF results

The SEM/ EDX results did not prove useful for giving a reliable elemental analysis of the ceramic glazes. So as an alternative, XRF analysis was used instead of the SEM/EDX. XRF detected the major and trace elements present in the bulk ceramic wares and that elemental information was very useful in determining which elements to follow in leaching studies of the elements of interest for ICP-MS analysis.

XRF results for the Victorian era and mid- 20th century samples

The XRF data gave a rich amount of elemental data for all the chinaware studied. **Table 13** summarises the various concentrations of the trace elements detected in the Chapman sample (B1) and Wileman bone china (B2). As expected a large amount of oxides of silicon, aluminium, calcium and phosphorous was detected along with very low concentrations of potassium, sodium and titanium (see **Appendix 4**). The main elements of interest for the leaching studies are given in **Table 13**.

Table 13: Amount of trace elements in ppm present in the Victorian era samples (B1 and B2) and mid- 20th century Alfred Meakin sample (B5)

Elements / ppm/	Cr	Co	Zn	Rb	Sr	Zr	Cd	Sn	Ba	Pb
B1	87	23	314	268	266	43	<0.5	11	218	12010
B2	26	35	130	256	281	38	<0.5	39	378	8231
B5	10.2	92	70	402.4	163	56	<0.7	13	121	27470

It is obvious that the level of Pb in these samples is relatively high compared to other trace elements (Ba, Cd, Co and Cr) analysed. The above values show that the concentration of lead ranges from 8231 to 27470 ppm. Lead glazes were known to be added for obtaining shiny transparent glazes {Perez-Arantegui, 2004 #166. Chapman (B1), Wileman (B2) and Alfred Meakin samples have a very shiny appearance and this might be due to the added lead oxide in the glazes. Cadmium was detected below <0.5 ppm in B1 and B2, it can be anywhere between (0 to 500 ppb. But this is not an element of significance in these materials. Barium was also detected in very low levels compared to lead. (see **Table 13**).

XRF results for the Crown Lynn samples

The XRF results pertaining to the bulk Crown Lynn wares are shown in **Table 14**.

Table 14: Amount of trace elements in ppm present in the Crown Lynn wares (C1-C8)

Elements /ppm	C1	C2	C3	C4	C5	C6	C7	C8
Cr	31	116	41	54	45	28	43	10
Co	500	58	15	0.46	58	86	74	61
Zn	80	1360	43	53	64	38	47	35
Rb	62	64	64	47	61	80	72	116.5
Sr	41	78	89	67	305	71	382	63.5
Zr	795	3586	1309	49	286	235	< 0.5	297
Cd	< 0.5	88	< 0.5	215	< 0.5	< 0.5	330	1.1
Sn	2082	448	290	< 0.5	14	12	9.6	8.8
Ba	367	777	121	590	242	139	311	231
Pb	3974	5478	5229	4087	9992	17180	18010	9756

The concentration of lead in all the Crown Lynn chinaware was found to be surprisingly high in the range of 3900 to 18010 ppm. The largest amount of lead was detected in the yellow coloured plate (C7) and a brown glazed plate with a yellow design under the glaze (C6). It was even higher than the Victorian era samples (see **Figure 27**). C7 also interestingly shows relatively high cadmium content compared to all analysed ceramic wares. Cadmium might be added to obtain the yellow coloured glaze in C7 see (**Section 1.8**). Also C2, C4 and C8 have cadmium in them. In some Crown Lynn samples, the Cadmium concentration is shown as <0.5 in (i.e. C1, C3, C5 and C6) this could mean the level could be anywhere between 0 to 500 ppb as commented in the Victorian era samples. Barium is detected in all Crown Lynn samples but its amount is lower than what was observed in modern Chinese, Indian and Thailand ceramic wares (see **Table 15**). Barium acts as a strong flux and combined with lead can give a smooth matte finish to ceramics at low firing (Hopper, 2006).

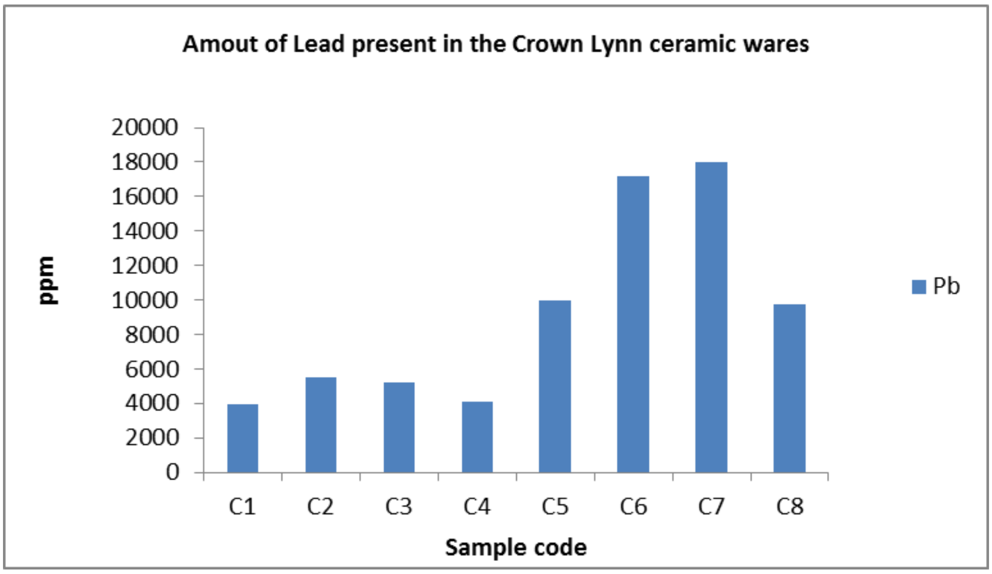


Figure 27: Amount of lead present in the Crown Lynn ceramic wares C1 – C8 in ppm

Literature says that lead was always added in the glazes in the safe form (i.e. form of frit) that is lead silicate which was a technique developed in the mid- 20th century for overcoming the lead poisoning in the pottery industries (Hopper, 2006). Sulphur was also detected in all Crown Lynn wares (see **Appendix-4**) and it could be from the main source of lead galena (PbS) used (Wood et al., 2007).

Sample C2 had slightly higher concentration of chromium, zinc, zirconium and barium in comparison with the other Crown Lynn wares (see **Figure 28**). Tin detected (see **Appendix 4**) could have been used in the form of a tin oxide for ensuring whiteness in the ceramic body which would have made a good white backdrop for decorations to be applied (Mason and Tite, 1997).

All the Crown Lynn wares had silica and aluminium in much higher concentration than calcium and phosphorous. This is obviously due to the kaolinite and quartz in the bulk of the clay body as detected in SEM and FTIR studies of Crown Lynn wares (see **Appendix 4**).

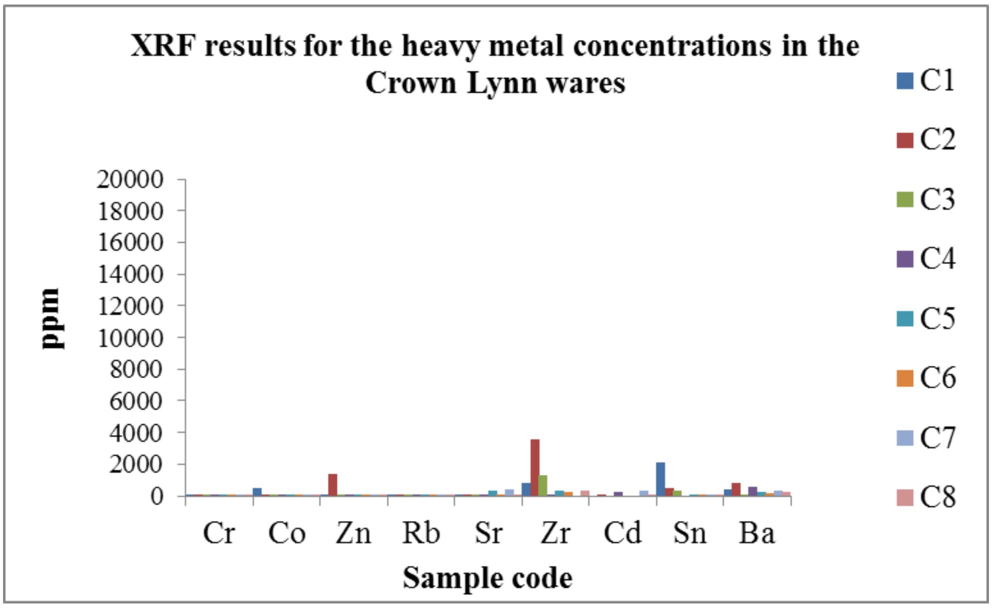


Figure 28: Amount of lead present in the Crown Lynn ceramic wares C1 – C8 in ppm

XRF results for the modern ceramic wares made in China, India and Thailand

The XRF results for the metals present in the modern ceramic wares are given in **Table 15**. It is immediately evident from **Table 15** that modern ceramic wares made in China except (A4 and A10), India and Thailand had high amount of barium compared to Victorian era and mid- 20th century samples which had high lead than barium. For these modern items, it is likely that barium has been used to replace lead in frit formulations for glazes due to the known toxicity of lead. The concentration of lead in most of the modern ceramic wares is hence found to be comparatively lower than the Crown Lynn wares. Sample A10 is similar to the Crown Lynn ceramic wares with high amount of lead and low barium compared to other modern ceramic samples. Cadmium was detected in all the samples and the maximum concentration was about 191ppm detected in the brightly coloured red Chinese teacup (A3). Some of the samples (A1, A4, A9, A10) show cadmium <0.5 which means cadmium may still be present in the samples but below 0.5 ppm (500 ppb). Cobalt was seen in all samples and the slightly higher level was observed in blue (A9 and A2) and black glazed (A1) ceramic wares. Cobalt oxide has been used to obtain blue shades in the glazes (see **Section 1-8**) hence its detection is understandable. Sample A1 would have had high chromium most likely due to the added chromium oxide to obtain black coloured glaze (Britt, 2007).

The brightly coloured sample A3 had chromium, zinc, zirconium, cadmium, tin barium in higher range compared to the white glazed square plate A4. The high amount of metal might be added for producing those brightly coloured red glaze in the sample A3.

Table 15: Amount of trace elements present in the bulk modern ceramic wares in ppm

Element /ppm	Cr	Co	Zn	Rb	Sr	Zr	Cd	Sn	Ba	Pb
A1	882	317	824	127	38	454	< 0.5	29	3296	49
A2	98	211	284	111	292	415	0.8	6.9	1912	29
A3	106	23	1210	243	291	3397	191	1413	2534	132
A4	9	17	42	346	28	99	< 0.5	15	120	71
A5	110	52	551	84	124	773	17.6	7.9	1108	56
A7	36	16	100	78	2.9	127	2.9	18	1393	288
A9	473	262	568	260	< 0.5	1287	< 0.5	21	2784	154
A10	59	104	269	695	31	114	< 0.5	262	98	3907
A11	23	12.5	3230	420	115	739	1.3	43	4164	110

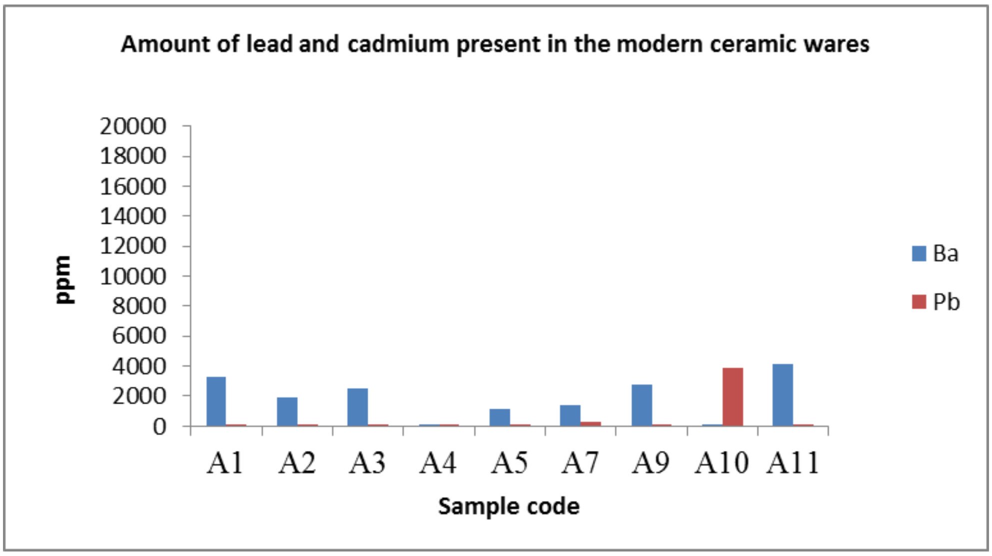


Figure 29: Amount of lead and barium in ppm in the modern ceramic wares made in China, India and Thailand

The amount of lead and barium in sample A10 shows similarity with that in Crown Lynn wares and hence stands apart from the other Chinese made samples. This is due to the glaze as the sample has a screen printed photographed on it. The Thailand teacup (A11) shows higher barium (see **Figure 29**). It indicates that barium has to be tested for its leaching potential in all the modern ceramic wares along with the other heavy metals like lead.

X-ray diffraction results (XRD)

The elements (silica, alumina, barium) identified with XRF analysis was confirmed by XRD using X-pert high score software for sample A5 as a representative for modern ceramic wares (see **Appendix 4**). Quartz was the main mineral identified in modern ceramic wares. Victorian era Wileman bone china identified calcium, silica, aluminium and lead as the main elements. XRD identified various phases of those elements identified with XRF and SEM analysis.

4.7 Inductively coupled plasma mass spectroscopy results

The XRF results gave some very useful elemental information that allowed a decision to be made on what elements to follow in ICP-MS studies of leaching potential. Hence,(Pb, Cd, Cr, Co, Ba, Zn, Zr, Sn, Sr and Rb shown to be present in the bulk ceramic wares may have a tendency to leach with various test solutions applied to the china. The results would be of interest in determining how the various coloured glazes would behave. In this study Victorian plus other later (though not new) chinaware such as Crown Lynn was added to the study to gain a perspective of how these ceramic wares behave. The most important aspect is to assess the behaviour of modern ceramic wares as it is the most used though Crown Lynn is still in popular use in New Zealand.

The ICP-MS technique was the most important technique used in this research for obtaining the concentration of trace and ultra- trace amounts of metals detected with XRF studies that was leached out of the ceramic wares when tested with 4% acetic acid following the ASTM (738-94) standard method. In addition, it was decided to test some commonly consumed liquids that would come into contact with these ceramic wares such as orange juice, hot water, cold water, black tea, lime tea and coca cola It was felt that most of these would be exposed to these ceramic wares. The ASTM method was followed for 1) preparing the 4% acetic acid, 2) the temperature range used in the test, 3) cleaning of the ceramic wares, and 4) the duration of leaching. Instead of AAS as traditionally used in older studies, ICP-MS is used for this investigation due to the lower detection limit of trace elements needed in this study (**Section 2.4-1**.). The detection limits of the ICP-MS instrument used for multi-elements analysis are given in **Table 16**.

Table 16: Instruments (ICP-MS) detection limit for multi-element analysis for metals of interest in the leaching studies

Cr 53 **ppb**	**Co 59** **ppb**	**Cd 111** **ppb**	**Ba 137** **ppb**	**Pb 207** **ppb**
0.10	0.00	0.01	0.04	0.02

Metal leached from the ceramic wares exposed to different leaching conditions analysed in ICP-MS gave concentrations of trace elements such as B, Na, Mg, Ca, V, Cr, Fe, Mn, Co, Ni, Cu, Zn, As, Se, Sr, Rb, Zr, Sn, Ag, Ba, Tl, Pb and U.

There are many health risks caused by the intake of Pb, Cd, Cr, Co and barium metals from the leachate of foods or liquids exposed to these glazed ceramic wares. Ingestion of even very low level of lead causes significant neurological and cognitive effects in humans (Valadez-Vega et al., 2011). It affects the central nervous system, liver and kidney. It mimics calcium and would greatly affects the functioning of these biological system (Phipps et al., 2012). Cadmium is more toxic than lead and is associated with the problems in the respiratory system that can lead to lung cancer. It also causes gastrointestinal problems. Cobalt is considered to be essential for nutrition by the WHO however, the inorganic compounds of cobalt (oxides and sulphides) poses health issues in humans (New Zealand Institute of Chemistry, 2008). Cobalt exposure can cause damage to the respiratory pathways and to the lungs, heart and thyroid (Valadez-Vega et al., 2011). The soluble form of barium compounds like barium carbonate is toxic and can cause vomiting, gastrointestinal problems and paralysis. Exact dosage of barium (i.e. the toxic limit) leading to health hazards in human is not well known (Assimon et al., 1997b). It is an important concern to discuss about the leaching level of Pb, Cd, Cr, Co and Ba than other detected essential trace elements (Fe, Zn, Cu, I, Mo, Ni, B and V).

4% acetic acid leaching results

2.5.1.1 Victorian era Chapman (B1) and Wileman (B2) and mid- 20th century ceramic wares (Alfred Meakin)

The leaching test results of the Victorian era and mid- 20th century samples with 4% acetic acid shown in **Table 17** and is obtained from leach test conducted with freshly prepared 4% acetic acid leaching solution at room temperature. Mean value of sample replicates (ICP-MS results for leached metals) with the error bars are shown in **Figure 30**.

The amount of lead leached into the testing solution is at a higher level for the Victorian era samples (B1 and B2) compared to the mid- 20th century samples (B5 and B6). The other metals (Co, Cr and Ba) are significantly lower compared to the level of lead leached from all these ceramic wares. As a second stage of the leaching process sample B1 and B2 were again leached with another freshly prepared 4% acetic acid solution for a duration of 24 hours to find the level of metal release after first extraction with repeated leach test on the same ceramic wares to find the amount of metal that will leach from these ceramic wares on routine domestic usage. The 95 % confidence error is given for each replicates analysed.

Table 17: Metal released into 4% acetic acid leachate solution in ppb (µg/L) from Victorian era and mid-20th century samples after a contact period of 24 hours (1st leaching test) ND means "not detected" and hence below detection limit)

Metals/ppb (ug/L)	B1	95% Confidence error	B2	95% Confidence error	B5	95% Confidence error	B6	95% Confidence error
Pb	4695	±93.70	16628	±145.80	61	±8.00	10	±0.00
Ba	4	±0.1	522	±3.9	13	±1.1	13	±0.6
Co	3	±0.1	94	±1.1	5	±0.4	ND	-
Cr	ND	-	35	±4.8	ND	-	ND	-
Cd	ND	-	1	±0.1	ND	-	ND	-

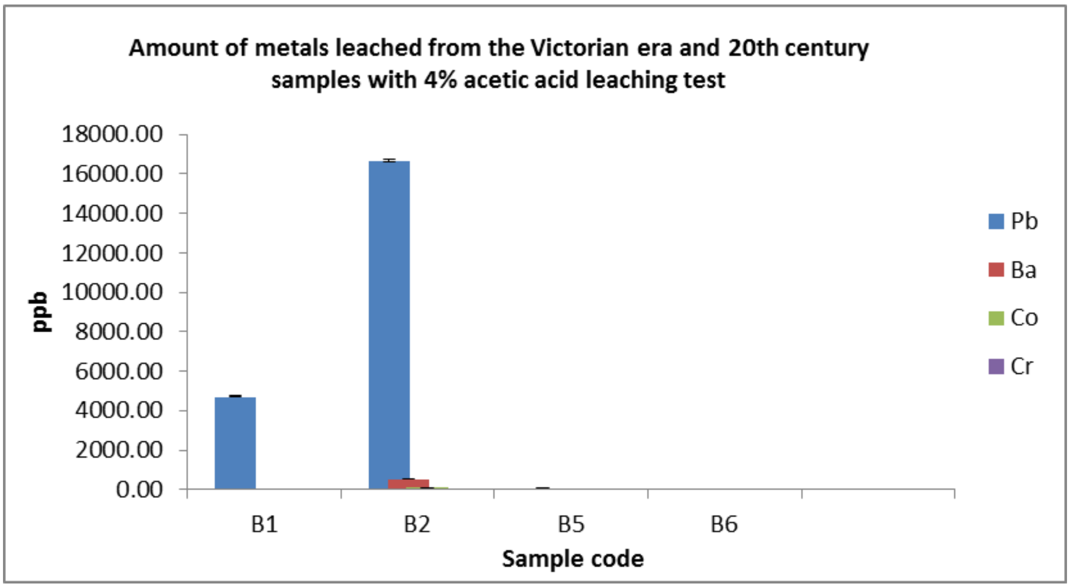


Figure 30**: Amount of metals (Cr, Co and Ba) leached out from the Victorian and mid- 20th century samples during a 24 hours leach test with 4%acetic acid. It is expressed in ppb (μg/L).**

Barium, cobalt and chromium are found in at low level in sample B2 compared to lead. Sample B2 released metals into the leachate solution in significant amount compared to all other samples given in the **Table 17**.

Sample B5 and B6 did not release a large quantity of lead that samples B1 and B2 were found to release. This is because they were a later manufactured form of China in which lead leaching from the glaze might have been solved by the use of Pb frits (Lehman, 2002). The results for the repeated leach test with 4% acetic acid conducted on a same sample (2^{nd} stage leach test) with their mean value of sample replicates (ICP-MS results for leached metals) with the error bars are shown in **Table 18**. The next stage of leaching test also identified significant lead leached out from them but this time the amount of leached lead is lower than the initial leaching test with 4% acetic acid.

Table 18: Metal released into 4% acetic acid leachate solution in ppb (μg/L) from Victorian era mid-20th century samples after a contact period of 24 hours (repeated leaching test) ND means "not detected" and hence below detection limit)

Metals/ ppb (ug/L)	B1	B2
Pb	1896	15587
Cd	ND	ND
Ba	3	525
Cr	2	25
Co	ND	99

Discussion

From the results obtained for the Victorian and mid- 20th century samples, the Victorian era samples released very high amount of lead on continuous leaching test conducted with 4% acetic acid for a duration of 24 hours. The lead released is from the sample itself and it is expected to occur given the significant amount of lead detected from the XRF results for Wileman and Chapman samples. The amount of lead leached from Wileman and Chapman samples exceeded the 4 mg/L leaching limit of lead as per Directive 84/500/EC (see **Table 1**) during repeated leaching test. Mid-20th century Alfred Meakin samples has shown the highest amount of lead in XRF results than Victorian era samples. However the leach results show that a very less lead leaching was found in B5 compared to B1 and B2. Lead might be added in its insoluble frit form (Lehman, 2002) which is more stable and resistant to acidic solutions than glazes with raw lead added in their glaze mixture.

Not much crazing was seen on samples B1 and B2. Crazing being cracks in the glazes might be considered to increase the tendency to leach via exposure of underlying glaze via the cracks. Sample B2 had a highly decorated design on the surface that was exposed to the acetic acid leach test and lead could be potentially released from those blue coloured glazes. The Alfred Meakin samples (B5 and B6) did not have highly coloured over glazed decorations on the surface of the plate or cup that came in contact with the leaching solutions. They were also more modern pieces and hence could have been manufactured differently to the Victorian pieces. The 4% acetic acid condition was chosen as the standard leaching agent for creating a more realistic condition to which the ceramic wares will be exposed on a daily usage (Belgaied, 2003). Lead leached in small amounts on repeated leaching test conducted on same ceramic dishes (Mohamed et al., 1995). The amount of lead leached from both Victorian samples was low in the repeated second leach test on a same sample.

2.5.1.2 Crown Lynn ceramic wares

Crown Lynn samples tested for leaching with 4% acetic acid included a mix of plates and teacups (**Table 2**). The results for the amount of Pb, Cd, Cr, Co and Ba leached from the Crown Lynn wares are given in the **Table 19.**

Table 19: Metal released into 4% acetic acid leachate solution in ppb (µg/L) from Crown Lynn samples after a contact period of 24 hours, ND means "not detected" and hence below detection limit)

Metals/ppb (ug/L)	C1	C2	C3	C4	C5	C6	C7	C8
Pb	2893	75	215	16	33	353	688	4880
Cd	ND	ND	ND	ND	ND	ND	ND	1
Ba	27	10	9	32	41	11	54	95
Cr	3	ND	4	7	ND	ND	14	5
Co	102	2	1	4	15	11	12	69

The results shows that lead was released from all the Crown Lynn samples but significantly high level of lead was leached from the grey teacup (C1) and brown teacup (C8) compared to the other Crown Lynn samples (see **Figure 31)**. Cadmium was below the detectable level for most of the Crown Lynn samples. Barium also leached from all the Crown Lynn samples but to levels below 100 µg/L. Sample C1 had a significant release of cobalt (see **Figure 32**).

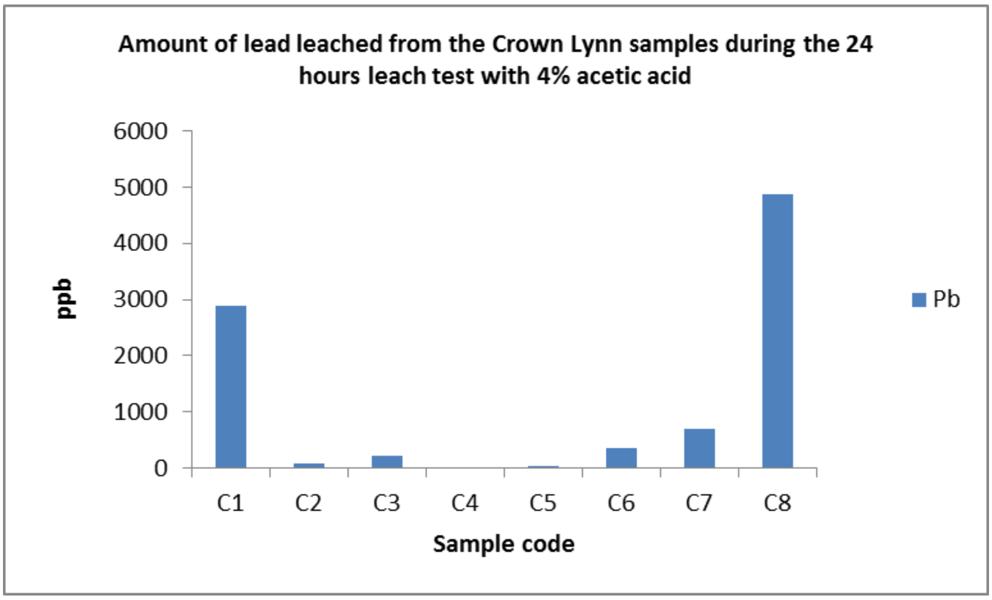


Figure 31: Amount of lead leached from the Crown Lynn ceramic wares during a 24 hours leaching test with 4% acetic acid. It is expressed in ppb (µg/L).

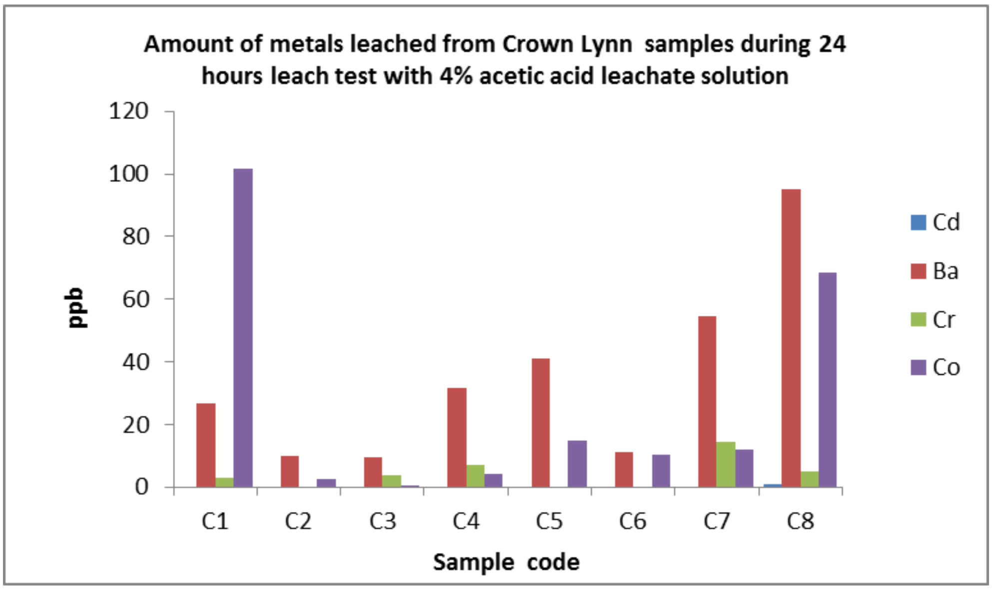


Figure 32: Amount of metals leached from the Crown Lynn ceramic wares during a 24 hours leaching test with 4% acetic acid in ppb (µg/L)

Discussion

The leaching of lead was lower for the Crown Lynn wares compared to the Victorian era samples. Sample C6 and C7 had high lead in the bulk analysis done on XRF but the leaching was significantly lower than C1 and C7. C1 and C8 release lead which was below or slightly higher than standard limit for lead released from the ceramic wares (4 mg/L). The leaching results of the Crown Lynn ceramic wares were in good agreement with the XRF results. The XRF results shows high cobalt in C1 compared to other Crown Lynn wares and the same was observed in leaching result for cobalt which was in significantly high level but very lower than the released lead. Standard limit of metal release from the ceramic wares was given only for lead and cadmium which may lead to several health hazards as discussed earlier compared to other analysed metals from the ceramic wares. Low level of lead migrated from the ceramic wares might lead to lead poisoning during the long term of use of the lead leaching ceramic wares (Feldman et al., 1999). So even though the detected lead was below or close to the standard limit (4 mg/L) it is probably a matter of concern. In New Zealand glazes used for ceramic wares were tested for their translucency, colour, hardness, maturing temperature, molten viscosity, flow, brilliance and thermal expansion to ensure compliance with the specifications. But leaching tests are not mentioned. Also chip resistance and glaze fit (i.e. thermal expansion between glaze and clay body) were measured after glazing. These testing were done for Crown Lynn manufactured ceramic wares according to the article published by New Zealand Institute of Chemistry (Daulton, 2005).

2.5.1.3 Modern ceramic wares made in China, India and Thailand

The amount of metals leached from the modern ceramic wares is shown in the **Table 20, Table 21 and Table 22**. Some of the highly coloured modern ceramic wares were successfully leached 2 or 3 times with fresh 4% acetic acid on the same sample (2 replicates per leaching test) as mentioned in **Section 3-8.** The results are given for three stages of repeated leaching test (1^{st}, 2^{nd} and 3^{rd}) with their sample codes.

Table 20: Metal released into 4% acetic acid leachate solution in ppb (µg/L) from modern ceramic samples (A1 to A4) after a contact period of 24 hours, ND means "not detected" and hence below detection limit)

Metals/ppb (ug/L)	A1			A2			A3		A4
	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	1st
Pb	8	16	3	15	14	ND	18	20	ND
Cd	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ba	33	34	5	7	7	31	7	7	1
Cr	1	2	1	20	5	2	4	ND	4
Co	10	62	3	7	6	21	ND	1	ND

Here 1st: Initial amount of metals leached with 4% acetic acid (24 hours) each values are mean of replicates.

2nd : repeated leach test values of metals leached with another freshly prepared 4% acetic acid (another 24 hours) each values are mean of replicates

3rd : repeated leach test for a third times with another freshly prepared 4% acetic acid (another 24 hours) each values are mean of replicates

All these values are to compare the amount of metals leached on repeated leaching and these results can be used to compare the level of metal that will leach from these ceramic wares on continuous usage.

Table 21: Metal released into 4% acetic acid leachate solution in ppb (µg/L) from modern ceramic samples (A5 to A9) after a contact period of 24 hours, ND means "not detected" and hence below detection limit)

Metals/ppb (ug/L)	A5			A6	A7	A8		A9
	1st	2nd	3rd	1st	1st	1st	2nd	1st
Pb	5	3	ND	6	ND	ND	ND	1
Cd	ND	ND	ND	15	ND	ND	ND	ND
Ba	12	11	8	815	6	46	18	34
Cr	ND	ND	ND	8	5	5	2	ND
Co	1	1	ND	ND	ND	13	6	ND

Table 22: Metal released into 4% acetic acid leachate solution in ppb (µg/L) from modern ceramic samples (A10 and A11) after a contact period of 24 hours, ND means "not detected" and hence below detection limit)

Metals/ppb (ug/L)	A10			A11	
	1st	2nd	3rd	1st	2nd
Pb	37	ND	2	3	ND
Cd	ND	ND	2	ND	ND
Ba	ND	ND	ND	15	6
Cr	6	ND	ND	ND	ND
Co	1	ND	ND	ND	ND

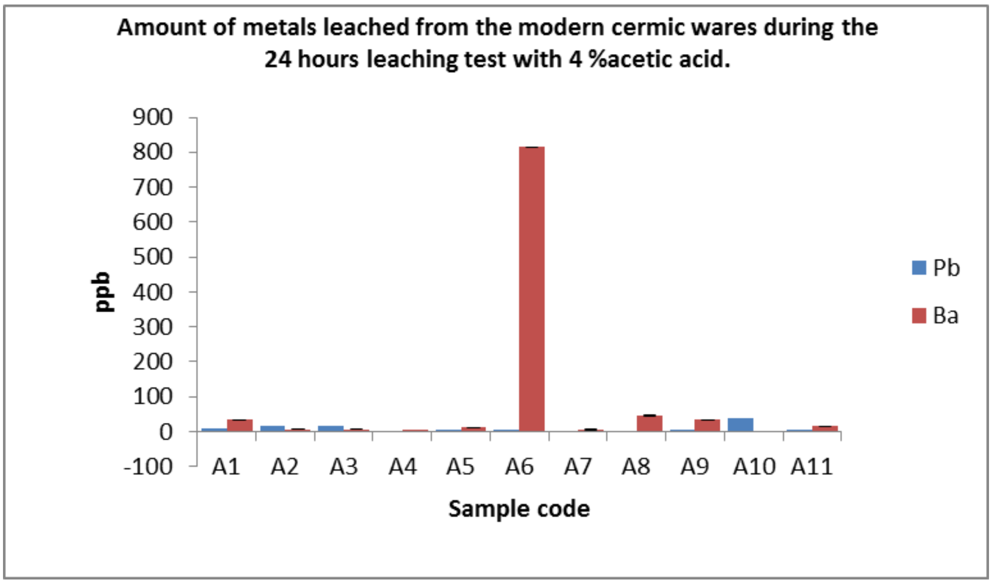


Figure 33: Amount of barium and lead leached from the modern ceramic wares during a 24 hours leaching test with 4% acetic acid (1st leaching test) in ppb (ug/L)

From the results obtained for the modern ceramic wares, barium was found to leach slightly from all the modern Chinese samples. The amount of barium leached is in the range of 1 µg/L to 815 µg/L. Not much cadmium leaching was observed in the modern ceramic wares except sample A6, a red Chinese plate which also had high barium compared to all other Chinese ceramic wares (see **Figure 33**). The Bulk sample analysis with XRF also show higher cadmium present in red coloured ceramic wares and is higher than other coloured modern ceramic wares. Indian bone china (A7) and Thailand (A11) samples did not show significant metal leaching in this analysis. Lead was detected in sample A10 only during the first leaching test and did not show any detectable level of lead during the repeated leaching test.

Discussion

Although XRF results of modern ceramic wares detected high barium in the bulk sample, only very low levels of barium was leached from these wares during the 24 hours 4% acetic acid leach test. The ASTM (738- 94) protocol was mainly developed for the leaching studies of lead and cadmium but more suitable leaching tests of barium from the ceramic wares were not investigated (Assimon et al., 1997a). 4% acetic acid was used as a suitable leaching solution for barium leaching test from literature studies (Demont et al., 2012). So assuming this method to be suitable for barium leaching the results can be treated as the maximum barium leached from the modern ceramic wares. Although health hazards related to the acute ingestion of barium especially barium carbonate or barium chloride are known, no standard limit for leaching of barium from ceramic wares was set. As per the US Environmental protection agency (EPA) the oral reference dose (RFD) for barium was 0.07 mg/kg/day that are 4 mg/person/day. The highest amount of barium leaching observed in the modern ceramic wares was well below the standard limit of barium as per the oral reference dose value. Also the leached lead was very low compared to the Victorian and Crown Lynn samples and is below the standard limit of leachable lead from the ceramic wares as mentioned in Crown Lynn and Victorian results.

The modern ceramic wares used were brand new without any chipping or scratches as discussed in the visual survey. Ceramic ware observed to be safe from metals like lead that may leach in high amount of metal once it is worn down by long term usage (Mohamed et al., 1995). According to these leaching results, modern ceramic wares were found to be safe with respect to metal leaching and so would not be of concern to human health. Both lead and cadmium were below the detectable limit of ICP-MS in the Indian bone china (A7) and the small white Chinese sauce plate (A4). They had plain white glazed surfaces that were exposed to the 4% acetic acid test (i.e. no coloured surface was exposed).

Orange juice leaching result

The orange juice leaching results are presented as solid matter results and liquid results for the ceramic teacups. The pH of the orange juice used for this leaching test was 3.84. All the teacups used for the orange juice leaching test were already leached with the 4% acetic acid and the ICP-MS results obtained for the liquid part of the orange juice is for 1mL of the sample diluted to 10 mL with Type 1 water as mentioned in **Section 3-8**.

The results presented in Table 23 **Table 23** shows the amount of lead, barium and cobalt leached from the ceramic teacups on exposure to orange juice for duration of 10 minutes.

Table 23: Amount of metals (lead, barium and cobalt) leached from Victorian era to modern ceramic tea cups leached with orange juice in μg/L.

Sample code	Lead in ppb	Barium in ppb	Cobalt in ppb
A3	ND	19	ND
A7	ND	25	ND
A9	ND	30	ND
A10	ND	48	ND
A11	ND	23	ND
B6	ND	20	ND
C1	46	47	3
C2	ND	17	ND
C8	4	39	ND
Orange Juice Blank	ND	193	1
The values shown have had the blank value for orange juice subtracted from them. The blank orange juice value is included to put the values in context of orange juice not exposed.			

The analysis of solid matter of the leached orange pulp results indicated that the amount of leached metals in the orange pulp were extremely low and not significantly different to blank values. Out of all the orange pulps analysed only in the sample exposed to the Crown Lynn cup (C1) was lead detected in significantly higher amount than the blanks. The amount of lead leached into the orange juice and associated with the pulp was calculated to be 1480 µg/L (see **Appendix -5**) and it is found to be higher than 46 µg/L in the liquid part of the orange juice from sample C1. The acetic acid leaching test conducted for the sample C1 also showed significantly higher lead (see **Table 19)**. The detected amount of lead leached from sample C1 with orange juice and 10 minutes exposure time is very low compared to the lead extracted with the 4% acetic acid leach test with the much longer 24 hours exposure.

The sample values for barium were very close to the blank value and not much leaching had taken place. The cobalt values were mostly below the detection limit of the ICP-MS instrument. The blank value for orange juice was very high in the blank itself which was not exposed to any ceramic wares.

2.5.1.4 Barium contamination from filter paper

During the initial work on orange juice leaching tests the liquid part of the centrifuged orange juice leachate was passed through the Buchner funnel using a Whatman glass fibre filter paper to avoid any blockage in the ICP-MS instrument with the particles from the orange juice. But unfortunately all the detected samples were noticed to have high amounts of barium including both the ceramic teacup and the blank. Analysis of some of the samples was repeated following the same procedure which also detected high level of barium which suggested that something in the method was a source of barium contamination. After going back through all the procedures followed for sample preparation it was suspected that the filter paper was releasing barium into the orange juice during the filtration process. This suspicion was confirmed after acid digesting the filter paper with concentrated nitric acid and analysing the digested solution with the ICP-MS instrument. Raw data from these initial trials where high barium levels were detected in samples which used filter paper are given in **Appendix-5.** Based on these findings the filter paper was replaced with a Minisart single use filters (0.45 µm) and this avoided the barium contamination issue above. This improved method has hence been used to generate all the data for the samples in **Table 23**.

Discussion

The Crown Lynn tea cup had small scratches inside from long term use compared to the modern teacups which was used as purchased. So the scratches may possibly be a reason for the continuous lead leaching observed from the 4% acetic acid and the orange juice leach test. However, the amount of barium and cobalt leached from the ceramic teacups were very low in both tests. The amount of barium level found in the blank using improved method where Minisart single use filters used instead of filter paper (confirmed for barium contamination) was also high. This result is a matter of concern if the product itself had barium contamination in it.

Black Tea and Lemon Tea results

The leaching results for the ceramic teacups with lemon tea (pH noted as 3.2) are shown in **Table 24** and **Figure 34**.

Table 24: Amount of metals leached from Victorian era to modern day ceramic teacups leached with hot lemon tea as leachate solution in ppb (μg/L).

Metals/ppb (ug/L)	Modern ceramic teacups					Victorian era tea cups	Crown Lynn tea cups	
	A3	A7	A9	A10	A11	B6	C1	C2
Pb	2	2	1	1	1	14	17	98
Ba	ND	ND	ND	14	10	ND	ND	43
Cd	ND	1	1	ND	1	1	1	ND
Co	ND	ND	ND	2	2	1	2	3
Cr	ND	ND	ND	ND	ND	ND	12	ND

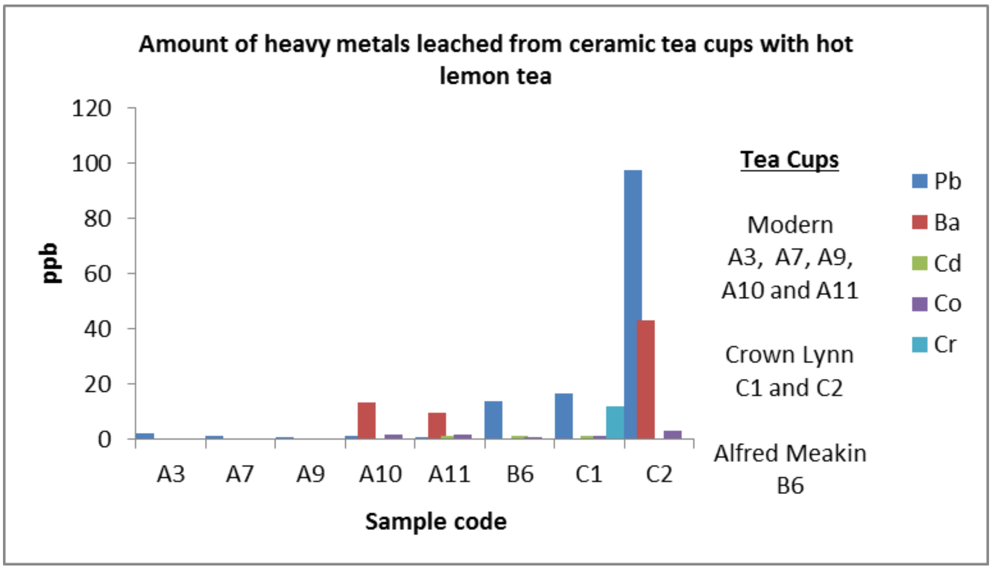


Figure 34: Amount of metals leached from ceramic tea cups with 10 minutes leaching test with hot lemon tea in ppb (μg/L).

All ceramic cups leached lead but the amount of leaching was insignificant compared to the 4% acetic acid leach test on the same samples. The Crown Lynn sample C2 which did show noticeable leaching with 4% acetic acid and orange juice compared with other ceramic cups leached a comparatively high amount of lead about 98 μg/L within the 10 minutes that the lemon tea was used as a leaching solution. The modern ceramic cup A10 which did not leach barium with the 4% acetic acid leach test released barium with hot lemon tea but the amount leached was low compared to Crown Lynn teacup C2. Amount of cobalt leached from sample A10 was also higher than the other leachate solution (i.e. acetic acid and orange juice tests).

Amount of metals leached from the ceramic tea cups leached with hot black tea (80-95 ^{o}C) are shown in **Figure 35** and **Table 25**.

Table 25: Amount of metals leached from ceramic teacups with hot black tea as leachate solution in ppb (µg/L).

Metals/ ppb (ug/L)	Modern ceramic teacups					Victorian era tea cup	Crown Lynn tea cups	
	A3	**A7**	**A9**	**A10**	**A11**	**B6**	**C1**	**C2**
Pb	ND	ND	ND	ND	ND	1	15	ND
Ba	1	14	ND	ND	ND	ND	5	5
Cd	ND	ND	2	2	ND	ND	1	1
Co	ND	ND	ND	ND	ND	ND	2	ND
Cr	ND	ND	ND	2	1	2	10	2

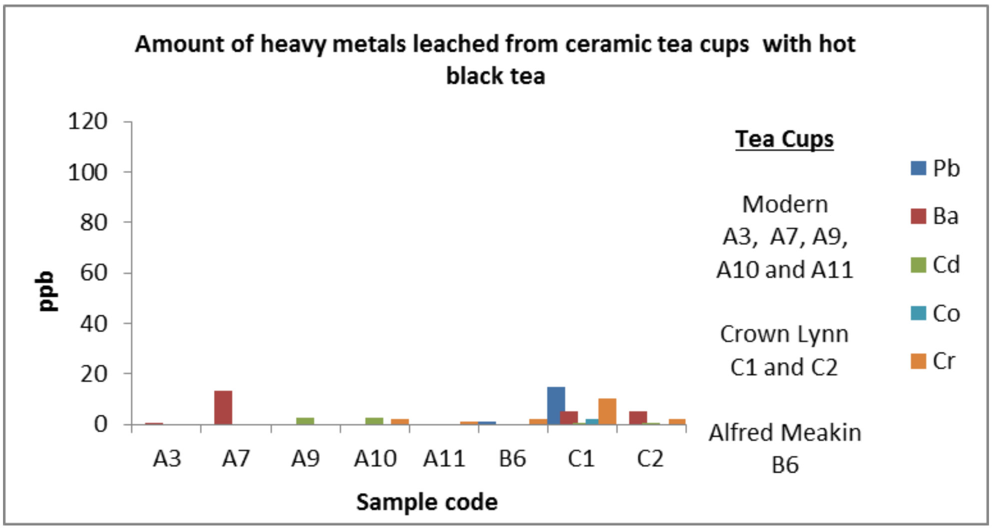


Figure 35: Amount of metals leached from ceramic tea cups with 10 minutes leaching test with hot black tea in ppb (µg/L).

The metals leached out from the ceramic tea cups were very low compared to that observed in the low pH lemon tea and 4% acetic acid which is expected given the pH difference between these samples and the more acidic samples.

Discussion

Temperature had great influence in the migration of metals from the ceramic teacups. An increase in temperature and a decrease in pH results in increase in migration of trace elements from the glazed ceramic wares (Demont et al., 2012). The amount of metals leached with the lemon tea is higher than that observed for black tea. Lead was found to leach from most of the ceramic cups on successive leaching with different pH solutions and Crown Lynn teacups leached higher amount of metals like lead and cadmium even after four to five repeated leaching tests conducted with same samples. However it was obvious that the extent of lead leaching was different given the different leaching solutions. The amount of lead and cadmium leached from all ceramic teacups are well below the standard limit given in the European Council Directive 84/500/EC which is 4 mg/L for lead and 0.3 mg/L for cadmium see **Table 1-2.**

Hot water leaching result

The results for the ceramic teacups exposed to hot water leach test for duration of 10 minutes is explained with the data shown in **Table 26**. The pH of Type 1 water was measured to be 6.34.

Table 26: Amount of metals leached from ceramic teacups with 10 minutes leaching test with hot water in ppb (ug/L).

Metals/ ppb (ug/L)	A3	A7	A9	A10	A11	B6	C1	C2
Pb	ND	ND	ND	ND	ND	ND	1	ND
Ba	ND	1	ND	ND	ND	ND	7	ND
Cd	68*	ND	ND	ND	ND	3	ND	ND
Co	ND	ND	ND	ND	ND	ND	ND	ND
*This value is inconsistent with other leaching results hence this value is suspected to be the result of some contamination from other sources.								

The Crown Lynn tea cup C1 shows low level of metal leaching even after four to five successive leaching tests with different leaching solutions. All other metals leached with hot water were either detected at very low or non-detectable levels.

Discussion

Modern ceramic wares analysed did not leach any metals of interest studied with the hot water leaching solution. The Crown Lynn tea cup which was giving results for leaching metals throughout the entire suite of leaching tests done did not leach any detectable levels of metals with the hot water leach test.

Cold water leaching results

The amount of metals leached from the ceramic teacups subjected to cold water leaching test are shown in **Figure 36**.

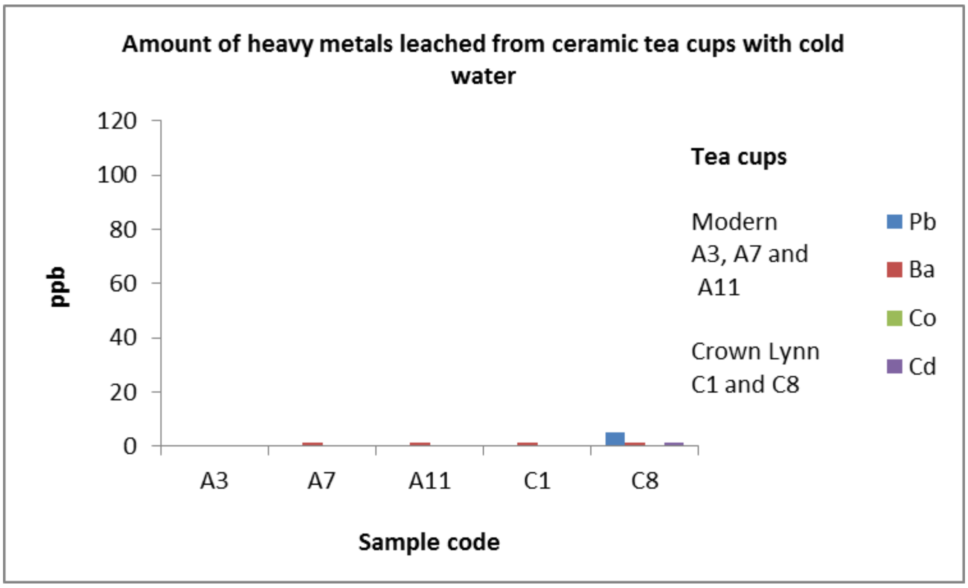


Figure 36: Amount of metals leached from the ceramic teacups of various eras during a 10 minutes leach test with cold water.

Lead was detected in very low level in Crown Lynn tea cup. All other samples did not release or showed very low level of metal during the 10 minutes leach test.

Discussion

Negligible leaching was observed in almost all samples. This is entirely expected with the leaching with neutral solution for all tested ceramic teacups.

Coca Cola leaching results

The leach test results of ceramic tea cups leached with Coca Cola at room temperature is given in the **Figure 37** and **Table 27**.

Samples C1, C2 and B6 are found to leach lead during the 10 minutes leach test with low pH (1.97) Coca Cola as leaching solution. Cadmium was not detected or below detectable level in all the ceramic teacups. Cobalt was detected in very low level from the Crown Lynn cup C2. Barium was also seen at comparatively higher levels in C2 than in other cups exposed to same leach test.

Table 27: Amount of metals leached from ceramic teacups with 10 minutes leaching test with cold water in ppb (µg/L).

Metals/ppb (ug/L)	A3	A7	A9	A10	A11	B6	C1	C2
Pb	ND	ND	ND	ND	ND	9	16	61
Ba	1	ND	ND	1	2	ND	1	10
Cd	ND	ND	ND	ND	ND	ND	ND	ND
Co	ND	ND	ND	ND	ND	ND	ND	5

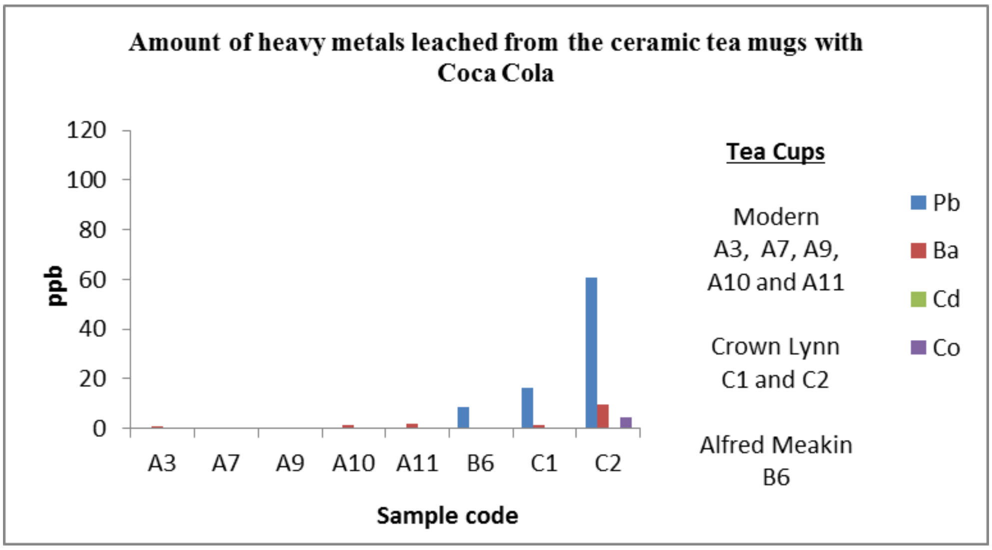


Figure 37: Amount of metals leached from the ceramic tea cups with highly acidic coca cola leach solution for a duration of 10 minutes given in ppb (µg/L).

Discussion

The results show that the Crown Lynn teacups tend to leach lead of varying amounts in all leaching tests done. However, the amount of lead leached was below the standard safe limit of released lead in ceramic wares as based on the 4% acetic acid leach test. The Alfred Meakin teacup (B6) showed lead leaching with low pH Coca Cola at room temperature but the amount of lead leached was at a lower level than that observed for the leaching test with hot lemon tea.

Summary and Conclusion

Characterisation studies with SEM, solid state NMR, FTIR gave only basic information of the clay bodies and no useful information of the glazes was obtained. However, the characterisation studies of the bulk ceramic wares done on XRF were highly informative about the metals present in the bulk ceramic wares. These XRF results informed the selection of metals to study in leachates with ICP-MS. However,

From the leaching studies, conducted with various eras' ceramic wares available in New Zealand, it was found that the pH of food, temperature and duration of exposure of the ceramic wares with the acidic foods each play a very important role in the leaching of metals from the ceramic glazes. Amount of cadmium leached from Victorian, mid- 20th century, Crown Lynn and modern ceramic wares was very negligible or non-detectable in all the leaching solution at different conditions. Red, yellow based glazes which had high amount of cadmium in their bulk XRF analysis were found to leach negligible or non-detectable level of that metal. High levels of a metal in XRF results do not always lead to high levels of that metal in the leachate solution.

Victorian era Wileman bone china released high amount of lead (15587 to 16628 µg/L) exceeding the standard safety limit of lead proposed by FDA (3 mg/L) and European council of Directive 84/500/EC (4 mg/L) for ceramic wares. The bright blue coloured over glaze decorative designs, longer exposure time and low pH conditions might have leached high amount of lead from the Wileman bone china. Barium, cobalt and chromium level in 4% acetic leachate solution were in very low level below the standard safety limit for this metals known in drinking water as there is no standard safety limit of these metals leaching from ceramic wares.

The Crown Lynn teacups released lead in different level in various leachates solutions. 4% acetic acid exposure for 24 hours leached high level of lead than other leaching solution (orange juice, hot tea, hot water and cold water) exposed for a short duration time but it was well below the standard safety limit of lead leached from the ceramic wares.

The modern ceramic wares (made in China, India and Thailand) studied in this research did leach very low levels of lead, barium, cadmium, cobalt and chromium and was well below the standard safety limit of this metals. The hot water and the hot lemon tea leach test proved that the pH plays a very important role in leaching as the amount of lead leached from the ceramic wares exposed to lemon tea was higher than the hot water leaching. Cold water did not release significant metals when compared to the hot water leaching test. The longer the ceramic wares were exposed to the low pH leaching solution higher amount of lead was released. All these different leachate solution gave varying results indicating that the leaching is influenced by various factors. Durability and damage of the glazes (crazing of the glazes) are likely to influence leaching rate of metals as seen in used ceramic wares (Victorian era and Crown Lynn) compared to unused modern ceramic wares but was not studied in detail in this work.

This research conducted with limited ceramic wares from various eras was also an indication that modern ceramic wares leached far less lead than the antique samples which suggest they are passing through improved safety testing before being sold in the New Zealand markets as well as improved techniques might be used by the potters to protect the glazes from leaching metals.

Recommendation for future work

- The results suggested that temperature plays a role in the amounts of metals released into the leachate solutions. 80 to 95 ^{o}C was the highest temperatures studied in this current work. However it would be very realistic if we could do some real domestic cooking (microwave) in these ceramic dishes and test the foods cooked in this wares for leaching metals.

References

Agrawal, S. Crockery with a Touch of Class. http://www.tata.com/company/articles/inside.aspx?artid=007DtsaA/0M= (accessed 19th April 2013)

Anonymous Fourier-Transform Spectroscopy. *Spectroscopy* 2005, 32-32.

Apperley, D. C.; Harris, R. K.; Hodgkinson, P. *Solid - State NMR Basic Priciples & Practice*; Momentum Press, LLC: New York, 2012.

Assimon, S. A.; Adams, M. A.; Jacobs, R. M.; Bolger, P. M. Preliminary assessment of potential health hazards associated with barium leached from glazed ceramicware. *Food Additives & Contaminants* 1997a, *14*, 483-490.

Assimon, S. A.; Adams, M. A.; Jacobs, R. M.; Bolger, P. M. Preliminary assessment of potential health hazards associated with barium leached from glazed ceramicware. *Food Additives and Contaminants* 1997b, *14*, 483-490.

Balci, M. *Basic 1H-and 13C-NMR spectroscopy*; Elsevier Philadelphia, 2005.

Becker, J. S.; Dietze, H.-J. Precise and accurate isotope ratio measurements by ICP-MS. *Fresenius Journal of Analytical Chemistry* 2000, *368*, 23-30.

Belgaied, J. E. Release of heavy metals from Tunisian traditional earthenware. *Food and Chemical Toxicology* 2003, *41*, 95-98.

Bell, C. 'Not really beautiful, but iconic': New Zealand's Crown Lynn Ceramics. *Journal of Design History* 2012, *25*, 414-426.

Berzina-Cimdina, L.; Borodajenko, N. Research of Calcium Phosphates Using Fourier Transform Infrared Spectroscopy. *Infrared Spectroscopy Materials Science, Engineering and Technology, Edited by Theophile Theophanides* 2012, 123-149.

Breuer, S. The Chemistry of Pottery. *Royal Society of Chemistry* 2012.

Britt, J. *The Complete Guide to High-Fire Glazes: Glazing and Firing at Cone 10*; Lark Books, 2007.

Burleson, M. *The Ceramic Glaze Handbook: Materials, Techniques, Formulas*; Lark Books, 2003.

Casavant, C. Lead Exposure in Avian Species, Worceter Polytechnic Institute, 2008.

Christie, A. B.; Thompson, B.; Brathwaite, B. Mineral commodity report 20 - clays. New Zealand Mining 2001, 27, 26-43.

Craig, N.; Speakman, R. J.; Popelka-Filcoff, R. S.; Glascock, M. D.; Robertson, J. D.; Shackley, M. S.; Aldenderfer, M. S. Comparison of XRF and PXRF for analysis of archaeological obsidian from southern Peru. *Journal of Archaeological Science* 2007, *34*, 2012-2024.

Daulton, T. L. Advanced Nanocomposites for High-Temperature Structural Aplications. http://www7430.nrlssc.navy.mil/facilities/emf/nanocomp.htm (accessed 21st June 2013)

Davis, R.; Mauer, L. J. Fourier transform infrared (FT-IR) spectroscopy: a rapid tool for detection and analysis of foodborne pathogenic bacteria. *Current research, technology and education topics in applied microbiology and microbial biotechnology. Formatex Research Center, Spain* 2010, 1582-1594.

Demont, M.; Boutakhrit, K.; Fekete, V.; Bolle, F.; Van Loco, J. Migration of 18 trace elements from ceramic food contact material: Influence of pigment, pH, nature of acid and temperature. *Food and Chemical Toxicology* 2012, *50*, 734-743.

Duwe, S.; Neff, H. Glaze and slip pigment analyses of Pueblo IV period ceramics from east-central Arizona using time of flight-laser ablation-inductively coupled plasma-mass spectrometry (TOF-LA-ICP-MS). *Journal of Archaeological Science* 2007, *34*, 403-414.

e-Bay 3 Jingdezhen Porcelain Qing Hua Tea Cup e-bay store, 2012.

e-Bay. e-bay: Shelley Wileman Foley Snowdrop Cameo Orange Antique Cake Plate. http://www.ebay.com/itm/SHELLEY-WILEMAN-FOLEY-SNOWDROP-Cameo-ORANGE-ANTIQUE-CAKE-PLATE-/281044094008?pt=LH_DefaultDomain_2&hash=item416f888c38 (accessed May 2013 2013)

e-Bay. e-Bay: Wileman Shelley Aqua Blue Cameo On Snowdrop Trio c1901. http://picclick.com/WILEMAN-Shelley-AQUA-BLUE-CAMEO-290533928630.html (accessed 8th May 2013)

e-Bay. ebay: Crown Ceramics India Fine Bone China Mug Floral Pattern. http://www.ebay.ca/itm/Crown-Ceramics-India-Fine-Bone-China-Mug-Floral-Pattern-/370633800360 (accessed May 8th 2013)

Eisazadeh, A.; Kassim, K. A.; Nur, H. Solid-state NMR and FTIR studies of lime stabilized montmorillonitic and lateritic clays. *Applied Clay Science* 2012, *67 - 68*, 5-10.

Encyclopedia Coesite. In McGraw-Hill Concise Encyclopedia of Science and Technology; McGraw-Hill, 2006.

Feldman, N.; Lamp, C.; Craigmill, L., Arthur. Lead leaching in Ceramics difficult to predict. *California Agriculture* 1999, *53*.

Ferrero, J. L.; RoldÃ¡n, C.; Ardid, M.; Navarro, E. X-ray fluorescence analysis of yellow pigments in altarpieces by Valencian artists of the XV and XVI centuries. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* 1999, *422*, 868-873.

Flight, G.; Lane, P. *Ceramics Manual: A Basic Guide to Pottery Making*; HarperCollins Publishers Limited, 1990.

Froh, J. Archaeological Ceramics Studied by Scanning Electron Microscopy. *Hyperfine Interactions* 2004, *154*, 159-176.

Gunther, D.; Hattendorf, B. Solid sample analysis using laser ablation inductively coupled plasma mass spectrometry. *TrAC Trends in Analytical Chemistry* 2005, *24*, 255-265.

Gupta, K. C. *Progress and Prospects of Pottery Industry in India: A Case Study of U.P*; Mittal Publishers Distributors, 1988.

Hamer, F.; Hamer, J. *The Potter's Dictionary of Materials and Techniques*; A & C Black, 2004.

Henden, E.; Cataloglu, R.; Aksuner, N. Determination of arsenic leaching from glazed and non-glazed Turkish traditional earthenware. *Science of The Total Environment* 2011, *409*, 2993-2996.

Hight, S. C. Determination of lead and cadmium in ceramicware leach solutions by graphite furnace atomic absorption spectroscopy: Method development and interlaboratory trial. *Journal of AOAC International* 2001, *84*, 861-872.

Hopper, R. *Robin Hopper Ceramics: A Lifetime of Works, Ideas and Teachings*; F+W Media, 2006.

Horiba Scientific. XRF Spectroscopy. http://www.horiba.com/scientific/products/x-ray-fluorescence-analysis/tutorial/xrf-spectroscopy/ (accessed 15 July 2013)

Hudgins, S. Pottering Around the Potteries. *World & I* 2002, *17*, 104.

Jakes, K. A.; American Chemical Society. Division of the History of, C.; American Chemical Society, M. *Archaeological chemistry: materials, methods, and meaning*; American Chemical Society, 2002.

James, M. Overview of X- ray Fluorescence http://archaeometry.missouri.edu/xrf_overview.html (accessed 20th April 2013)

Jernegan, J. *Dry Glazes*; A&C Black, 2009.

Jones, L. L. Ceramics. http://www.chemistryexplained.com/Bo-Ce/Ceramics.html#b (accessed 18/04/2013 2013)

Jones, T. *Bone China: A Richard Lacey Detective Mystery*; iUniverse, 2000.

Kelloway, S.; Birmingham, J. Profiling Nineteenth-century Australian Potteries: Approaches to Provenancing Ceramics and Identifying Potting Practices. *Australasian Historical Archaeology* 2010, *28,* 35-42.

Khursheed, A. *Scanning Electron Microscope Optics and Spectrometers*; World Scientific Publishing Co.: River Edge, NJ, USA, 2010.

Kitouni, S.; Harabi, A. Sintering and mechanical properties of porcelains prepared from algerian raw materials. *Ceramica* 2011, *57*, 453-460.

Klinowski, J. *New Techniques in Solid-State NMR*; Springer, 2005.

Kogel, J. E.; Trivedi, N. C.; Society for Mining, M.; Exploration; Barker, J. M. *Industrial Minerals and Rocks: Commodities, Markets, and Users*; Society For Mining, Metallurgy and Exploration, Incorporated, 2006.

Laird, D. F. *Reinforced Sintered Cancellous Bovine Bone as a Potential Bone Replacement Material*; University of Waikato, 2010.

Lehman, R. L. Lead glazes for ceramic foodware. *Internet]. Research Triangle Park, NC: International Lead Management Center* 2002.

Li, B.; Zhao, J.; Collerson, K. D.; Greig, A. Application of ICP-MS trace element analysis in study of ancient Chinese ceramics. *Chinese Science Bulletin* 2003, *48*, 1219-1224.

Lobo, H.; Bonilla, J. V. *Handbook of Plastics Analysis*; Marcel Dekker, 2003.

Lynch, R.; Elledge, B.; Peters, C. An assessment of lead leachability from lead-glazed ceramic cooking vessels. *Journal of environmental health* 2008, *70*, 36.

Macedo, D. A.; Cesário, M. R.; Souza, G. L.; Cela, B.; Paskocimas, C. A.; Martinelli, A. E.; Melo, D. M. A.; Nascimento, R. M. Infrared Spectroscopy Techniques in the Characterization of SOFC Functional Ceramics. In *Infrared Spectroscopy - Materials Science, Engineering and Technology*; T. Theophile, Ed.; InTech: ONLINE, 2012.

MacKenzie, K. J. D.; Smith, E. *Multinuclear Solid-State Nuclear Magnetic Resonance of Inorganic Materials*; Elsevier Science, 2002.

Macomber, R. S. *A complete introduction to modern NMR spectroscopy*; Wiley, 1998.

Mason, R. B.; Tite, M. S. The beginnings of tin-opacification of pottery glazes. *Archaeometry* 1997, *39*, 41-58.

Mazzocchin, G. A.; Agnoli, F.; Colpo, I. Investigation of roman age pigments found on pottery fragments. *Analytica Chimica Acta* 2003, *478*, 147-161.

Mirti, P.; Davit, P. Technological Characterization of Campanian Pottery of Type A, B and C and of Regional Products from Ancient Calabria (Southern Italy). *Archaeometry* 2001, *43*, 19-33.

Mohamed, N.; Chin, Y. M.; Pok, F. W. Leaching of lead from local ceramic tableware. *Food Chemistry* 1995, *54*, 245-249.

Monk, V. M. *Crown Lynn A New Zealand Icon*, 2006.

New Zealand Institute of Chemistry. Ceramic Products. http://nzic.org.nz/ChemProcesses/inorganic/ (accessed 13 July 2013)

Nixon, W. C. The General Principles of Scanning Electron Microscopy. *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences* 1971, *261*, 45-50.

Omolaoye, J. A.; Uzairu, A.; Gimba, C. E. Heavy metal assessment of some ceramic products imported into Nigeria from China. *Archives of Applied Science Research* 2010, *2*, 120-125.

Ong, S. C. *China Condensed: 5000 Years of History and Culture*; Marshall Cavendish: Singapore, 2005.

Palanivel, R.; Velraj, G. FTIR and FT-Raman spectroscopic studies of fired clay artifacts recently excavated in Tamilnadu, India. *Indian Journal of Pure and Applied Physics* 2007, *45*, 501-508.

Patwardhan, N. *New Handbook for Potters*; Allied Publishers, 2005.

Perez-Arantegui, J.; Larrea, A.; Molera, J.; Pradell, T.; Vendrell-Saz, M. Some aspects of the characterization of decorations on ceramic glazes. *Applied Physics A* 2004, *79*, 235-239.

Perryman, J. *Traditional pottery of India*; A and C Black, 2000.

Peterson, S.; Peterson, J. *The Craft and Art of Clay: A Complete Potter's Handbook*; LAURENCE KING PUBLISHERS, 2003.

Phipps, A.; Fels, H.; Burns, M. S.; Gerstenberger, S. L. Lead poisoning due to geophagia: The consumption of miniature pottery. *Open Journal of Pediatrics* 2012, 60-66.

Prabakaran, K.; Musthafa, A. M.; Hemamalini, R.; Velraj, G. FT-IR and Micro-Raman Spectroscopic Studies of Archaeological Potteries Recently Excavated in Tamilnadu, India. *Recent Research in Science and Technology* 2010, *2*.

Reilly, C. *Metal Contamination of Food: Its Significance for Food Quality and Human Health*; Wiley, 2008.

Rhodes, D.; Hopper, R. *Clay and glazes for the potter*, Third ed.; Krause Publications, 2000.

Saikia, B. J.; Parthasarathy, G. Fourier transform infrared spectroscopic characterization of kaolinite from Assam and Meghalaya, Northeastern India. *J. Mod. Phys* 2010, *1*, 206.

Saikia, B. J.; Parthasarathy, G.; Sarmah, N. C. Fourier transform infrared spectroscopic estimation of crystallinity in SiO2 based rocks. *Bulletin of Materials Science* 2008, *31*, 775-779.

Sanchez-Ramos, S.; Bosch-Reig, F.; Gimeno-Adelantado, J. V.; Yusa-Marco, D. J.; Domanech-Carba, A.; Berja-Parez, J. A. Validation of a method for the determination of boron in ceramic materials by X-ray fluorescence spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy* 2000, *55*, 1669-1677.

Sharma, B. K. *Industrial Chemistry*; Krishna Prakashan, 1997.

Sheean, J. L. Chinese pottery. *Journal of Chemical Education* 1931, *8*, 1249.

Sheets, R. W. Release of heavy metals from European and Asian porcelain dinnerware. *Science of The Total Environment* 1998, *212*, 107-113.

Shelah, G. On The Invention Of Pottery. *Science Magazine* 2012, *336*.

Shelley and Wileman Backstamps. http://www.shelleychinaclub.com/backstamps.html (accessed May 8th 2013 2013)

Shelly, P. *The Oldest Craft in the World: A Simple Description of the Processes Employed in the Manufacture of English Bone China*; Shelly Potteries, 1937.

Shoval, S.; Beck, P. Thermo-FTIR spectroscopy analysis as a method of characterizing ancient ceramic technology. *Journal of Thermal Analysis and Calorimetry* 2005, *82*, 609-616.

Shoval, S.; Yadin, E.; Panczer, G. Analysis of thermal phases in calcareous Iron Age pottery using FT-IR and Raman spectroscopy. *Journal of Thermal Analysis and Calorimetry* 2011, *104*, 515-525.

Sivasankar, B. *Engineering Chemistry*; McGraw-Hill Education (India) Pvt Limited, 2008.

Speakman, R. J.; Neff, H. *Laser Ablation-ICP-MS In Archaeological Research*; University of New Mexico Press, 2005.

The Press Trust of India World's Oldest Pottery Found in India, Say Anthropologist. In *The Citizen* Ottawa, 1986.

Thomas, R. *Practical Guide to ICP-MS*; Marcel Dekker Incorporated, 2003.

Tunstall, S.; Amarasiriwardena, D. Characterization of lead and lead leaching properties of lead glazed ceramics from the Solis Valley, Mexico, using inductively coupled plasma-mass spectrometry (ICP-MS) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFT). *Microchemical Journal* 2002, *73*, 335-347.

Valadez-Vega, C.; Zuniga-Perez, C.; Quintanar-Gomez, S.; Morales-Gonzalez, J. A.; Madrigal-Santillan, E.; Villagomez-Ibarra, J. R.; Sumaya-Martinez, M. T.; Garcia-Paredes, J. D. Lead, cadmium and cobalt (Pb, Cd, and Co) leaching of glass-clay containers by pH effect of food. *Int. J. Mol. Sci.* 2011, *12*, 2336-2350.

Velraj, G.; Janaki, K. Spectroscopic Studies of some Fired Clay Artifacts Recently Excavated at Tittagudi in Tamilnadu. *Recent Research in Science and Technology* 2011, *3*.

Watanabe, T.; Shimizu, H.; Nagasawa, K.; Masuda, A.; Saito, H. 29Si-and 27Al-MAS/NMR study of the thermal transformations of kaolinite. *Clay Miner* 1987, *22*, 37-48.

Watkins, C.; Harvey, W.; Robert, S. *Shelley Potteries : The History And Production of a Staffordshire Family*; Barrie and Jenkins: London, 1980.

Wood, N.; Tite, M. S.; Doherty, C.; Gilmore, B. A technological examination of ninth-tenth century AD Abbasid blue-and-white ware from Iraq, and its comparison with eighth century AD Chinese blue-and-white Sancai ware. *Archaeometry* 2007, *49*, 665-684.

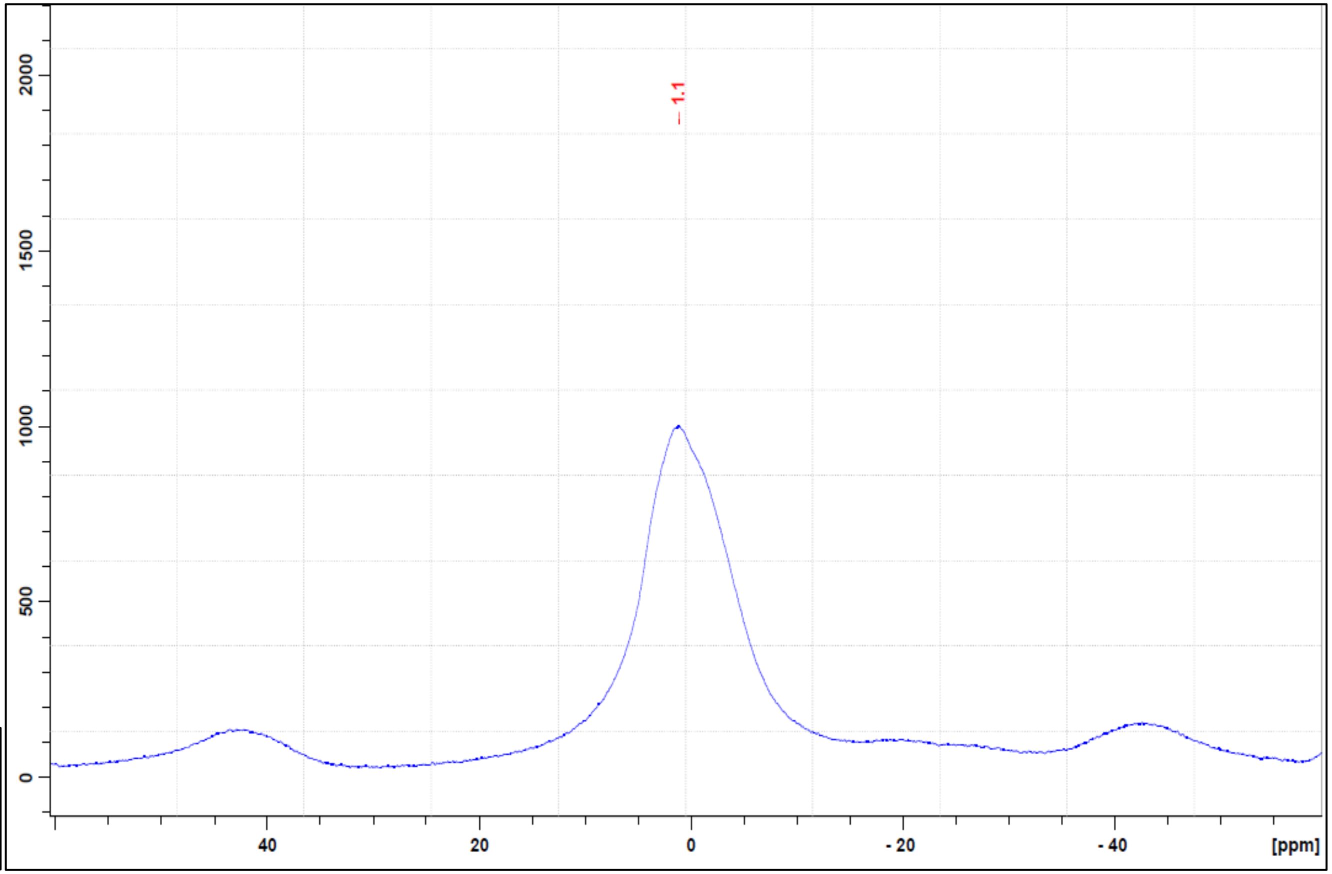
World Health Organisation “Ceramic Foodware Safety: Sampling, Analysis and Limits for Lead and Cadmium Release,” 1976.

Wu, X.; Zhang, C.; Goldberg, P.; Cohan, D.; Pan, Y.; Arpin, T.; Bar-Yosef, O. Early Pottery at 20, 000 Years Ago in Xianrendong Cave, China. *Science Magazine* 2012, *336*, 1696-1700.

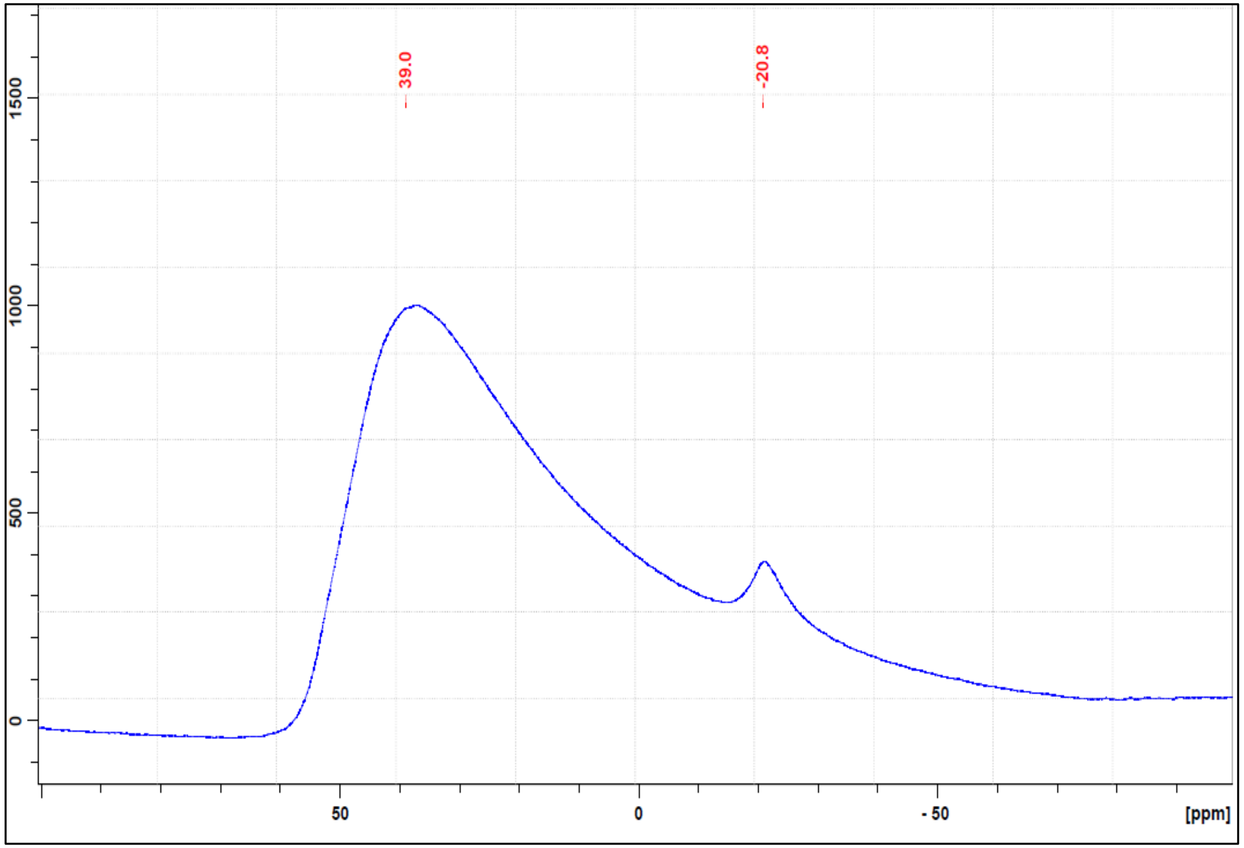
Yu, L.-x.; Wang, H.-d.; Qiu, G.-z.; Liang, D.-y. Comprehensive utilization of kaolin ore accompanying muscovite. *Journal of Central South University of Technology* 2010, *17*, 954.

Appendix-1

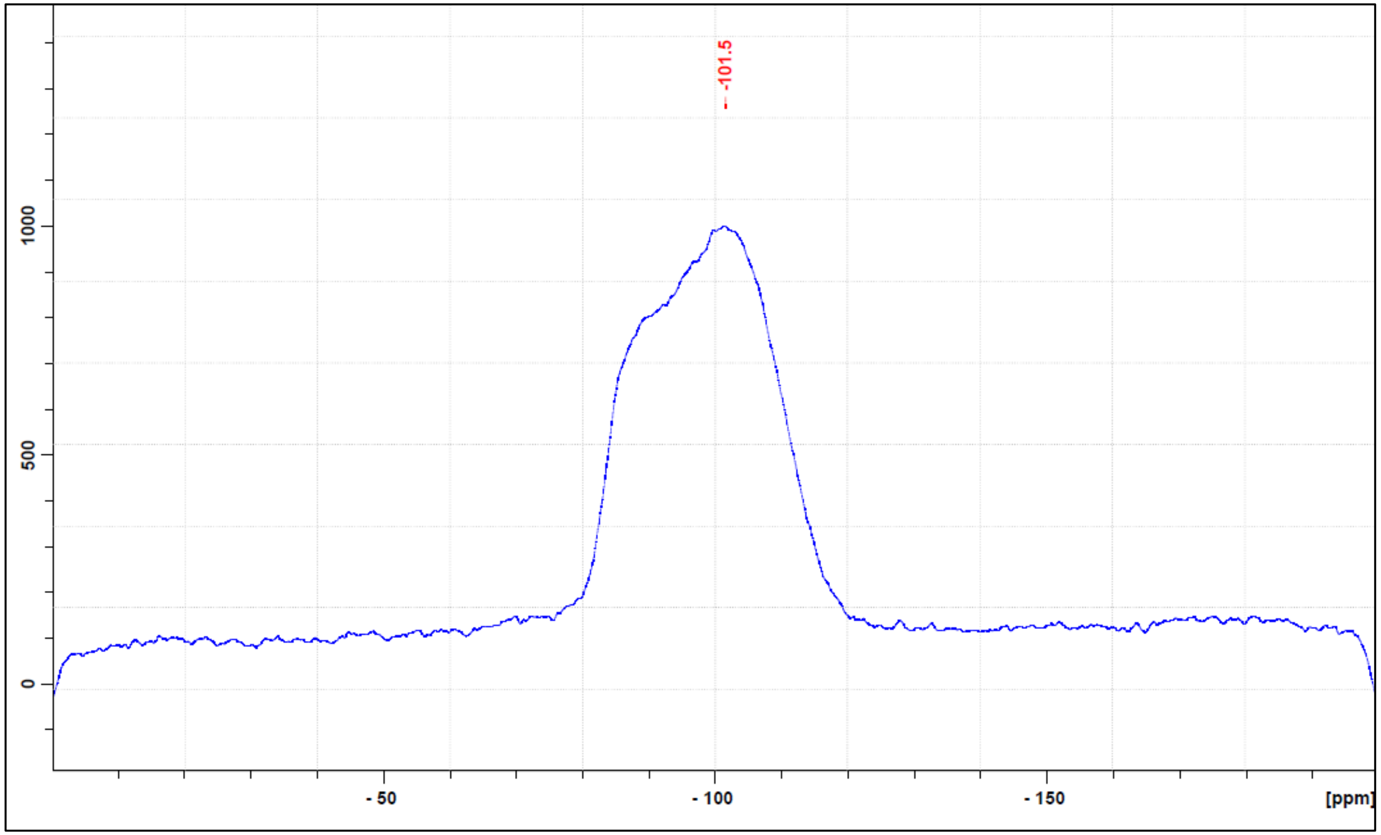
^{31}P solid state NMR spectrum of the ground mid- 20th century Alfred Meakin ceramic bowl B5



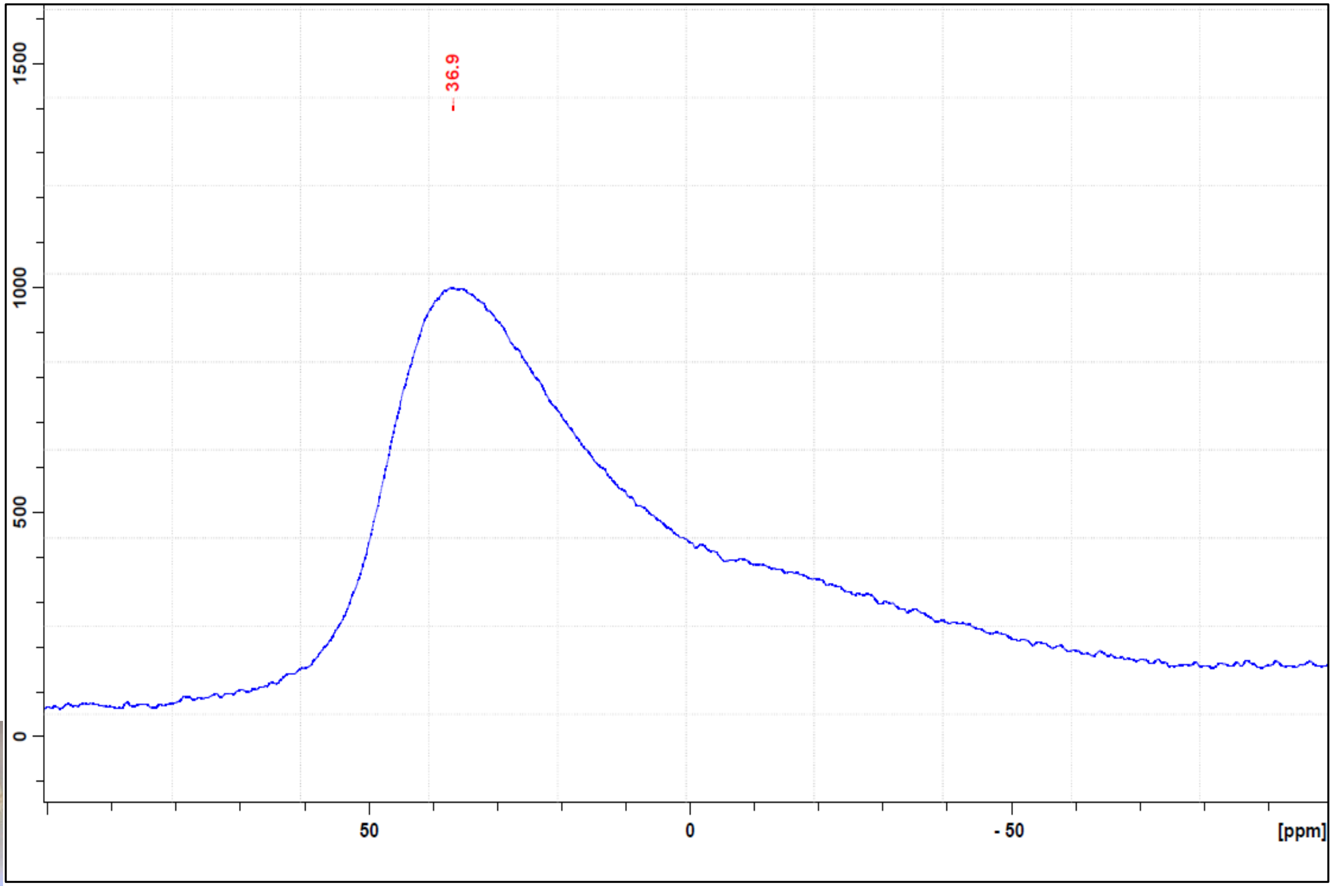
^{27}Al solid state NMR spectrum of the ground mid- 20th century Alfred Meakin ceramic bowl B5



^{29}Si solid state NMR spectrum of the ground mid- 20th century Alfred Meakin ceramic bowl B5



^{27}Al solid state NMR spectrum of the ground Crown Lynn plate C4



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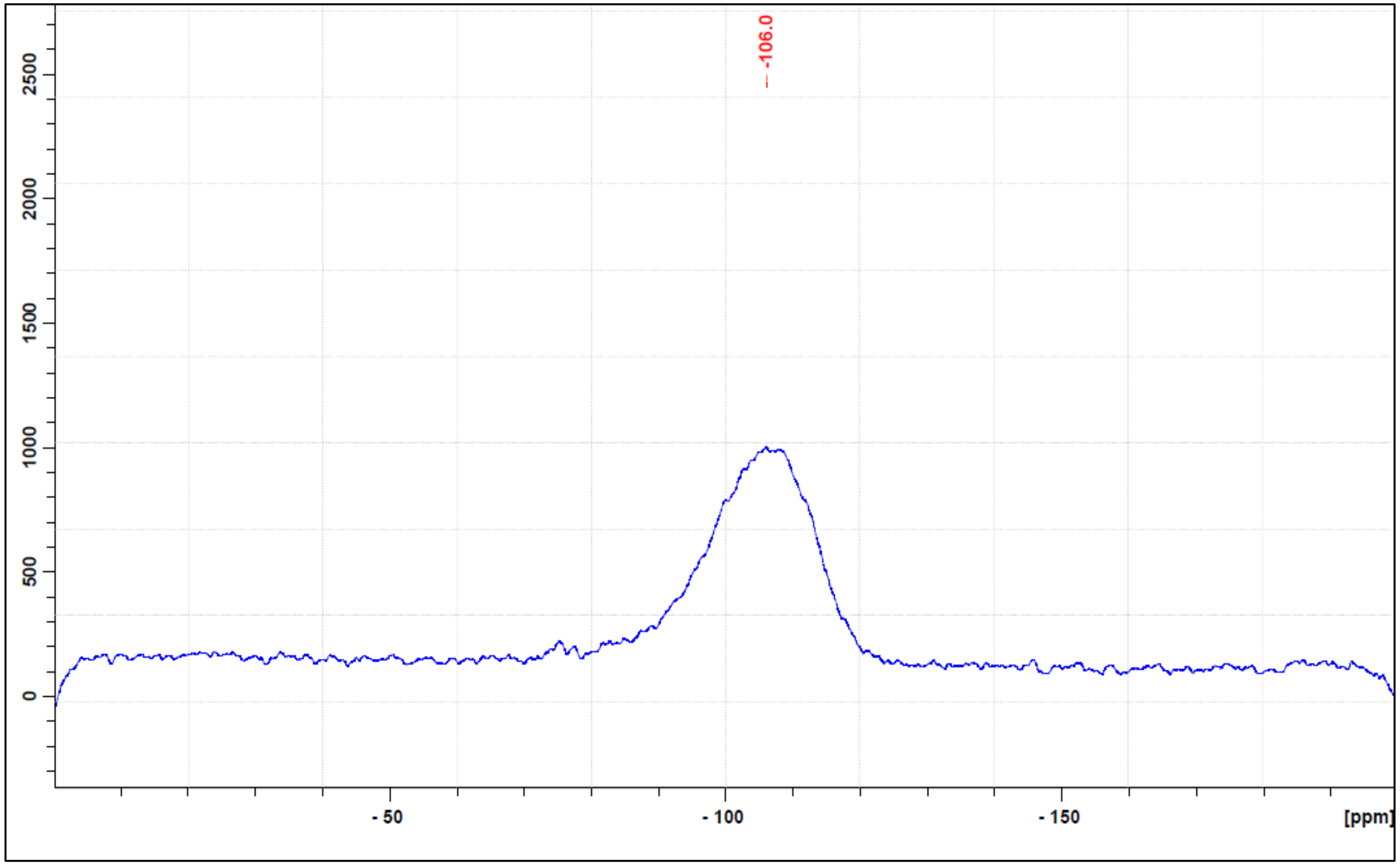

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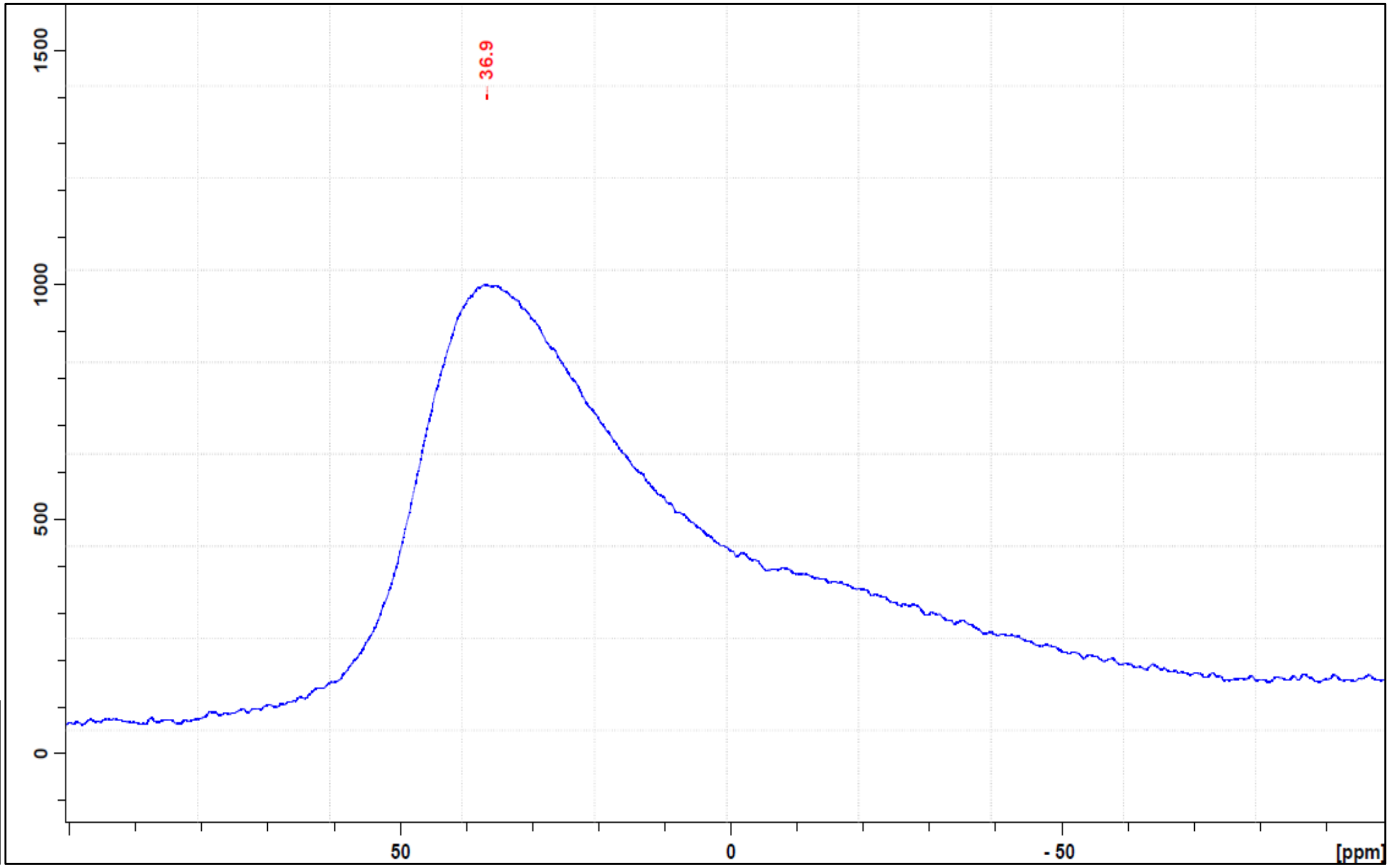

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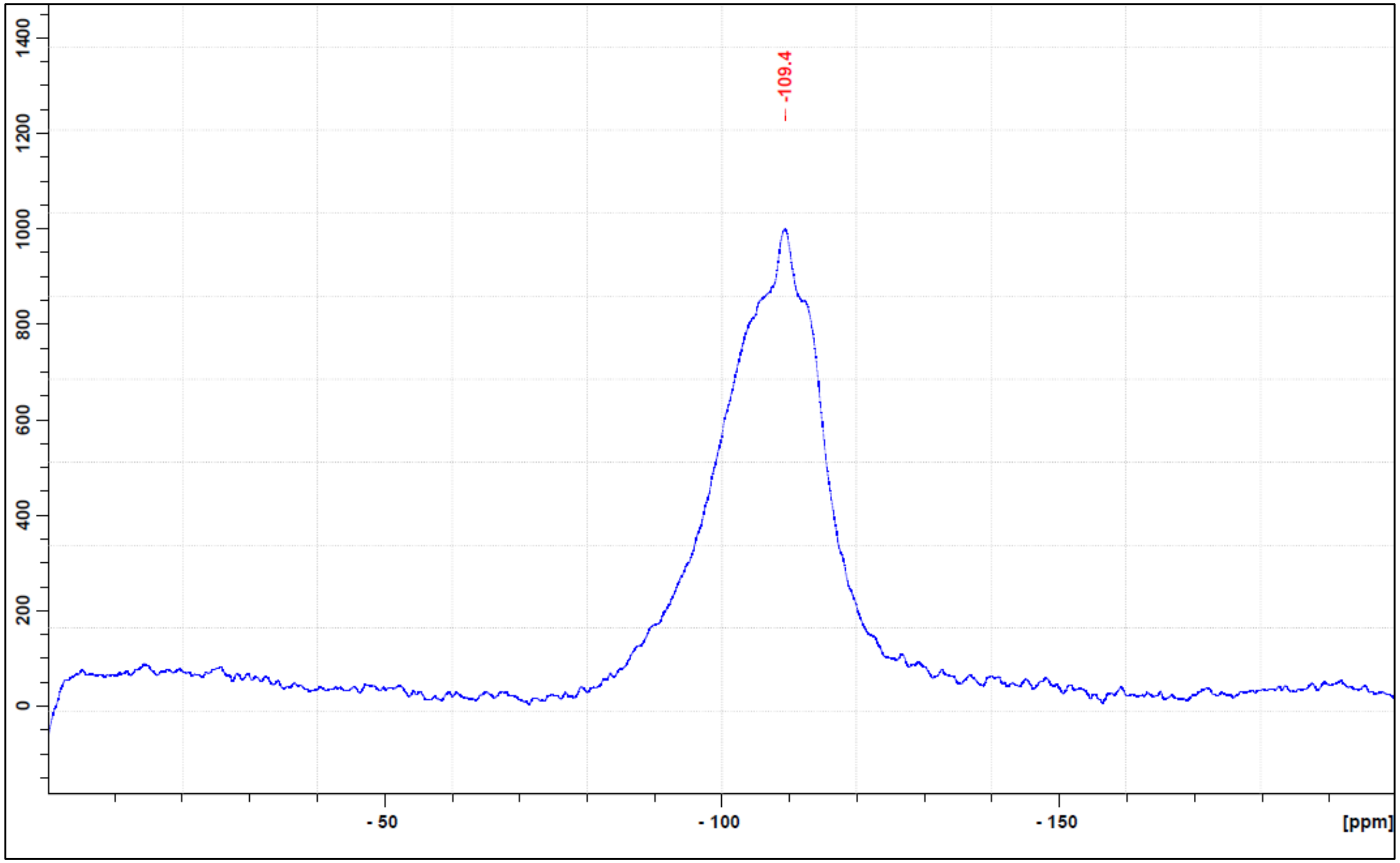
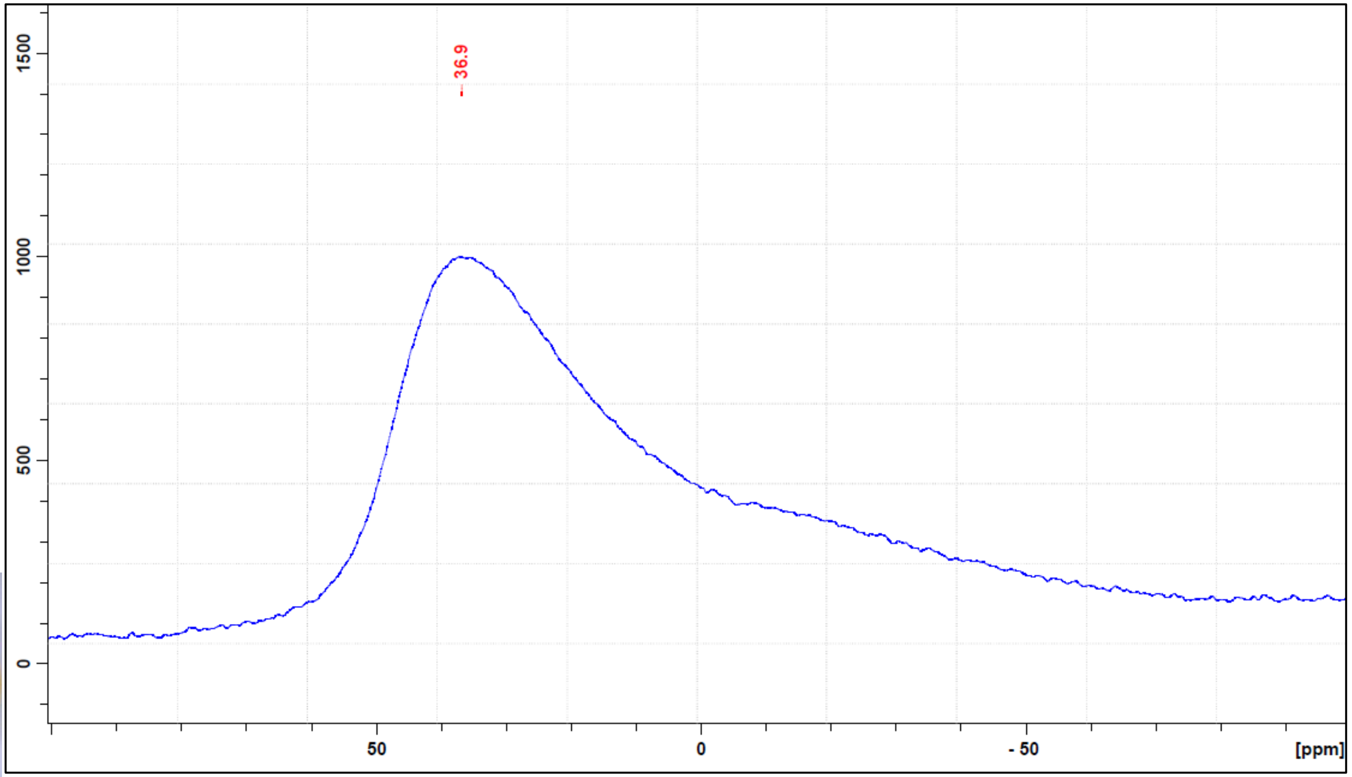


^{27}Al solid state NMR spectrum of the ground Crown Lynn plate C7



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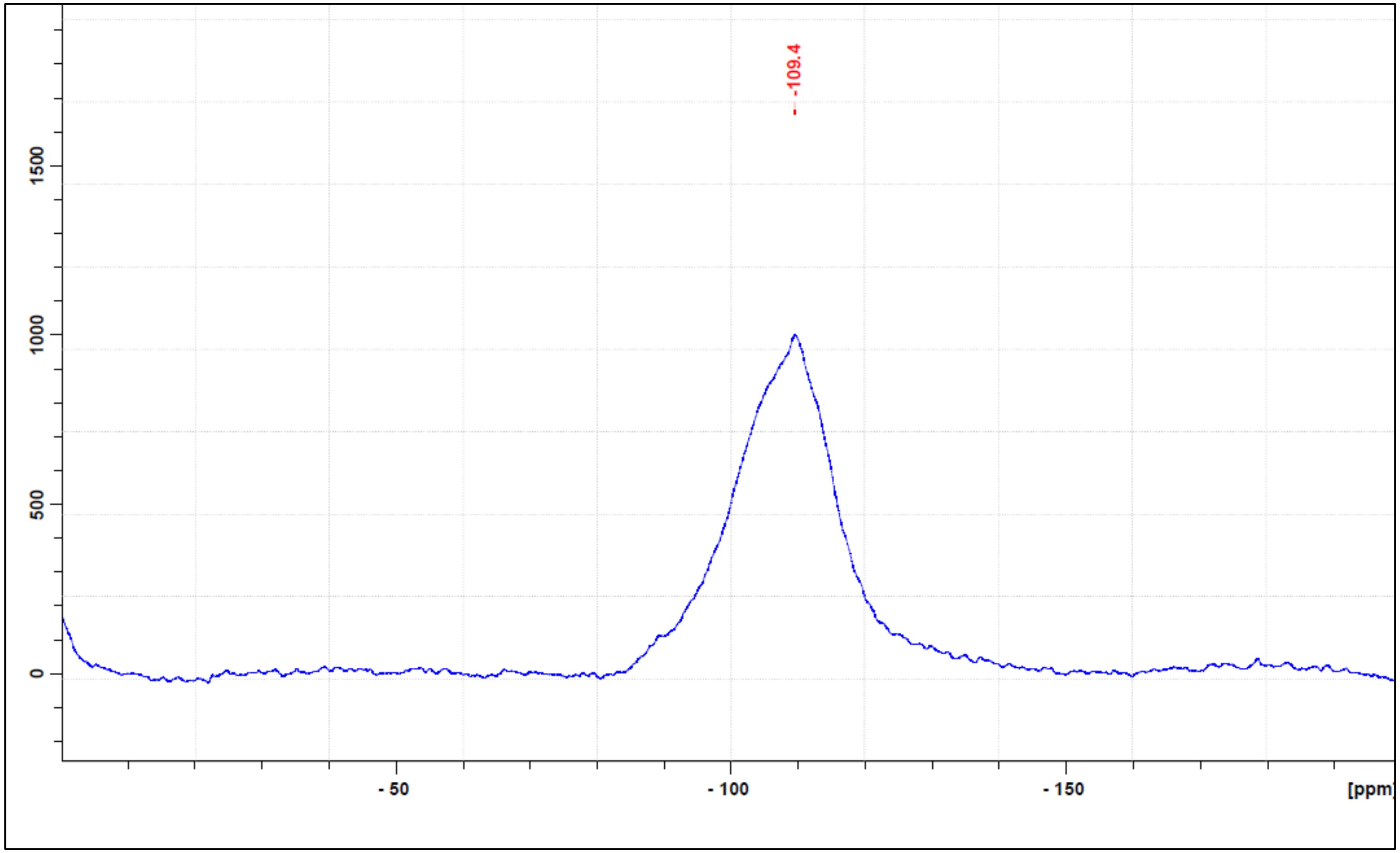
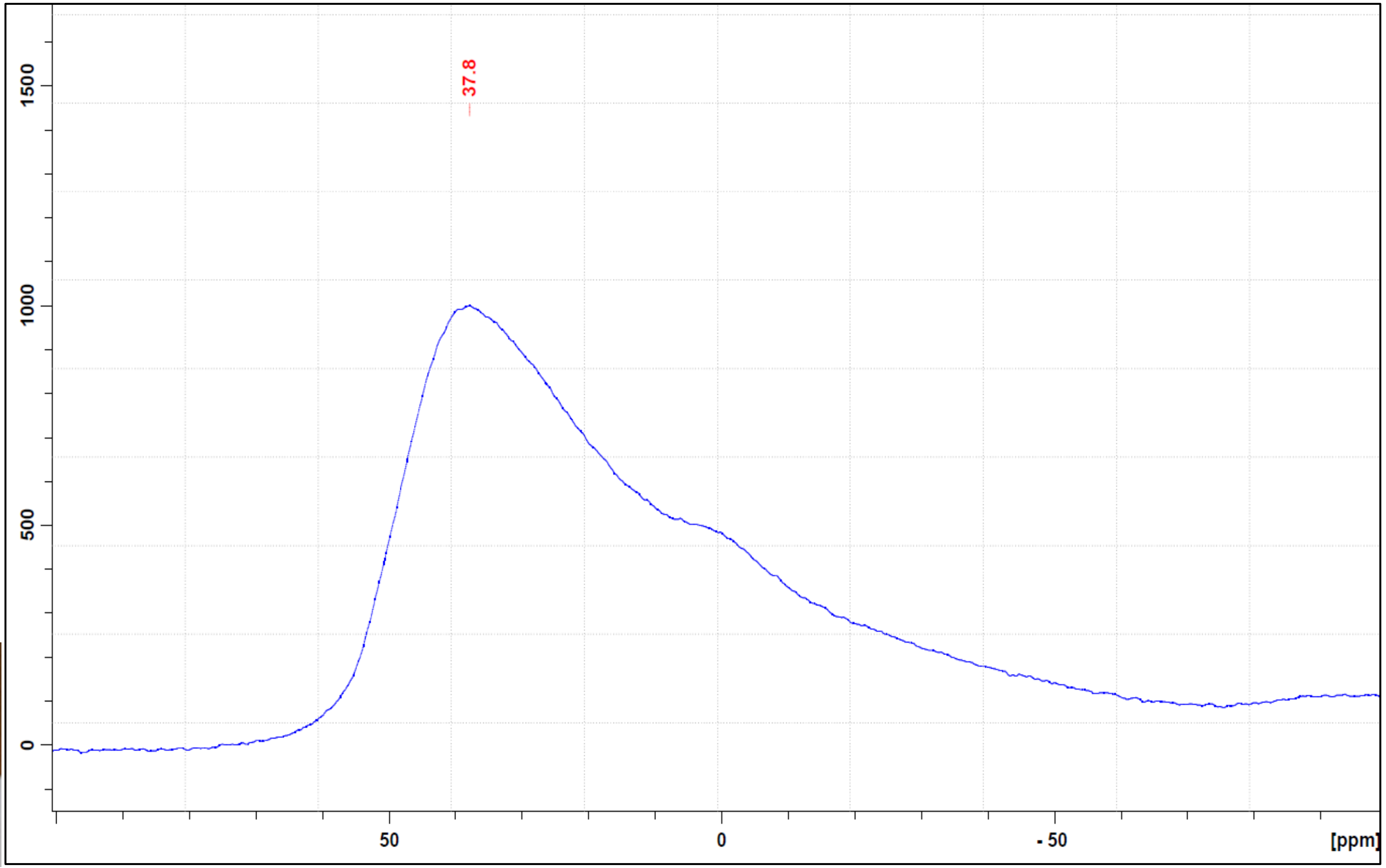
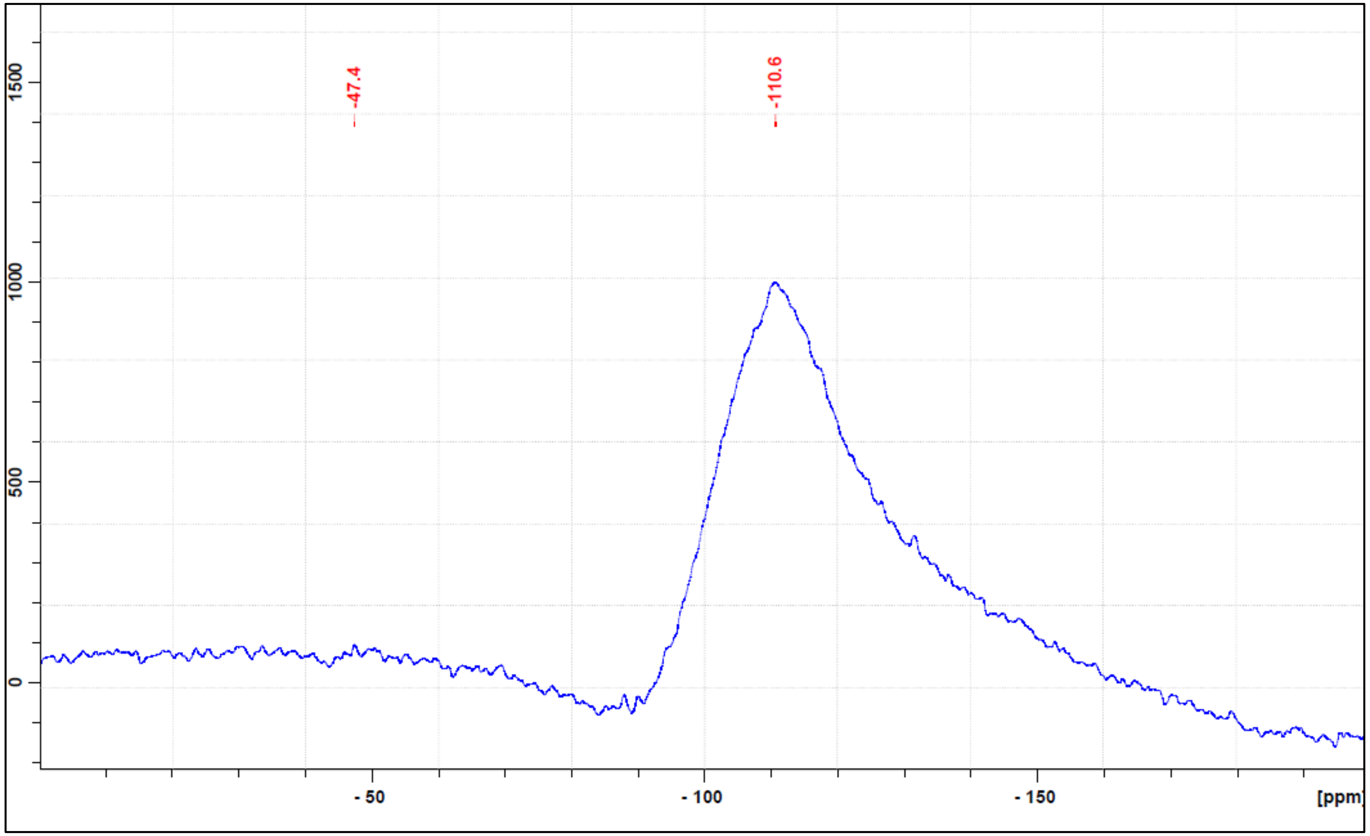


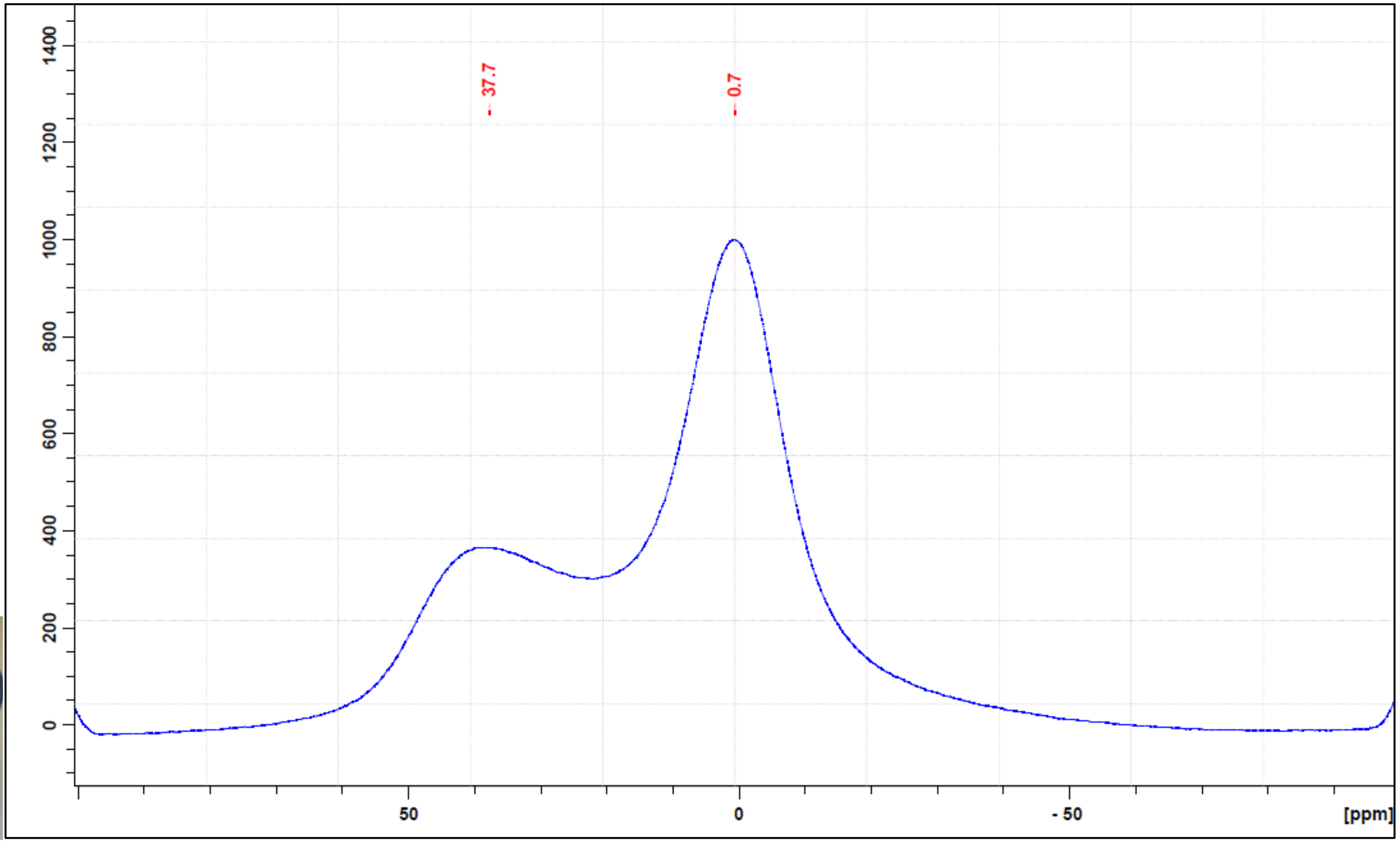
^{27}Al solid state NMR spectrum of the ground modern Chinese bowl A1



^{29}Si solid state NMR spectrum of the ground modern Chinese bowl A1



^{27}Al solid state NMR spectrum of the ground modern Chinese ceramic bowl A2



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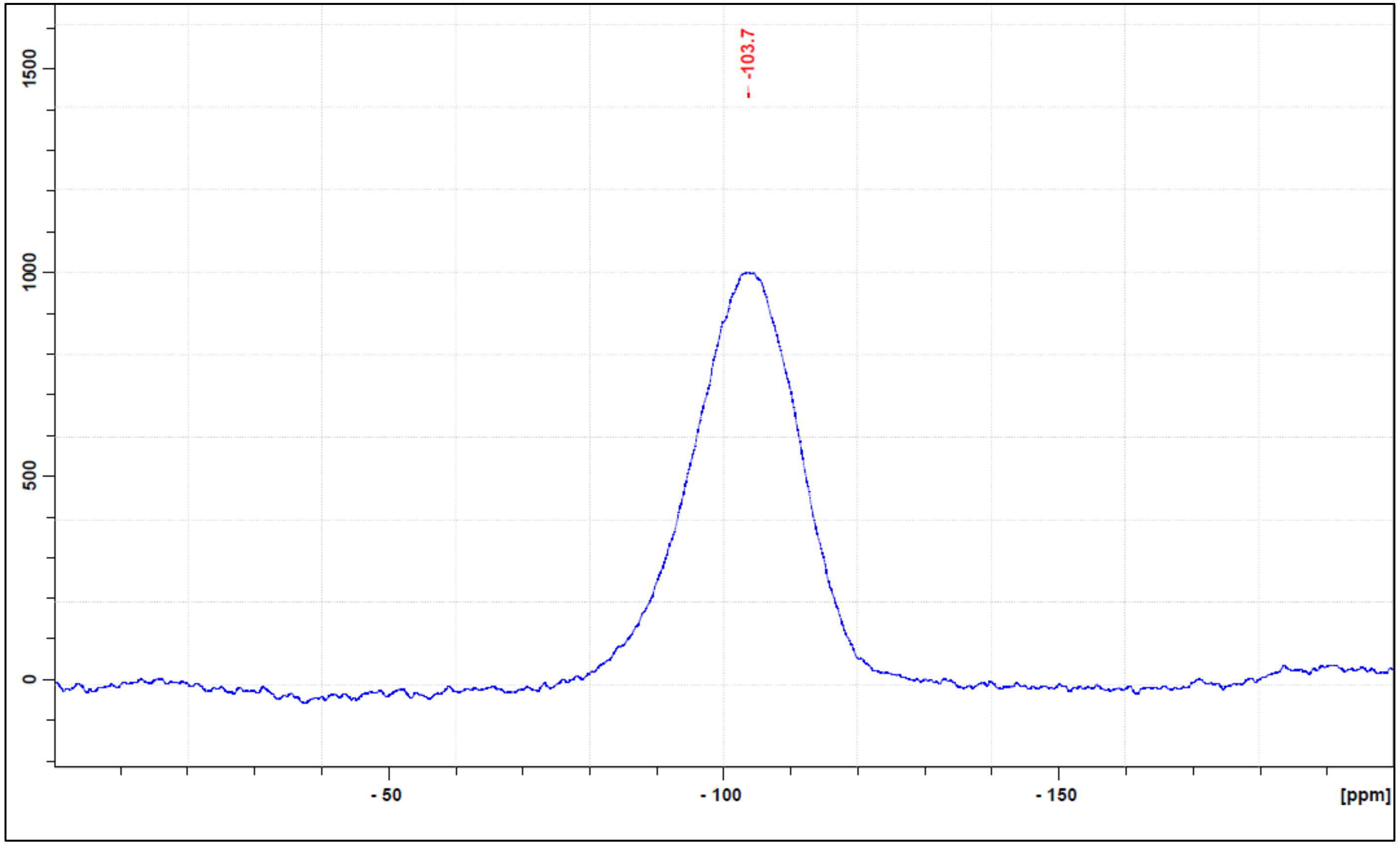
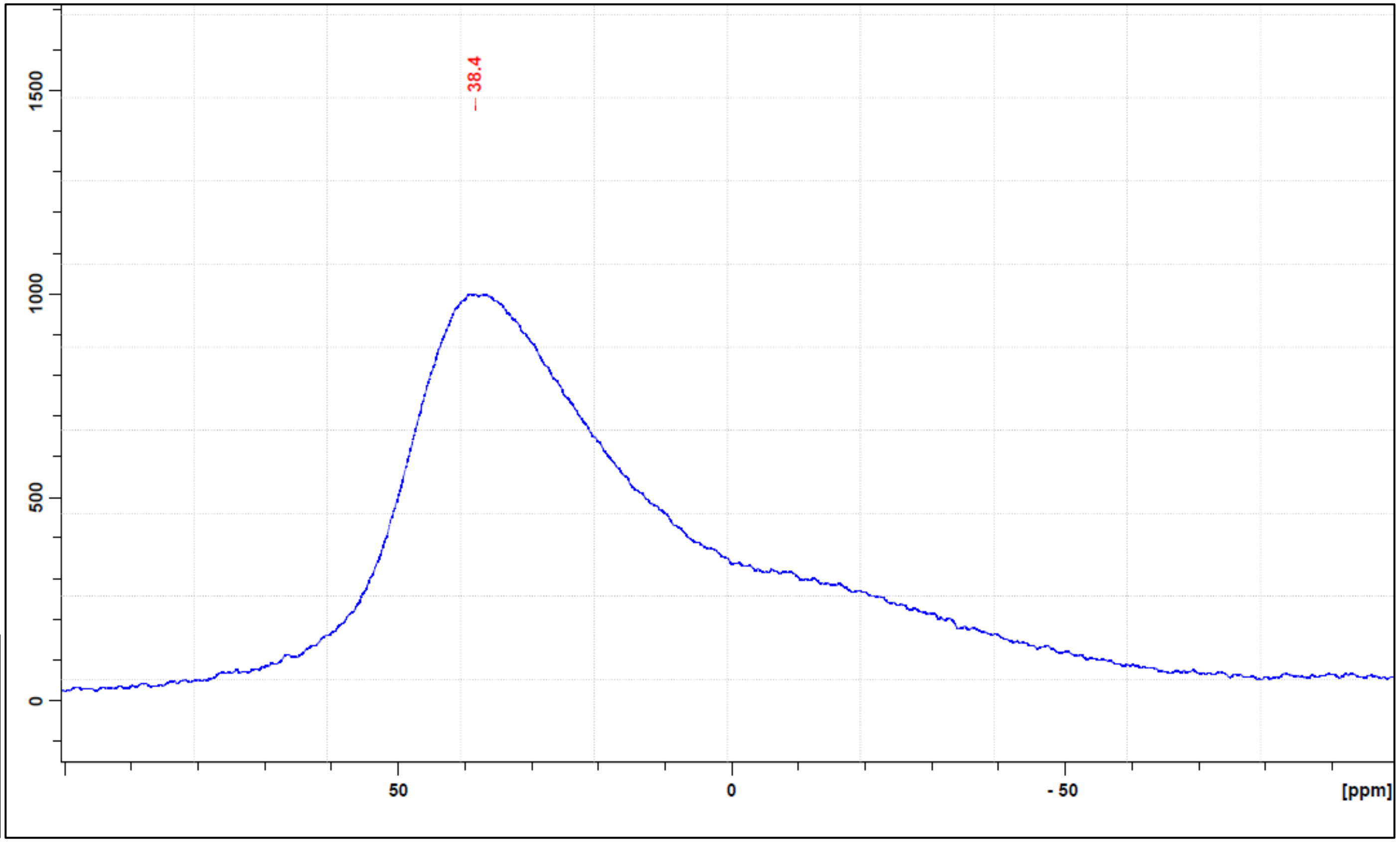
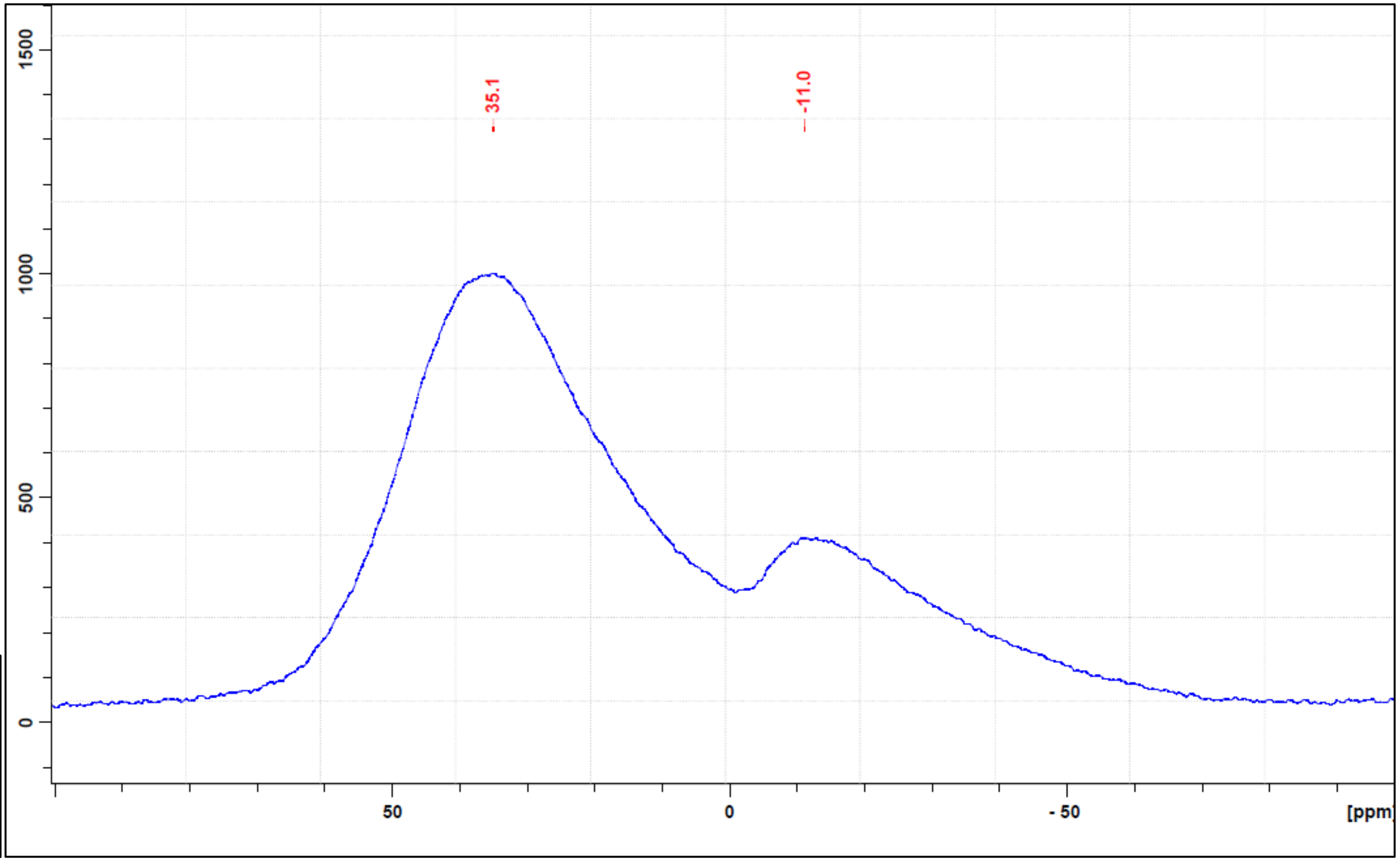


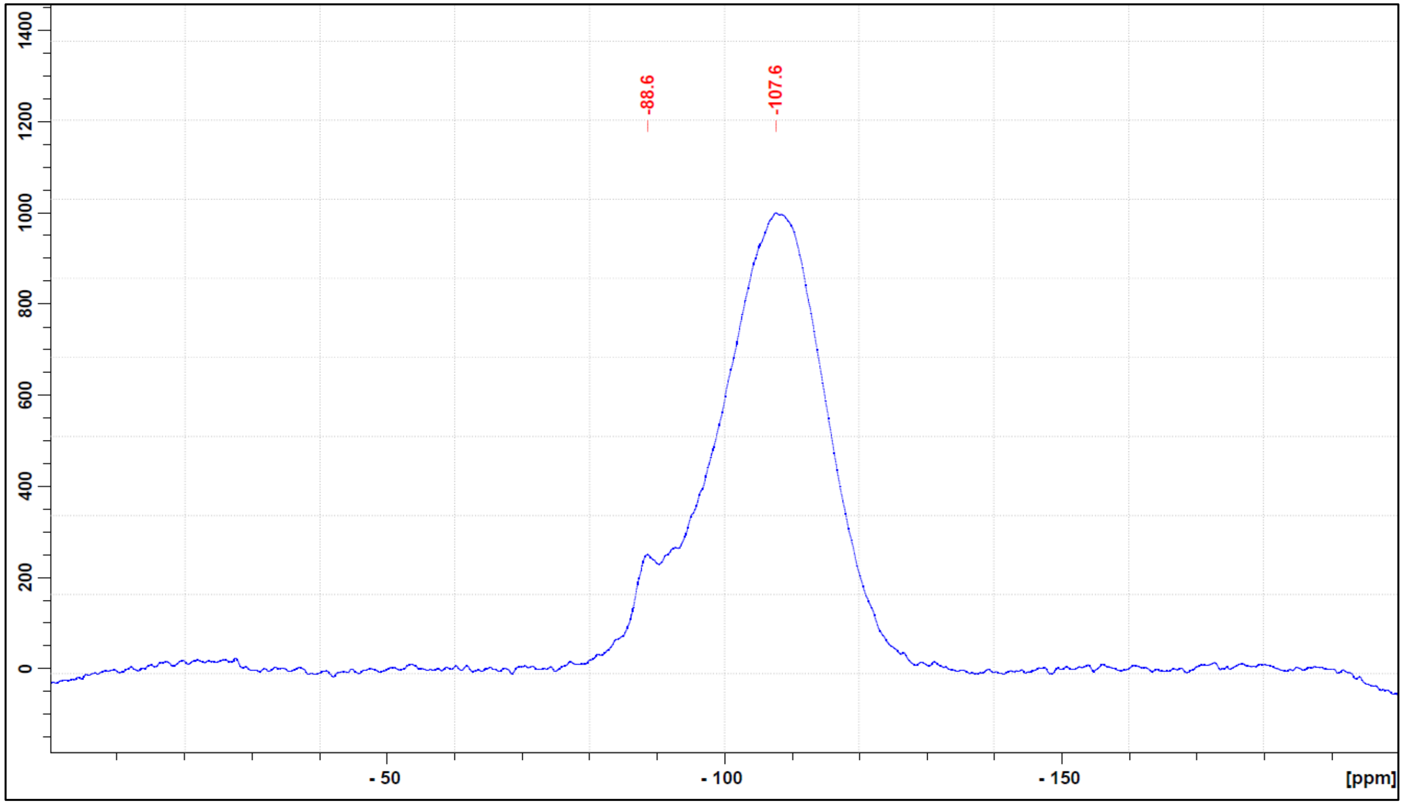
^{27}Al solid state NMR spectrum of the ground modern Chinese teacup A3



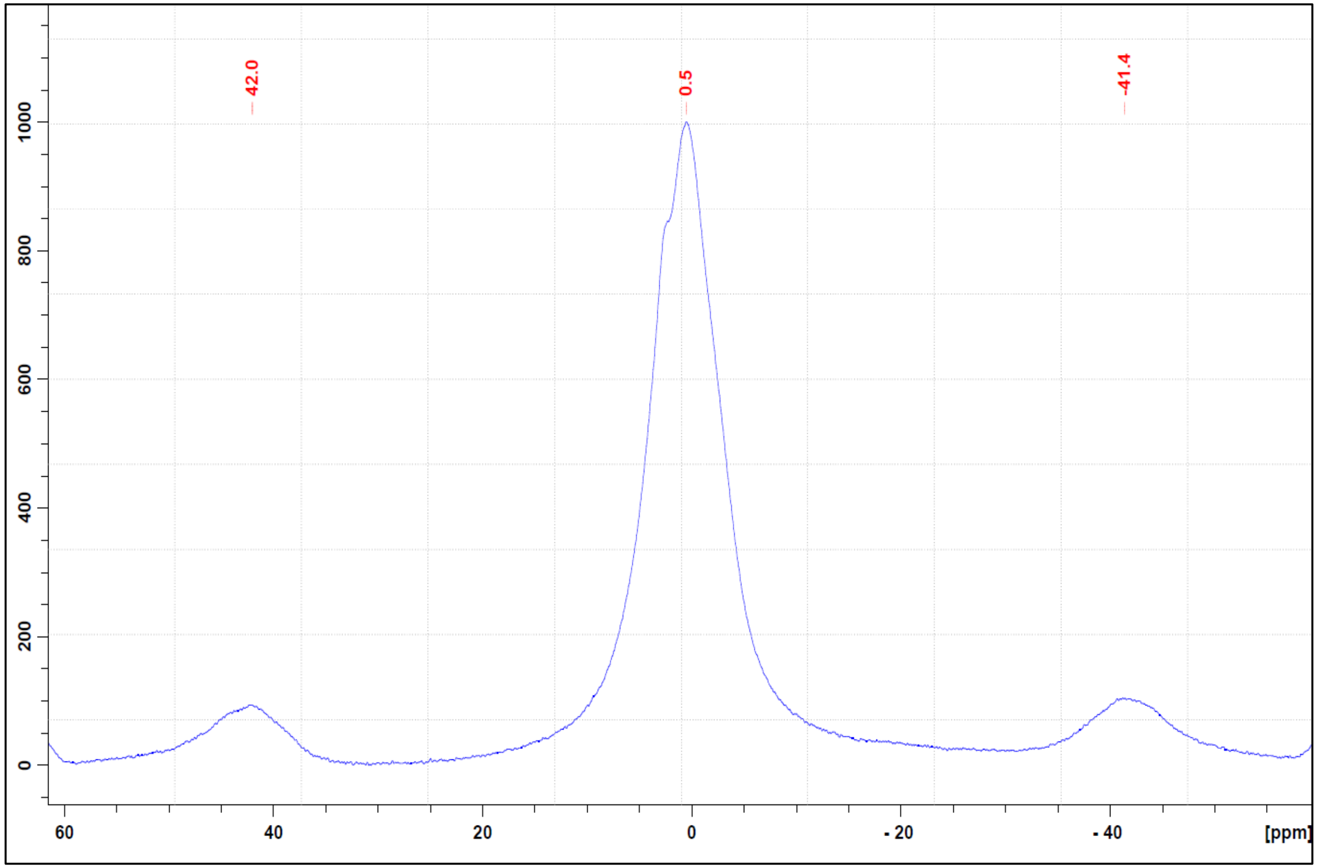
^{27}Al solid state NMR spectrum of the ground modern Chinese square plate A4



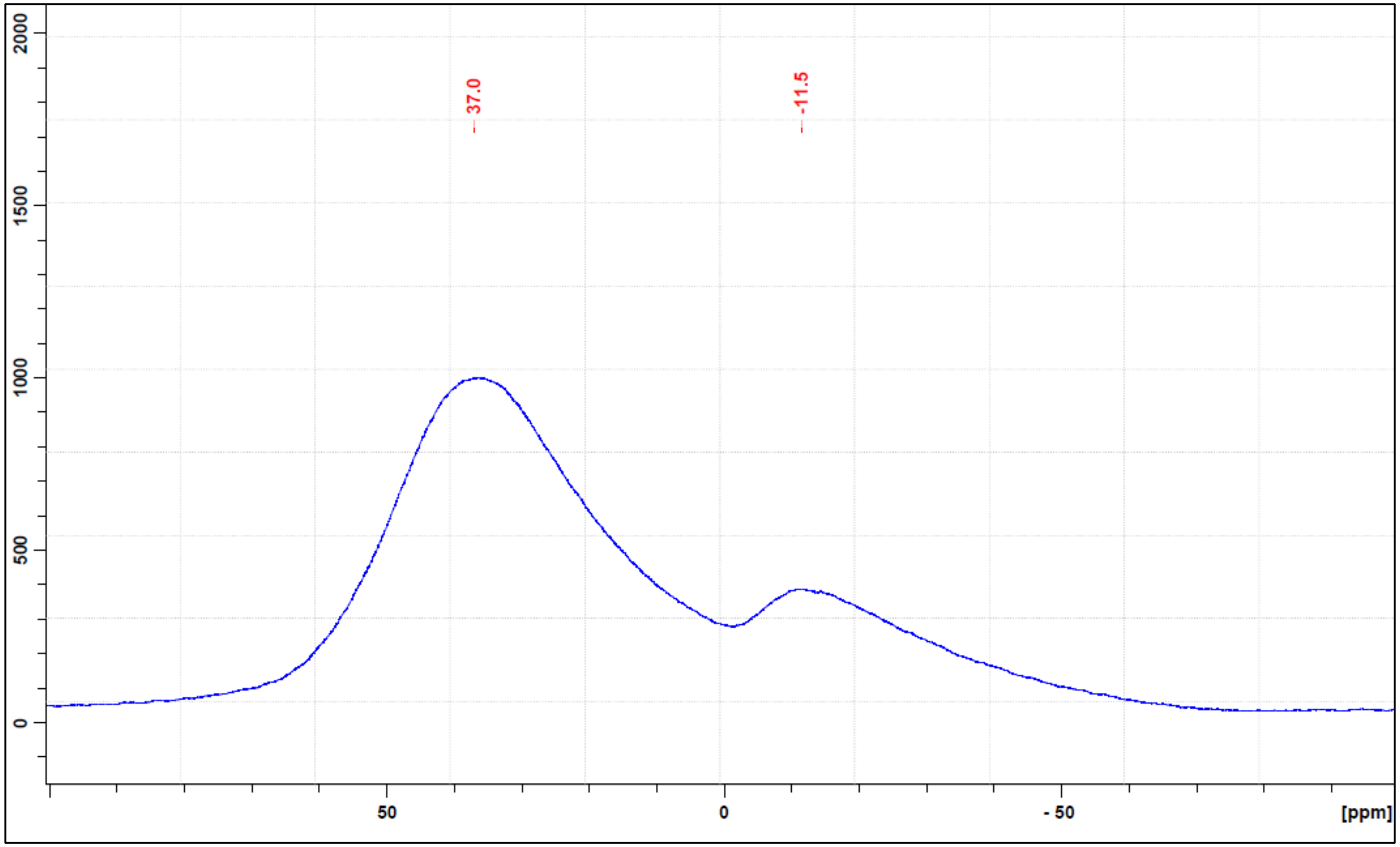
^{29}Si solid state NMR spectrum of the ground modern Chinese square plate A4



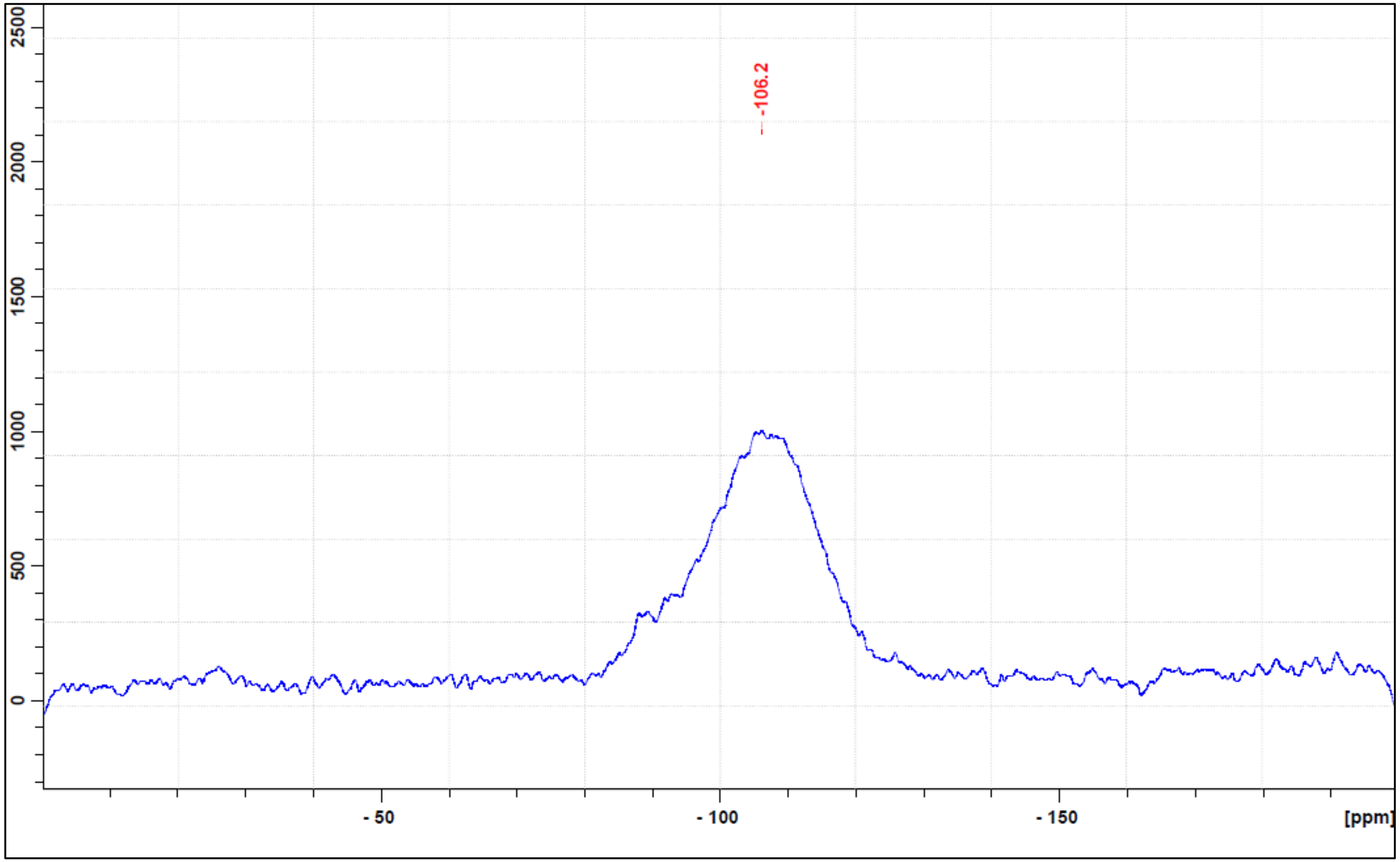
^{31}P solid state NMR spectrum of the ground Indian bone china teacup A7



^{27}Al solid state NMR spectrum of the ground modern Chinese teacup A10

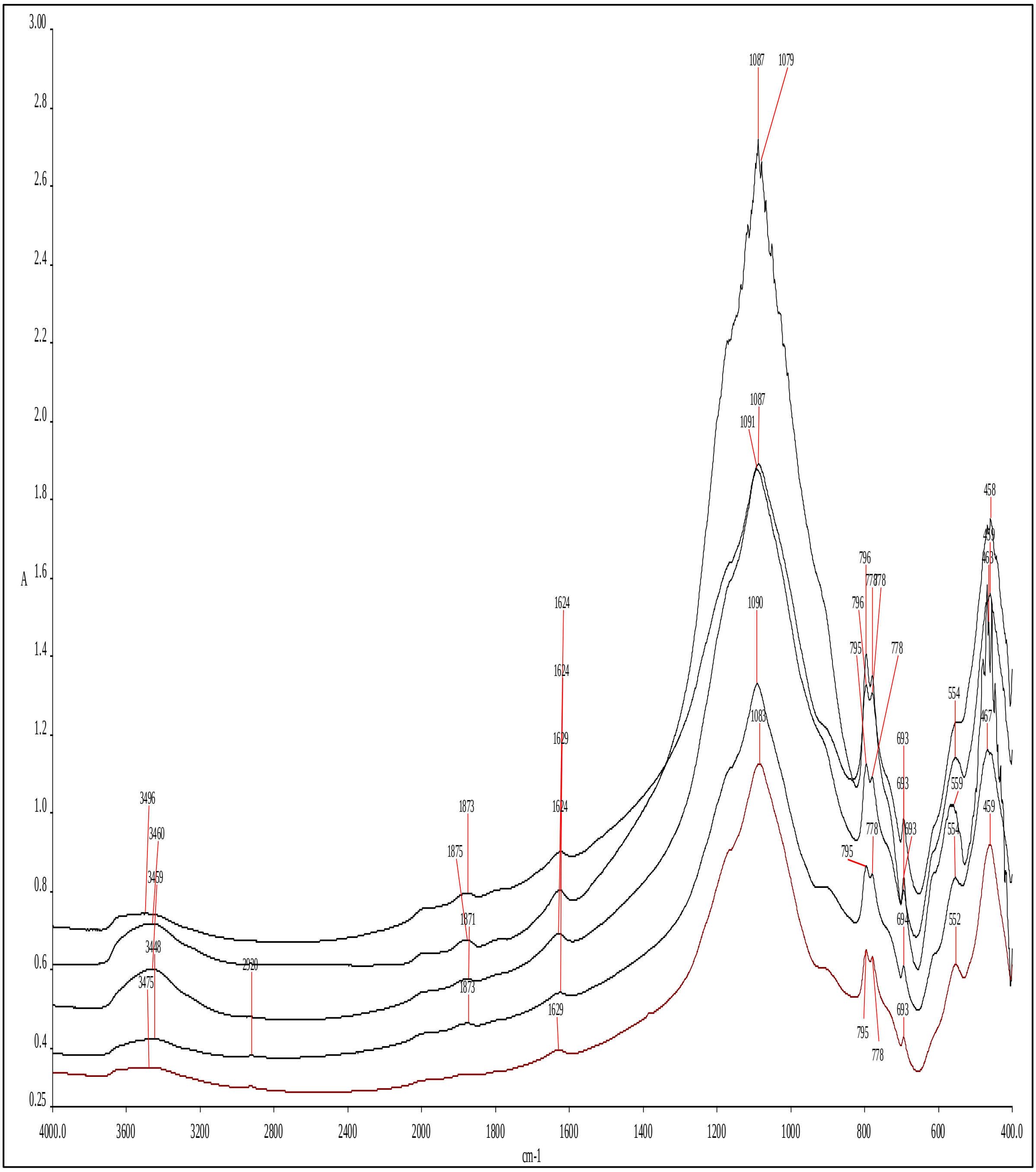


^{29}Si solid state NMR spectrum of the ground modern Chinese teacup A10



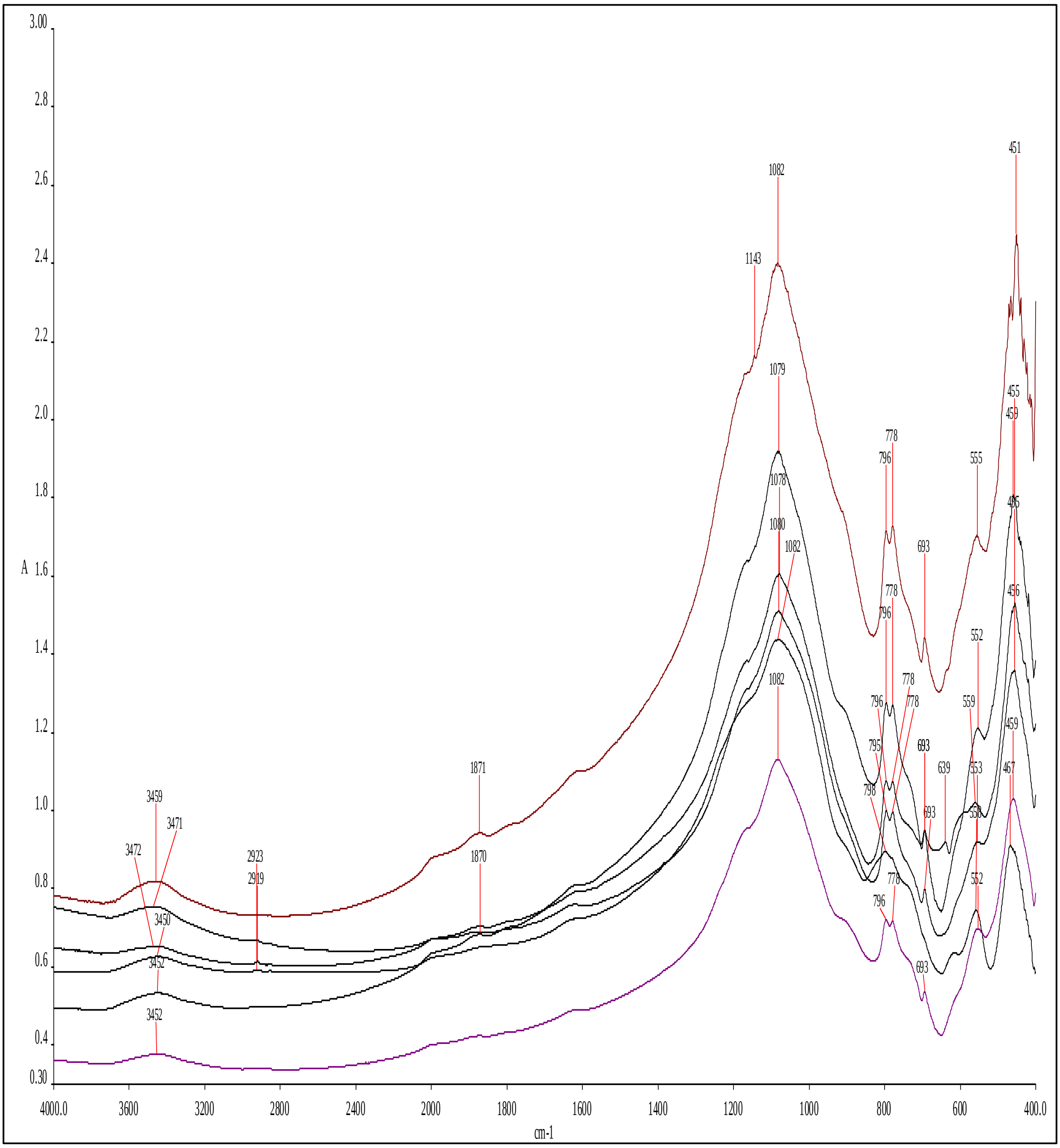
Appendix -2

FTIR spectra of Crown Lynn samples (C2, C3, C4, C5 and C7)*



*Samples codes from top to bottom are C7, C5, C4, C3 and C2.

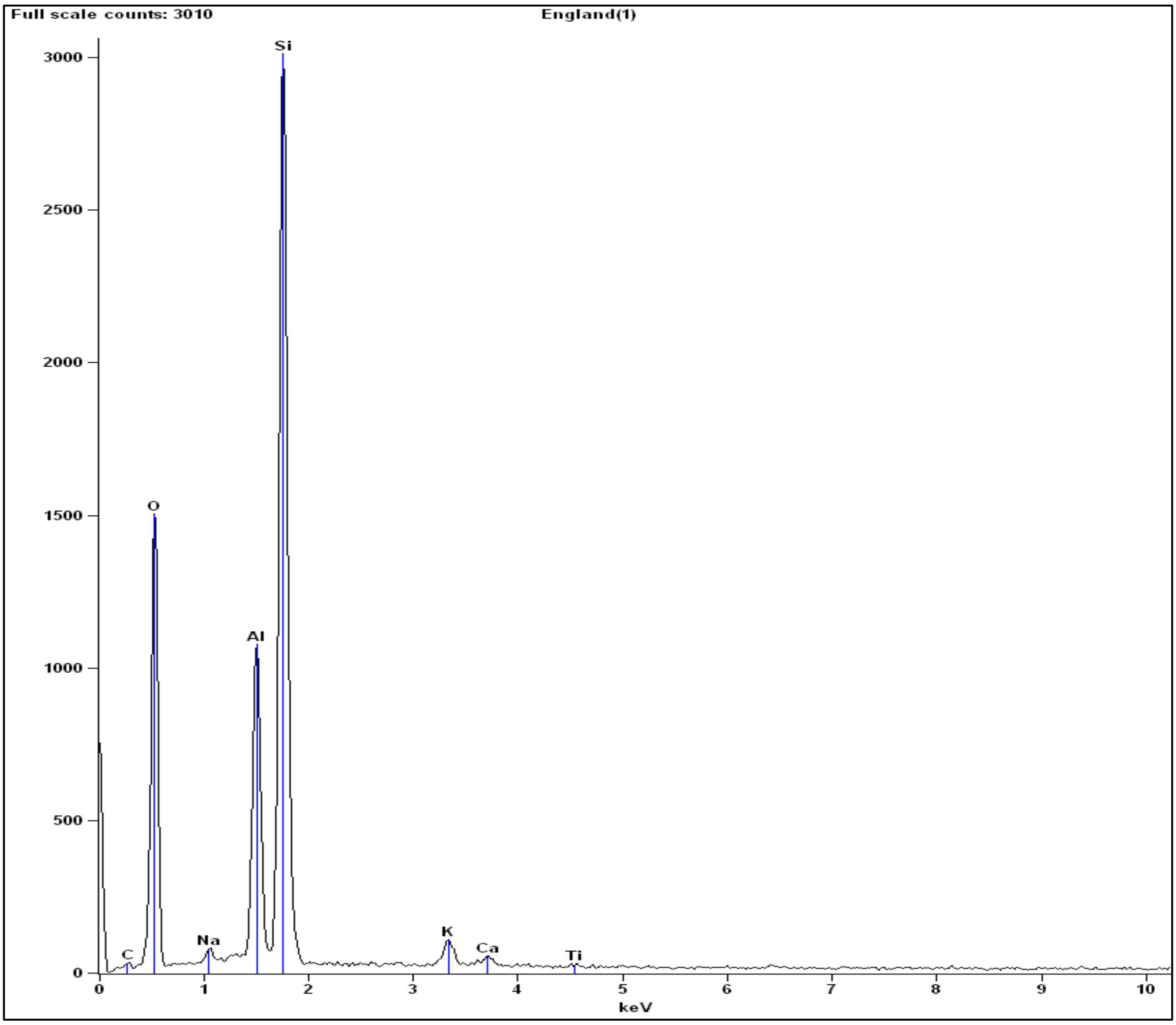
FTIR spectra of modern ceramic samples (A1, A2, A3, A4, A5, A10)*



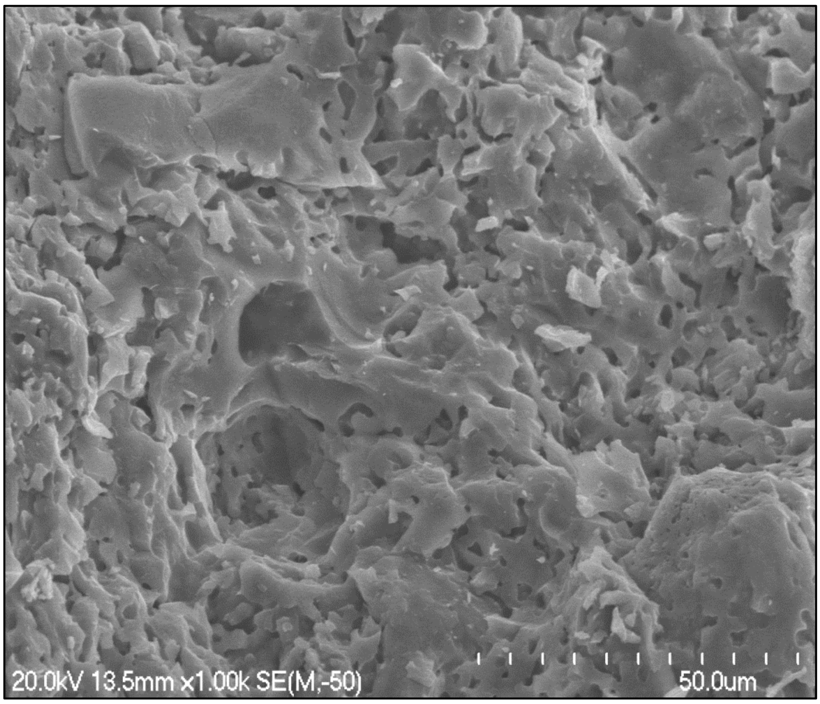
* Samples codes from top to bottom A5, A1, A2, A10, A3 and A9

Appendix-3

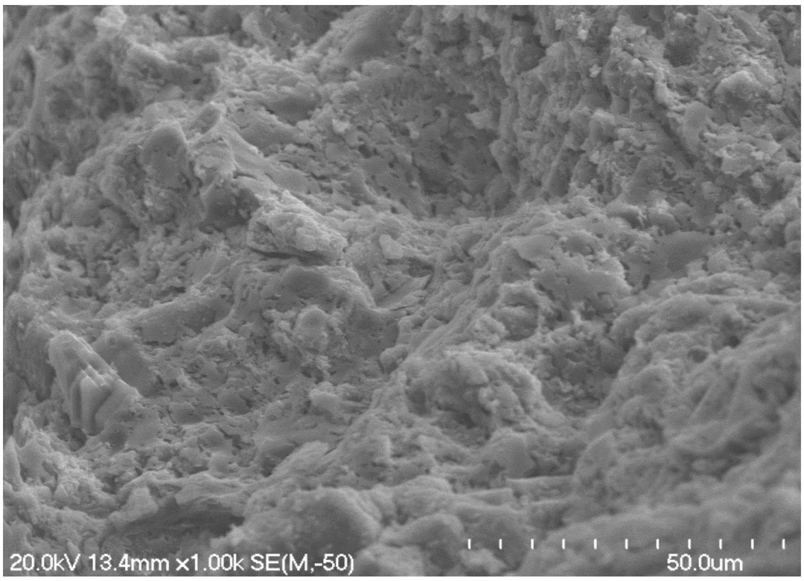
SEM/EDX spectra of Victorian era, Chapman sample B1



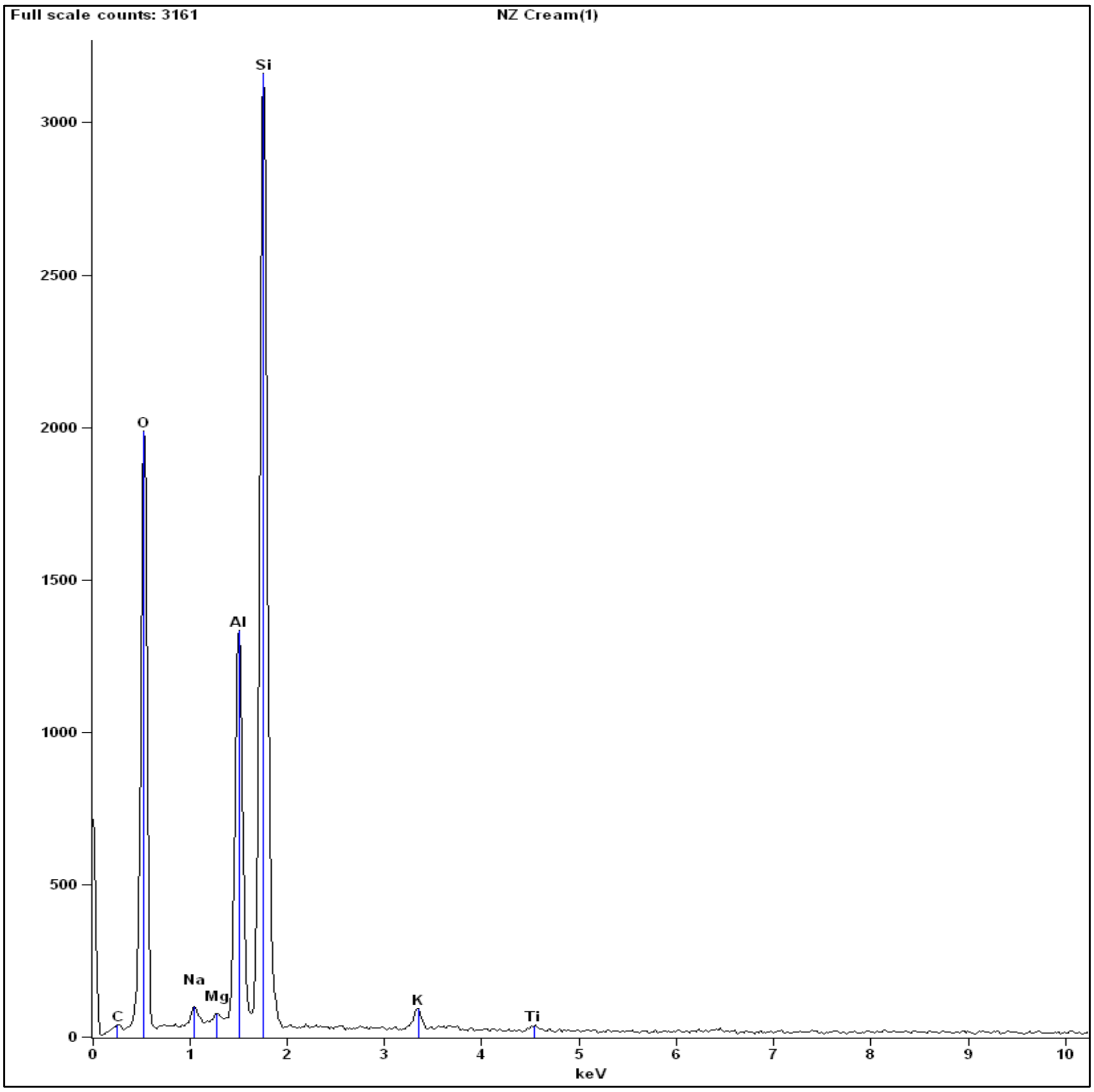
SEM image of Victorian era, Chapman sample B1



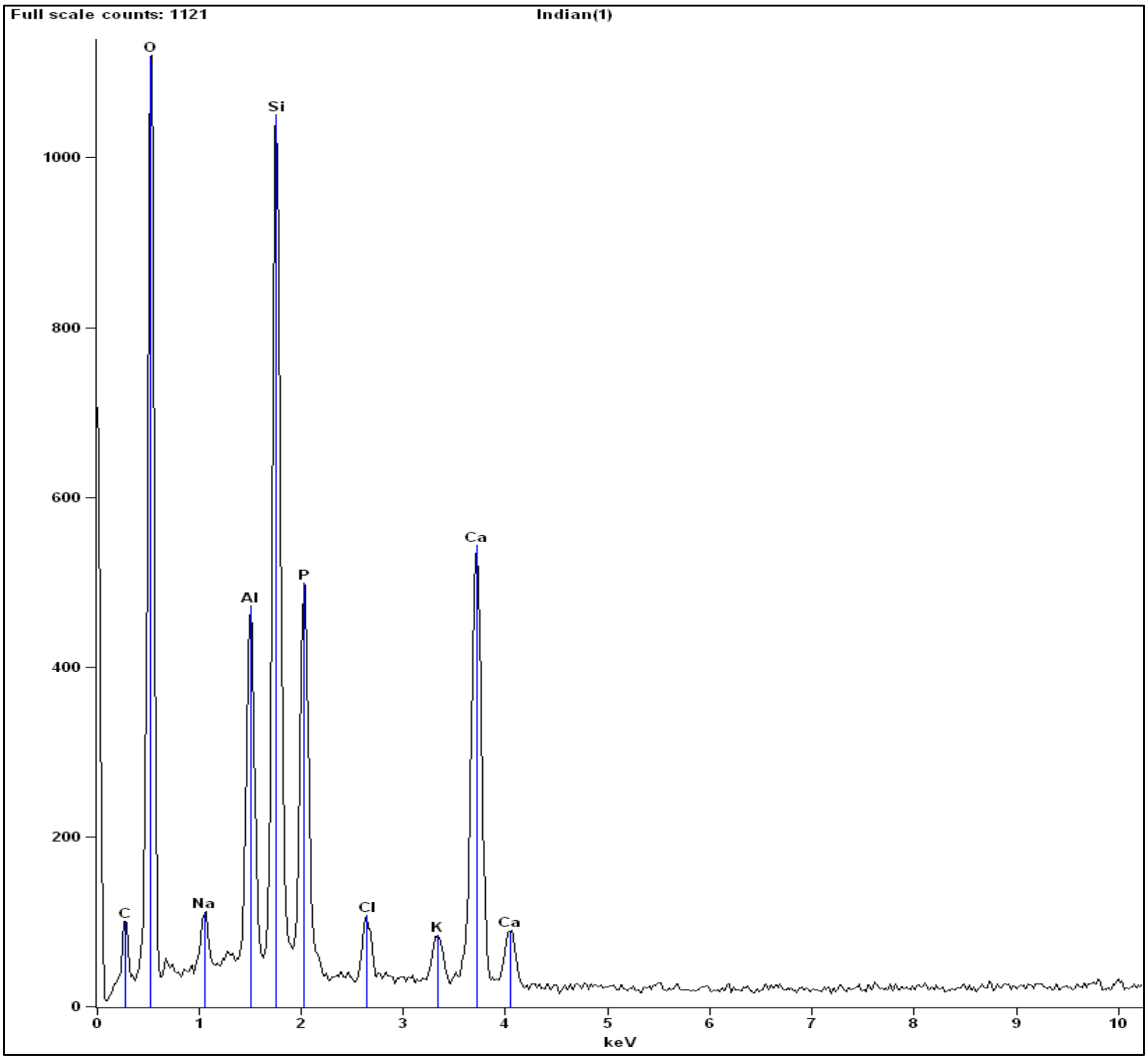
SEM image of Crown Lynn sample C4



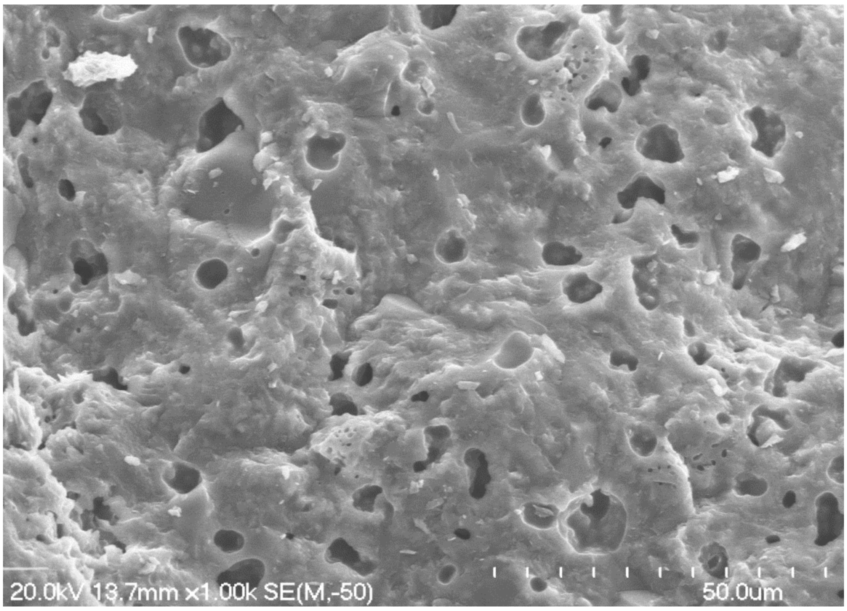
SEM/EDX spectra of Crown Lynn sample C4



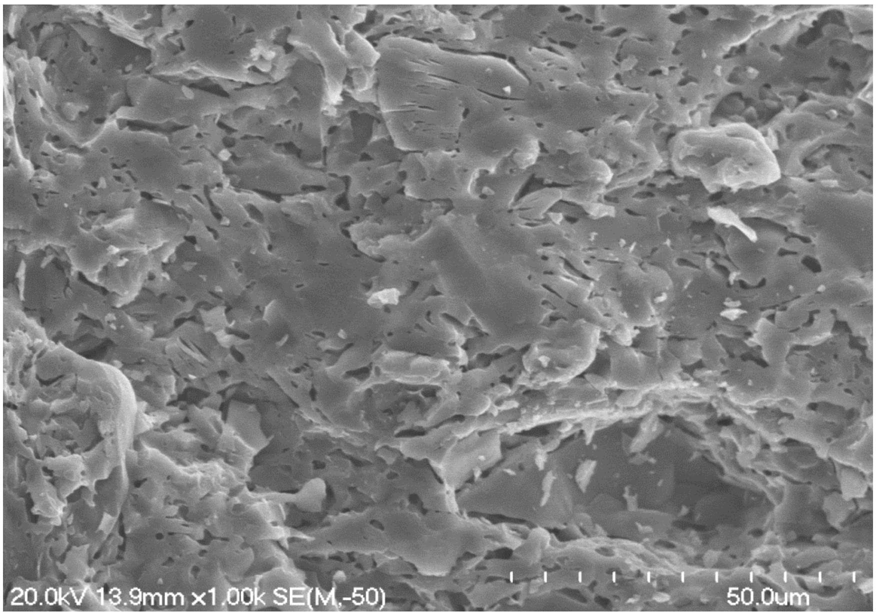
SEM/EDX spectra of Indian bone china A7



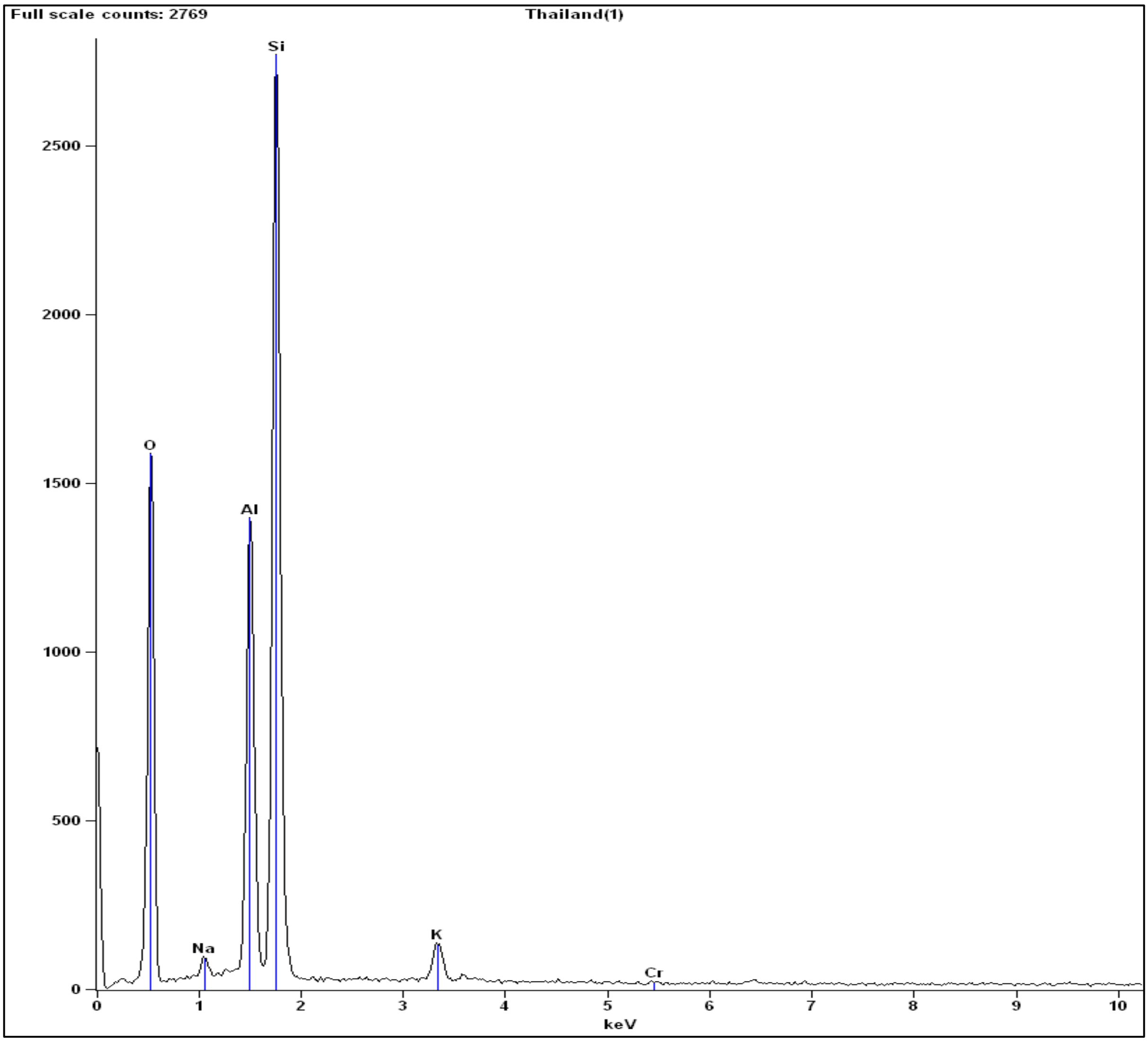
SEM image of Indian bone chinaA7



SEM image of Thailand samplesA11



EDX spectra of Thailand sample A11



Appendix-4

XRF results data

Element	Dimension	BX-N standard reference used for XRF analysis of bulk ceramic wares
Na2O	%	1.28
MgO	%	< 0.019
Al2O3	%	54.85
SiO2	%	10.02
P2O5	%	0.18
K2O	%	0.06
CaO	%	0.26
TiO2	%	2.84
MnO	%	0.05
Fe2O3	%	23.34
S	ppm	281
Cl	ppm	88.4
V	ppm	419
Cr	ppm	322
Co	ppm	111
Ni	ppm	197
Cu	ppm	11.2
Zn	ppm	81
Ga	ppm	60
Ge	ppm	< 0.5
As	ppm	117.4
Se	ppm	< 0.4
Br	ppm	1.3
Rb	ppm	4.8
Sr	ppm	109
Y	ppm	119
Zr	ppm	546
Nb	ppm	54
Mo	ppm	9.9
Ag	ppm	< 0.4
Cd	ppm	< 0.5
In	ppm	< 0.7

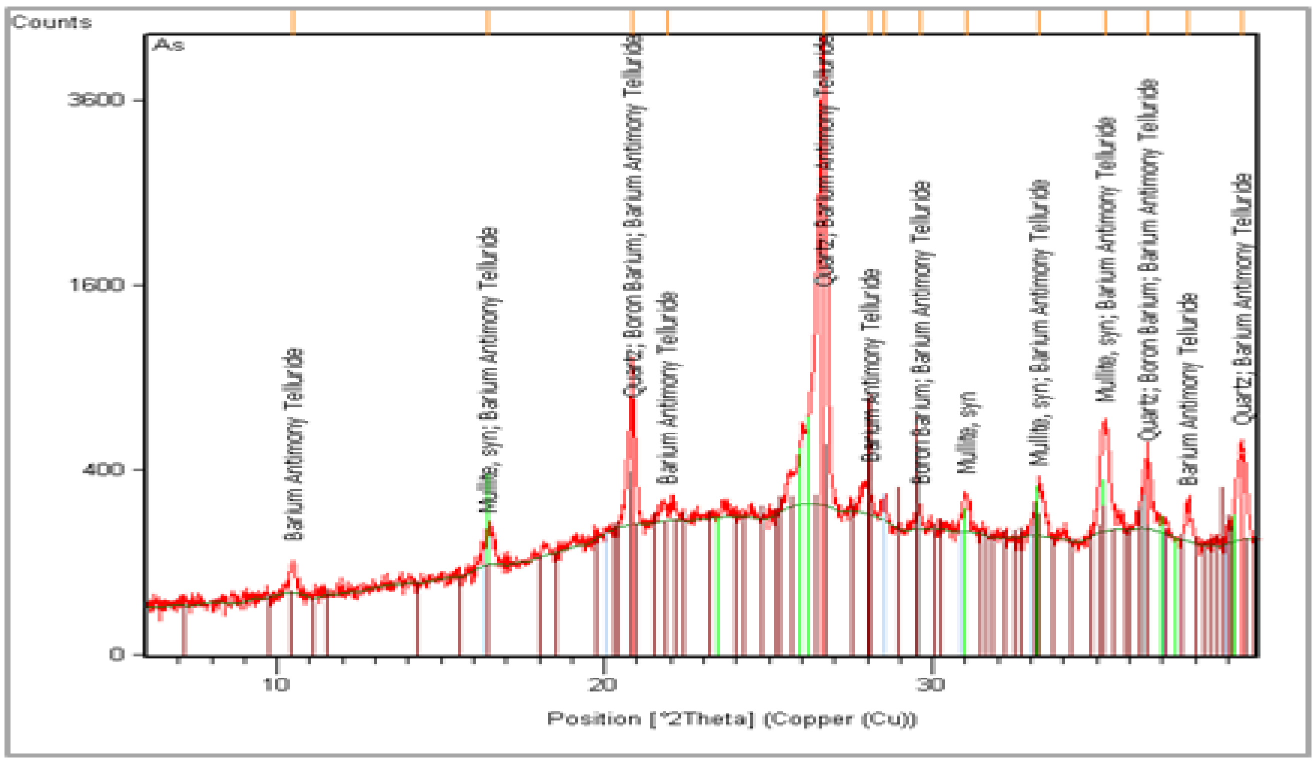
Sn	ppm	12.5
Sb	ppm	7.6
Te	ppm	0.7
I	ppm	< 1.5
Cs	ppm	< 2.6
Ba	ppm	16.4
La	ppm	358
Ce	ppm	530
Pr	ppm	27
Nd	ppm	138
Hf	ppm	13.9
Ta	ppm	< 4.9
W	ppm	5.6
Hg	ppm	< 0.8
Tl	ppm	< 1.3
Pb	ppm	134
Bi	ppm	< 1.2
Th	ppm	49
U	ppm	9.9

XRF results for bulk ceramic wares studied

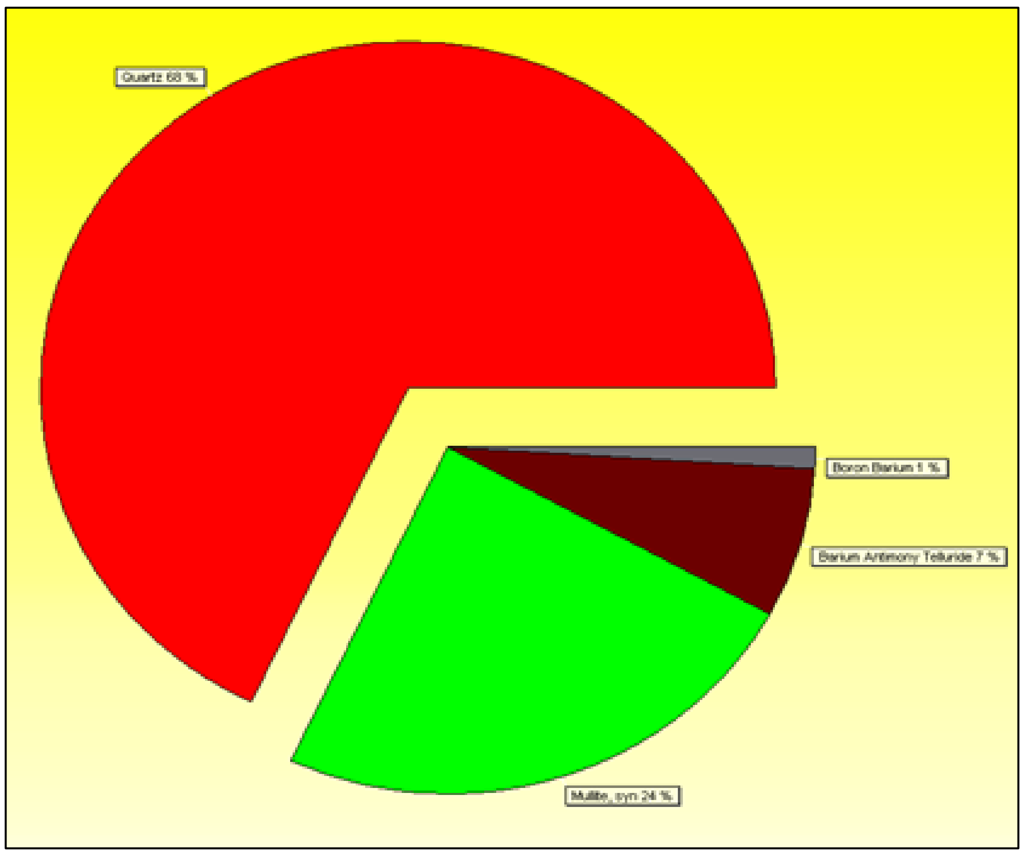
Element	Dimension	A1	A2	A3	A4	A5	A7	A9	A10	A11	B1	B2	B5	C1	C2	C3	C4	C5	C6	C7	C8	Blank 1 Al2O3	Blank 2 Al2O3
																						Directly sampled	Motor &pesto used
Na	%	3.075	0.735	1.16	1.06	0.685	1.18	1.115	1.06	1.35	1.4	0.655	1.116	1.33	1.51	1.21	1.43	0.93	1.31	1.03	1.27	0.36	0.43
Mg	%	0.15	0.13	0.42	0.32	1	0.38	0.4683	0.53	0.08	0.26	0.23	0.262	0.34	0.29	0.28	0.14	0.27	0.36	0.38	0.10	< 0.0067	< 0.0068
Al	%	10.345	13.27	10.48	10.84	12.275	7.43	11.97	11.52	9.42	7.98	7.515	8.655	10.53	12.54	12.07	9.89	12.64	12.58	14.28	12.96	49.71	50.41
Si	%	30.465	27.26	30.04	33	28.005	20.93	33.8	32.19	30.74	21.53	16.8	20.76	32.14	33.6	31.69	33.19	34.3	33.95	36	34.63	0.10	0.35
P	%	0.05	0.03	0.05	0.01	0.05	6.38	0.05031	0.03	0.04	5.54	5.705	5.815	0.08	0.05	0.06	0.02	0.03	0.09	0.04	0.08	< 0.0030	< 0.0030
S	ppm	84.5	93	169	85	142.5	57	162.8	1034	95.00	< 19	< 14	< 27	997	240	185	1047	240.7	259	443	227.5	132.8	153.1
Cl	ppm	113	116	53	< 1.2	114	77.7	< 1.3	187	119.00	< 3.6	63.45	< 4.3	82	30	33	77	< 2.9	< 3.8	< 3.6	< 2.7	< 10	< 10
K	%	1.08	2.77	1.8	1.92	1.25	1.51	1.949	2.97	1.75	1.63	1.5	2.016	1.1	1.21	1.26	1.15	1.06	0.96	1.24	1.38	0.00	0.01
Ca	%	0.8	0.615	0.54	0.15	1.1	15.08	0.409	0.16	0.63	14.05	14.5	14.45	0.55	1.74	1.69	0.32	0.35	0.34	0.24	0.38	0.04	0.05
Ti	%	0.14	0.415	0.05	0.03	0.345	0.06	0.06535	0.04	0.05	0.01	0.01	0.01115	0.41	0.3	0.31	0.34	0.42	0.47	0.58	0.50	0.00	0.00
V	ppm	<4.0	117	4	13.7	112	< 5.3	< 3.6	26	<4.1	< 2.2	< 2.4	< 2.1	58	49	61	63	71	50	85	72	3.4	4.6
Cr	ppm	880	99.5	106	9.3	110.5	36	473.2	59	23.50	87	26	10.2	31	116	41	54	44.5	28	43.3	9.8	< 0.3	14.7
Mn	%	0.04	0	0.03	0.03	0.01	0.00	0.02942	0.06	0.03	0	0	0.00467	0	0.01	0	0	0	0.03	0	0.30	0.00	0.00
Fe	%	0.97	0.47	0.41	0.28	0.44	0.20	0.4131	0.42	<4.2	0.23	0.20	0.20	0.37	0.45	0.45	0.46	0.46	0.59	0.47	0.60	0.01	0.01
Co	ppm	320	209	23	16.5	51	15.8	261.6	104	12.70	23	36	92	500	58	15	53	58	86	74	61	< 0.5	< 0.6
Ni	ppm	40	22	29	17.1	25.5	< 1.9	16.4	24	2.55	5	5.55	31.6	24	38	11.4	11.5	9.9	11.2	9.6	12.3	3.9	3.4
Cu	ppm	18.7	7.4	4.2	11.1	12.4	13.4	7.8	29	4.50	33	26.5	33.1	4.4	6.6	4.9	4.1	7.2	6.1	10.6	24	< 0.3	< 0.3
Zn	ppm	822.5	282.5	1210	42	550	100	568.1	269	3243.50	314	129.5	69.7	80	1360	43	47	64	38	47	35	6.8	6.2
Ga	ppm	26.5	28.5	33	34	25.5	12.3	36	15.2	31.50	17.3	23.5	< 6.2	11.1	19.3	9.9	11.1	< 2.9	< 4.0	< 4.1	< 2.8	59	58
Ge	ppm	2.35	3.05	2.2	0.9	2.1	< 0.7	2.9	3.1	4.30	< 0.9	<0.8	< 1.5	< 0.5	< 0.6	1.5	< 0.5	< 0.7	< 1.0	< 1.0	< 0.7	< 0.2	< 0.2
As	ppm	13.85	3.75	< 0.9	< 0.6	1.8	126	1.2	< 5.3	29.50	19	11.9	< 22	< 5.2	< 6.6	< 6.2	< 5.2	< 9.6	< 14	< 15	< 9.4	< 0.2	< 0.2
Se	ppm	1.3	2.15	55	0.3	5.7	< 0.5	0.7	< 0.6	0.90	< 1.1	<0.9	< 2.1	< 0.5	< 0.7	< 0.6	< 0.5	< 0.9	< 1.4	< 1.5	< 0.9	0.6	0.5
Br	ppm	0.8	1	0.4	0.2	1.9	< 0.5	0.5	1.4	<4.5	< 0.6	2.3	9.1	0.9	0.9	0.9	0.6	1.7	2.9	3	1.1	0.2	< 0.1
Rb	ppm	127.5	111	243	346	83.5	78	259.6	695	421.00	268	255.5	402.4	62	64	64	67	61	80	72	117	0.6	1.2
Sr	ppm	38	291.5	291	28	124	386	381	31	115.50	266	279.5	163.2	41	78	89	49	305	71	382	64	1.7	1.5
Y	ppm	30	30.5	66	152	23.5	9.4	99.2	16.7	43.50	< 0.5	<0.5	< 0.5	26	36	40	32	5.1	< 0.5	< 0.5	6.1	1	0.9
Zr	ppm	453.5	413	3397	99	774.5	127	1287	114	738.00	43	38	55.7	795	3586	1309	215	286	235	330	297	18.6	18.8
Nb	ppm	19.45	23	35	36	19.1	10.2	33.9	23	42.00	27	22.5	29.8	28	23	21	19	22	29	31	24	0.9	1
Mo	ppm	2.45	4.05	7.3	2.7	4.25	1.5	5.7	0.8	2.90	0.7	0.4	< 1.0	4.3	8.7	4.5	2.3	2.8	2.1	3.1	4.7	0.8	0.6
Ag		<0.4	<0.4	1.1	< 0.4	<0.4	< 0.4	< 0.4	10.6	< 0.4	0.8	0.8	< 0.5	2.1	1	0.5	< 0.4		1	1.3	< 0.4		
Cd	ppm	<0.5	0.55	191	< 0.5	17.4	2.9	< 0.5	< 0.5	1.20	< 0.5	<0.5	< 0.7	< 0.5	88	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1.1	< 0.5	< 0.5
In	ppm	<0.7	<0.7	< 0.7	< 0.7	<0.7	< 0.7	< 0.7	< 0.7	<0.7	< 0.7	<0.7	137.8	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7	< 0.7
Sn	ppm	29.5	7.4	1413	15.3	7.9	18	20.7	262	44.50	10.6	39	13.3	2082	448	290	9.7	14.2	12	9.6	8.8	< 0.7	0.7
Sb	ppm	2.55	<0.9	0.8	< 0.9	<0.9	8.4	< 0.9	294	<4.6	4.2	0.4	< 1.2	2.5	6.9	1.4	1.5	25	3	0.4	1.2	0.9	0.7
Te	ppm	4.8	1.55	2.8	< 1.2	1.6	< 1.2	3.8	< 1.2	6.50	< 1.2	<1.2	< 1.5	< 1.2	1	< 1.2	2.3	< 1.2	0.7	< 1.2	< 1.2	2	1.3
Cs	ppm	40.5	19.4	16.5	13	20.25	3.8	35.8	45	87.00	9.6	9.75	10.2	6.1	11.1	7	24	5.7	3.4	3.4	8.1	10.2	8.7
Ba	ppm	3345	1906	2534	120	1122	1393	2784	98	4203	218	376	121.1	367	777	121	590	242	139	311	231	10.7	14.1
La	ppm	61	61	47	61	48	< 4.9	94.9	18.4	44.50	< 4.9	<4.9	< 4.9	11.2	19.3	14.5	49	10.9	10.7	10.2	23	18.6	23
Ce	ppm	110.5	114	71	77	93.5	8.2	127.6	38	69.00	11.8	<5.8	< 5.8	27	208	34	75	28.9	33	29	52	24	22
Nd	ppm	29	42.5	42	68	43	< 10	64.6	19.4	44.00	< 10	<10	< 10	10.5	13.5	< 10	54	< 10	10.9	< 10	< 10	29	47
Hf	ppm	16.3	14.35	77	12	20.05	< 3.7	33.1	7	2.80	11.8	9.3	8.9	22	78	31	9.8	14.5	13.2	10	13.1	3.3	3.3
Ta	ppm	10.15	6.95	14.9	16.4	7.7	< 5.9	12.9	9	110.00	< 4.0	<3.5	< 5.1	< 2.0	< 2.7	< 2.1	< 1.9	< 2.5	< 2.9	< 3.1	< 3.0	3.5	2.6
W	ppm	15.25	6.65	4.1	13.6	3.7	2.9	4.3	22	7.80	20	22.5	< 3.5	12.9	< 4.7	15.1	10.3	11.4	13.1	12	9.8	3.5	2.7
Hg	ppm	1.1	0.55	1.7	< 0.4	0.7	< 1.0	0.9	< 0.9	23.00	< 1.5	<1.2	< 2.6	< 0.8	< 0.9	< 0.9	< 0.8	< 1.3	< 1.8	< 1.8	< 1.2	1.3	1.1
Tl	ppm	3	2.45	2.1	1.7	1.65	< 1.6	2	< 2.1	14.90	< 4.2	<3.4	16.6	< 2.0	< 2.6	< 2.5	< 2.0	< 3.6	< 5.3	< 5.5	< 3.5	1.7	1.4
Pb	ppm	49.5	29	132	71	56	288	154	3907	111	12010	8179	27420	3974	5478	5229	4087	9992	17180	18010	9756	2.1	3.5
Bi	ppm	6	2.7	6.1	< 0.4	1.75	< 1.6	5.2	< 1.9	7.8	< 4.6	<3.5	< 8.8	< 2.0	< 2.7	< 2.4	< 2.1	< 3.8	< 5.6	< 5.1	< 3.3	1.1	0.8
Th	ppm	28.5	32.5	50	35	29	13.5	48.4	2.6	23	< 1.5	<1.5	< 1.5	17.7	48	16.3	9.1	26.3	< 1.5	< 1.5	6.1	2.3	2.4
U	ppm	15.6	12.1	7.5	13.5	10.4	2.1	< 1.5	10.5	14.5	13.7	7.6	5.4	9.4	9	8	9.7	8.1	8.3	5.6	4.8	4.4	4.1

XRD data of modern Chinese ceramics wares A5 with the table showing the compound name, chemical formula and their semi quantitative (%), spectra showing the main minerals.

Compound Name	Chemical Formula	Score	SemiQuant [%]
Quartz	Si O2	71	68
Mullite, syn	Al4.75 Si1.25 O9.63	43	24
Boron Barium	B6 Ba	44	1
Barium Antimony Telluride	Ba Sb Te3	22	7

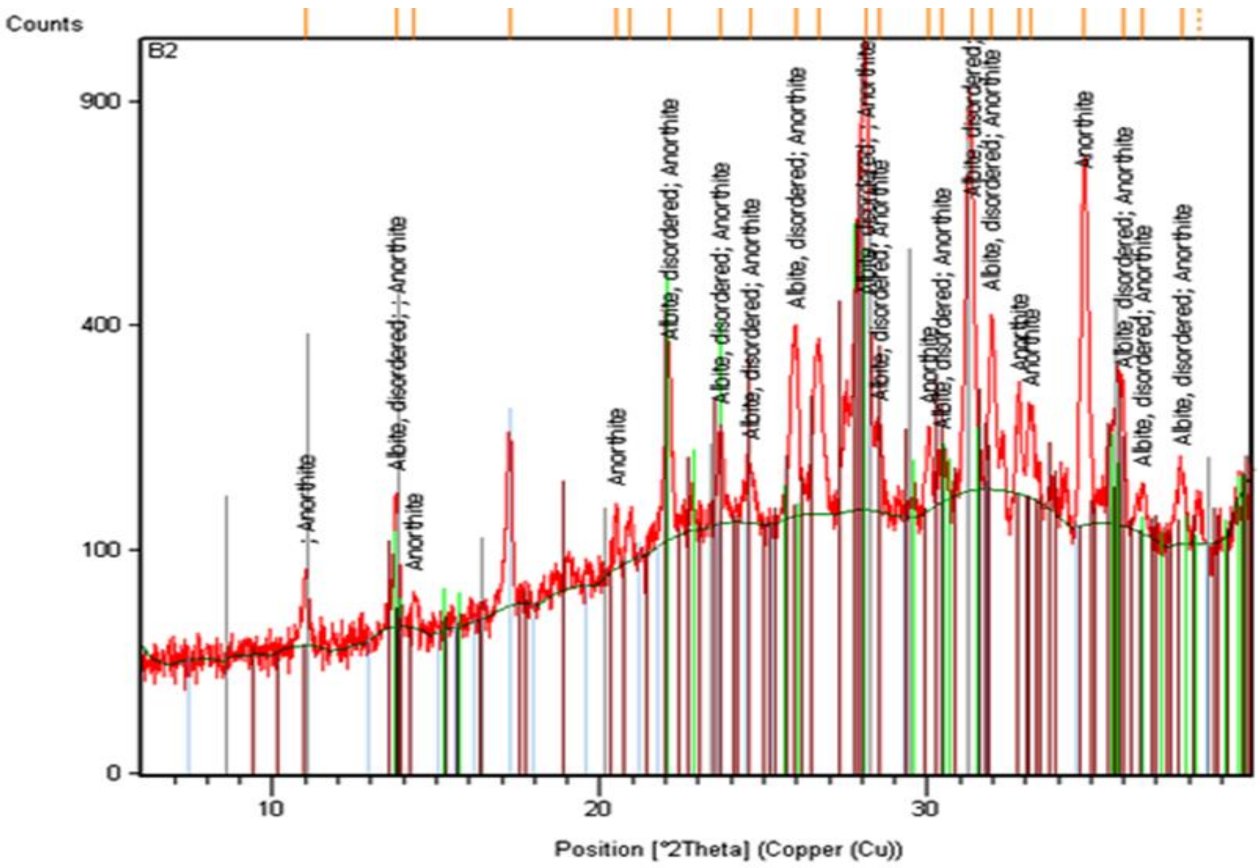


Amount of various compounds identified with XRD



XRD data of Victorian eras bone china B2 with the table showing the compound name, chemical formula and their semi quantitative (%) and spectra showing the main minerals.

Compound Name	Chemical Formula	Score	SemiQuant [%]
Albite, disordered	Na Al Si3 O8	37	-
Lead Oxide Hydroxide Hydrate	Pb13 O8 (O H)1...	27	-
Anorthite	Ca0.94 Na0.06 Al...	25	-



Appendix-5

ICP-MS results for orange juice leaching test

Amount of barium detected in blank orange juice, water and sample C1 exposed to orange juice leach test in ppm (ug/L) with 95% confidence error given

.

Blank orange juice in Polypropylene Beakers	Blank water in Polypropylene Beakers	C1 leachate gone through filter paper	C1 without Filter paper
431.99 ±242	231.96 ±8	432.25 ±89	24.07±8

95% Confidence error =(12.7*SD/√ the number of duplicates)

Calculation done in Excel sheet for the above values given in the above table

Sample code	Ba-1	Ba-2	Mean	95% student's t-static value	Standard Deviation	95% Confidence error =(12.7*SD/√2)
Blank	413	451	432	12.7	27	242
Water	232.59	231.32	232	12.7	1	8
C1-Filterp paper	439.25	425.24	432	12.7	10	89
C1- no Filter paper	23.42	24.72	24	12.7	1	8

Orange juice pulp calculation done for sample C1 with improved method as discussed in results section

Amount of barium leached from sample C1 after exposure to orange juice for a duration of 10 minutes:

Sample weighed from dried orange pulp/actual orange pulp dry weight	0.067/0.10 = 0.67 g
0.67g of dried pulp digested in 3ml HNO_3: H_2O_2 (2:1)	
Digested solution diluted 200 times for ICP-MS analysis	
Test 1 -Pb	0.19 µg/L

Test 2 -Pb	0.14 µg/L
Mean of Test 1 and Test 2 -Pb	0.165 µg/L
Dilution 200 times so the Mean value *200 times -Pb	33 µg/L
Amount of lead in 3mL of digested sample	33 µg/L in 3mL=33*3/1000=0.099 µg
	0.099 µg/0.067g =1.48 µg/g
Amount of lead leached out from the sample C1 into the orange pulp (solid matter)	=1.48 ppm =1480 ppb =1480 ppb (µg/kg) or (µg/L)

4% acetic acid leach results for all ceramicwares

	B 10	Na 23	Mg 24	Al 27	K 39	Ca 43	V 51	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 65	Zn 66	As 75	Se 82	Sr 88	Rb 85	Zr 90	Ag 109	Cd 111	Sn 118	Ba 137	Tl 205	Pb 207	U 238	Cr 52
BLANK	-1.21	19.03	3.50	0.05	5.17	24.99	-1.79	2.30	-50.58	-0.01	0.00	-17.38	0.06	-0.16	-0.05	-0.40	0.05	0.04	-0.28	-0.02	0.55	-0.03	0.02	0.00	0.41	0.00	
BLANK	-1.45	18.74	3.50	-0.03	5.75	19.70	-1.83	2.11	-50.31	-0.01	0.00	-17.43	0.09	-0.09	-0.09	-0.42	0.05	0.04	-0.26	-0.03	0.50	0.03	0.30	-0.01	0.07	0.00	
Average	-1.33	18.88	3.50	0.01	5.46	22.34	-1.81	2.21	-50.44	-0.01	0.00	-17.41	0.08	-0.13	-0.07	-0.41	0.05	0.04	-0.27	-0.03	0.52	0.00	0.16	0.00	0.24	0.00	
A1	-0.40	381.83	19.86	133.35	42.97	209.87	-0.49	2.28	-17.65	3.71	2.03	-16.96	0.52	20.84	0.80	-0.30	0.29	0.36	-0.90	-0.01	0.47	-0.24	6.84	0.00	0.48	0.07	
A1	-0.76	400.34	21.09	142.91	44.15	246.02	-0.44	2.61	-11.01	4.02	2.18	-17.01	3.80	22.42	0.86	-0.33	0.30	0.38	-0.90	-0.01	0.51	-0.28	7.44	0.00	0.72	0.08	
A1	0.04	372.18	19.26	129.20	41.80	212.69	-0.54	2.12	-16.34	3.49	1.98	-17.07	0.55	20.05	0.83	-0.29	0.27	0.35	-0.93	-0.02	0.47	-0.25	6.63	0.00	0.48	0.08	
Average	-0.37	384.78	20.07	135.15	42.97	222.86	-0.49	2.33	-15.00	3.74	2.06	-17.01	1.62	21.10	0.83	-0.31	0.29	0.36	-0.91	-0.01	0.48	-0.26	6.97	0.00	0.56	0.08	
SA1-B 1st	-	365.90	16.56	135.14	37.52	200.52		0.13		3.74	2.06		1.55	21.10	0.83		0.24	0.32	-0.64	0.00	-0.04	-0.26	6.81	0.00	0.32	0.08	
BLANK	2.68	58.24	17.29	193.18	41.06	537.49	-0.12	-0.11	11.35	0.01	0.01	8.53	0.97	133.00	0.25	0.05	0.65	0.06	-0.31	-0.68	0.33	0.02	2.44	-0.23	15.23	-0.01	
BLANK	2.79	56.82	6.08	168.54	49.78	137.99	0.08	-0.04	-0.55	0.44	-0.25	13.90	1.50	132.31	0.12	-0.02	0.32	0.06	0.08	-0.76	0.21	0.92	2.74	-0.26	6.19	-0.03	
Average	2.73	57.53	11.69	180.86	45.42	337.74	-0.02	-0.08	5.40	0.22	-0.12	11.21	1.23	132.65	0.19	0.01	0.48	0.06	-0.12	-0.72	0.27	0.47	2.59	-0.24	10.71	-0.02	
A1	6.61	1213.64	61.67	1567.88	504.78	2121.63	3.06	4.05	420.38	12.75	15.09	3.38	13.10	64.11	1.35	0.16	4.75	2.41	0.76	0.10	0.31	2.38	279.65	-0.24	9.05	1.52	
A1	6.77	1191.38	61.11	1590.48	390.96	2146.65	3.15	4.25	446.51	13.66	15.25	6.84	3.17	55.97	2.05	0.15	4.65	2.24	0.72	0.25	0.85	2.44	277.95	-0.24	10.49	1.50	
Average	6.69	1202.51	61.39	1579.18	447.87	2134.14	3.10	4.15	433.44	13.20	15.17	5.11	8.13	60.04	1.70	0.15	4.70	2.32	0.74	0.17	0.58	2.41	278.80	-0.24	9.77	1.51	
SA1-B digeste	3.96	1144.98	49.70	1398.32	402.45	1796.40	3.10	4.15	428.04	12.98	15.17	-6.10	16.17	-72.61	1.51	0.14	4.22	2.26	0.86	0.89	0.31	1.94	276.22	0.00	-0.94	1.51	
BLANK	0.17	5.67	0.88	0.22	-7.90	-11.95	11.56	4.23	-56.56	-0.07	-0.04	-0.02	0.32	-1.58	0.00	-0.26	-0.05		-0.13	-0.10	0.40	-0.06	0.02	-0.04	-0.37	0.00	
BLANK	0.13	7.01	1.07	0.37	-4.76	-13.15	12.20	4.60	-56.62	-0.07	-0.04	0.01	0.29	-1.41	-0.01	-0.19	-0.04		-0.18	-0.11	0.41	-0.06	0.06	-0.04	-0.40	0.00	
Average	0.15	6.34	0.98	0.30	-6.33	-12.55	11.88	4.41	-56.59	-0.07	-0.04	-0.01	0.30	-1.49	0.00	-0.22	-0.04		-0.15	-0.10	0.41	-0.06	0.04	-0.04	-0.39	0.00	
A1	28.72	43.93	19.18	87.69	10.45	245.04	12.14	6.93	57.36	6.12	12.48	0.03	4.03	3.62	0.70	-0.32	0.35		0.42	-0.10	0.16	-0.04	6.84	-0.04	0.62	0.03	
A1	28.87	45.11	18.65	85.46	12.37	233.23	12.05	6.89	59.40	5.92	12.09	0.01	4.01	3.69	0.69	-0.33	0.42		0.36	-0.07	0.15	-0.07	6.66	-0.04	0.64	0.03	
Average	28.80	44.52	18.91	86.58	11.41	239.14	12.09	6.91	58.38	6.02	12.29	0.02	4.02	3.65	0.69	-0.32	0.39		0.39	-0.08	0.16	-0.06	6.75	-0.04	0.63	0.03	
SA1-B 2nd	28.65	38.18	17.93	86.28	17.74	251.69	0.21	2.49	114.96	6.09	12.29	0.03	3.71	5.15	0.70	-0.10	0.43		0.55	0.02	-0.25	0.01	6.71	0.00	1.02	0.03	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.06		-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.02		-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17		11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.04		-0.02	0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	
A1	2.07	22.77	3.46	28.05	-13.14	35.68	10.78	3.71	-39.05	0.25	0.54	-0.09	-1.48	-2.45	-0.04	-0.20	0.47		0.24	-0.01	0.09	-0.24	0.98	-0.01	0.20	0.00	
A1	2.49	24.48	3.63	29.07	-12.37	41.65	10.78	4.10	-38.86	0.24	0.55	-0.01	-1.38	-0.08	-0.04	-0.23	0.16		0.10	-0.02	0.07	-0.23	0.94	-0.01	0.23	0.00	
Average	2.28	23.62	3.55	28.56	-12.76	38.67	10.78	3.90	-38.95	0.24	0.54	-0.05	-1.43	-1.26	-0.04	-0.21	0.32		0.17	-0.01	0.08	-0.24	0.96	-0.01	0.22	0.00	
SA1-B 3rd	1.50	3.89	0.88	28.39		27.04	1.62	0.60	4.90	0.25	0.55	-0.03	0.27	1.80	0.06	0.04	0.27		0.19	0.00	0.00	0.03	0.92	0.00	0.13	0.00	
BLANK	0.38	34.87	9.40	1.09	2.49	52.58	18.20	65.49	-6.96	0.05	0.01	-0.04	0.33	4.04	0.05	-0.24	0.11	0.04	-0.13	-0.01	0.53	0.09	0.07	0.00	0.13	0.00	6.95
BLANK	0.46	34.10	9.05	0.96	1.95	41.32	17.69	63.79	-7.11	0.03	0.00	0.01	0.36	3.76	0.05	-0.25	0.10	0.03	-0.12	0.01	0.49	0.01	0.09	0.00	0.11	0.00	6.85
Average	0.42	34.48	9.23	1.03	2.22	46.95	17.94	64.64	-7.03	0.04	0.01	-0.01	0.35	3.90	0.05	-0.24	0.11	0.04	-0.12	0.00	0.51	0.05	0.08	0.00	0.12	0.00	6.90
A2	0.82	7.64	4.32	19.25	11.13	22.02	19.01	67.01	-9.28	0.08	1.32	0.79	0.50	3.71	0.09	-0.25	0.30	0.06	0.00	0.00	0.51	0.10	1.57	0.00	0.71	0.01	6.88
A2	0.60	7.64	4.43	19.05	11.54	28.61	19.20	67.23	-7.93	0.08	1.23	0.64	0.45	3.86	0.09	-0.28	0.29	0.05	-0.14	-0.01	0.55	0.03	1.52	0.00	0.63	0.01	7.13
A2	0.92	9.04	4.87	21.48	13.20	29.09	20.39	71.78	-9.90	0.10	1.42	2.17	0.55	4.00	0.10	-0.27	0.33	0.06	-0.19	-0.01	0.53	0.00	1.78	0.00	0.77	0.01	7.65
Average	0.78	8.11	4.54	19.92	11.96	26.57	19.54	68.67	-9.04	0.08	1.32	1.20	0.50	3.86	0.09	-0.27	0.31	0.06	-0.11	-0.01	0.53	0.04	1.63	0.00	0.70	0.01	7.22
SA2-B 1st	0.36	-26.38	-4.69	18.90	9.73	-20.38	1.59	4.03	-2.00	0.04	1.32	1.21	0.15	-0.04	0.04	-0.02	0.20	0.02	0.02	-0.01	0.02	-0.01	1.55	0.00	0.58	0.01	0.32
BLANK	-1.21	19.03	3.50	0.05	5.17	24.99	-1.79	2.30	-50.58	-0.01	0.00	-17.38	0.06	-0.16	-0.05	-0.40	0.05	0.04	-0.28	-0.02	0.55	-0.03	0.02	0.00	0.41	0.00	
BLANK	-1.45	18.74	3.41	-0.03	5.75	19.70	-1.83	2.11	-50.31	-0.01	0.00	-17.43	0.09	-0.09	-0.09	-0.42	0.05	0.04	-0.26	-0.03	0.50	0.03	0.30	-0.01	0.07	0.00	
Average	-1.33	18.88	3.46	0.01	5.46	22.34	-1.81	2.21	-50.44	-0.01	0.00	-17.41			-0.07	-0.41	0.05	0.04		-0.03	0.52	0.00	0.62	0.00	0.24	0.00	
SA2	-0.06	4.57	4.05	16.98	13.32	28.58	-0.78	3.28	-43.49	0.07	1.25	-16.26	0.00	1.95	-0.02	-0.39	0.28	0.06	-0.23	-0.01	0.46	-0.03	1.53	-0.01	1.16	0.01	
SA2	-0.52	4.14	3.91	16.45	12.36	20.62	-0.89	2.94	-46.76	0.07	1.16	-16.66	-0.06	1.85	0.00	-0.42	0.28	0.05	-0.19	0.01	0.46	0.02	1.46	0.00	0.65	0.01	
SA2	-0.89	5.11	4.17	17.55	14.06	20.63	-0.97	3.40	-43.46	0.08	1.29	-15.71	0.00	1.94	0.02	-0.43	0.28	0.05	-0.22	0.00	0.48	-0.02	1.60	-0.01	0.57	0.01	
Average	-0.49	4.60	4.04	16.99	13.25	23.28	-0.88	3.20	-44.57	0.07	1.24	-16.21		1.91	0.00	-0.42	0.28	0.05	-0.21	0.00	0.47	-0.01	1.53	0.00	0.80	0.01	
SA2-B 2nd	-	-14.28	0.58	16.98	7.79	0.93		1.00		0.08	1.24		0.00	1.91			0.23	0.02	-0.21		-0.06	-0.01	0.91	0.00	0.55	0.01	
BLANK	0.17	5.67	0.88	0.22	-7.90	-11.95	11.56	4.23	-56.56	-0.07	-0.04	-0.02	0.32	-1.58	0.00	-0.26	-0.05		-0.13	-0.10	0.40	-0.06	0.02	-0.04	-0.37	0.00	
BLANK	0.13	7.01	1.07	0.37	-4.76	-13.15	12.20	4.60	-56.62	-0.07	-0.04	0.01	0.29	-1.41	-0.01	-0.19	-0.04		-0.18	-0.11	0.41	-0.06	0.06	-0.04	-0.40	0.00	
Average	0.15	6.34	0.98	0.30	-6.33	-12.55	11.88	4.41					0.30	-1.49	0.00	-0.22	-0.04		-0.15	-0.10	0.41	-0.06	0.04	-0.04	-0.39	0.00	
A2 2	0.91	11.60	4.40	18.60	8.98	17.61	11.69	4.61	-54.15	0.08	4.16	0.07	0.91	4.40	0.11	-0.30	0.10		-0.17	-0.10	0.16	-0.07	6.01	-0.04	-0.29	0.01	
A2 1	1.49	11.92	4.66	19.12	6.16	21.08	12.62	5.05	-55.31	0.10	4.42	0.20	1.07	4.87	0.12	-0.31	0.11		-0.16	-0.10	0.14	-0.04	6.42	-0.04	-0.28	0.01	
Average	1.20	11.76	4.53	18.86	7.57	19.35	12.16	4.83	-54.73	0.09	4.29	0.14	0.99	4.63	0.11	-0.31	0.11		0.00	0.00	0.15	-0.05	6.21	-0.04	-0.28	0.01	
SA2-B3rd	1.05	5.42	3.55	18.56	7.57	19.35	0.28	0.42	0.00	0.09	4.29	0.14	0.69	4.63	0.11	0.00	0.11		0.00	0.00	0.00	0.00	6.17	0.00	0.00	0.01	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.06		-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.02		-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17	-19.57	11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.04			0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	

	B 10	Na 23	Mg 24	Al 27	K 39	Ca 43	V 51	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 65	Zn 66	As 75	Se 82	Sr 88	Rb 85	Zr 90	Ag 109	Cd 111	Sn 118	Ba 137	Tl 205	Pb 207	U 238	Cr 52
A2	1.37		4.82	9.44	-13.20		9.48	3.38	-41.34	0.09	1.22	0.00	-1.17	0.35	-0.07	-0.30	4.33		0.06	-0.02	0.10	-0.23	2.56	-0.01	0.13	0.00	
A2	0.99	6.84	3.23	7.07	-24.11	24.47	9.21	3.29		0.35	1.21	-0.11	-1.32	-0.16	-0.07	-0.20	1.03		0.08	-0.01	0.09	-0.26	2.20	-0.01	0.09	0.00	
Average	1.18	6.84	4.03	8.25	-18.65	24.47	9.34	3.33	-41.34	0.22	1.21	-0.06			9.84	-0.25	2.68			-0.02	0.09	-0.25	2.38	-0.01	0.11	0.00	
SA2-B 4th	0.40	-12.89	1.35	8.08	0.91	12.85	0.18	0.03	0.00	0.22	1.22	-0.03			9.94	0.00	2.64			0.00	0.02	0.00	2.35	0.00	0.02	0.00	
BLANK	2.68	58.24	17.29	193.18	41.06	537.49	-0.12	-0.11	11.35	0.01	0.01	8.53	0.97	133.00	0.25	0.05	0.65	0.06	-0.31	-0.68	0.33	0.02	2.44	-0.23	15.23	-0.01	
BLANK	2.79	56.82	6.08	168.54	49.78	137.99	0.08	-0.04	-0.55	0.44	-0.25	13.90	1.50	132.31	0.12	-0.02	0.32	0.06	0.08	-0.76	0.21	0.92	2.74	-0.26	6.19	-0.03	
Average	2.73	57.53	11.69	180.86	45.42	337.74	-0.02	-0.08	5.40	0.22	-0.12	11.21	1.23	132.65	0.19	0.01	0.48	0.06	-0.12	-0.72	0.27	0.47	2.59	-0.24	10.71	-0.02	
A2	3.19	231.61	43.06	678.76	289.51	652.28	3.20	0.88	111.30	0.68	4.38	51.35	1.38	622.23	1.85	0.16	8.00	0.77	0.85	-0.01	2.72	2.72	27.06	-0.25	3.00	0.06	
A2	3.45	277.67	53.72	743.69	307.15	915.67	3.35	0.97	101.64	1.20	4.47	54.61	2.18	622.76	0.89	0.17	8.36	0.81	0.57	0.32	4.09	2.64	28.14	-0.18	5.93	0.09	
Average	3.32	254.64	48.39	711.23	298.33	783.97	3.28	0.93	106.47	0.94	4.42	52.98	1.78	622.50	1.37	0.17	8.18	0.79	0.71	0.16	3.40	2.68	27.60	-0.21	4.46	0.07	
A2-B dig	0.59	197.11	36.70	530.36	252.91	446.23	3.28	1.00	101.07	0.72	4.42	41.77	0.55	489.85	1.18	0.16	7.70	0.73	0.71	0.87	3.13	2.21	25.01	0.03	-6.25	0.07	
BLANK	0.38	34.87	9.40	1.09	2.49	52.58	18.20	65.49	-6.96	0.05	0.01	-0.04	0.33	4.04	0.05	-0.24	0.11	0.04	-0.13	-0.01	0.53	0.09	0.07	0.00	0.13	0.00	6.95
BLANK	0.46	34.10	9.05	0.96	1.95	41.32	17.69	63.79	-7.11	0.03	0.00	0.01	0.36	3.76	0.05	-0.25	0.10	0.03	-0.12	0.01	0.49	0.01	0.09	0.00	0.11	0.00	6.85
Average	0.42	34.48	9.23	1.03	2.22	46.95	17.94	64.64	-7.03	0.04	0.01	-0.01	0.35	3.90	0.05	-0.24	0.11	0.04	-0.12	0.00	0.51	0.05	0.08	0.00	0.12	0.00	6.90
A3	0.69	106.69	24.69	85.53	103.27	40.65	18.66	65.75	-0.15	1.21	0.11	0.84	0.93	4.49	0.07	-0.23	0.32	0.79	-0.18	0.00	0.53	0.02	1.48	0.00	1.22	0.02	6.89
A3	1.09	109.33	24.73	86.24	105.33	36.49	18.70	65.78	-5.40	1.19	0.11	0.84	0.91	4.69	0.07	-0.19	0.33	0.83	-0.16	0.00	0.61	0.06	1.49	0.00	1.20	0.02	7.12
A3	1.06	105.35	24.59	85.15	107.05	35.60	18.44	64.97	-3.40	1.18	0.11	0.87	0.92	4.63	0.11	-0.21	0.32	0.81	-0.07	0.00	0.57	0.08	1.54	0.00	1.23	0.02	6.95
Average	0.95	107.12	24.67	85.64	105.22	37.58	18.60	65.50	-2.98	1.19	0.11	0.85	0.92	4.60	0.08	-0.21	0.32	0.81	-0.13	0.00	0.57	0.05	1.51	0.00	1.22	0.02	6.99
A3-B 1st	0.53	72.64	15.44	84.62	102.99	-9.37	0.66	0.86	4.05	1.15	0.11	0.86	0.57	0.70	0.04	-	0.22	0.78	-	0.00	0.06	0.01	1.43	0.00	1.09	0.02	0.08
BLANK	-1.21	19.03	3.50	0.05	5.17	24.99	-1.79	2.30	-50.58	-0.01	0.00	-17.38	0.06	-0.16	-0.05	-0.40	0.05	0.04	-0.28	-0.02	0.55	-0.03	0.02	0.00	0.41	0.00	
BLANK	-1.45	18.74	3.41	-0.03	5.75	19.70	-1.83	2.11	-50.31	-0.01	0.00	-17.43	0.09	-0.09	-0.09	-0.42	0.05	0.04	-0.26	-0.03	0.50	0.03	0.30	-0.01	0.07	0.00	
Average	-1.33	18.88	3.46	0.01	5.46	22.34	-1.81	2.21	-50.44	-0.01	0.00	-17.41	0.08	-0.13	-0.07	-0.41	0.05	0.04	-0.54	-0.03	0.52	0.00	0.16		0.24	0.00	
A3	-1.29	101.55	23.72	76.62	149.85	30.25	-1.48	2.24	-41.61	1.23	0.11	-16.36	0.43	2.58	-0.02	-0.44	0.32	0.79	-0.18	0.00	0.57	0.00	1.50	0.00	1.10	0.02	
A3	-0.84	101.97	23.50	75.57	120.67	34.70	-1.58	1.86	-43.37	1.18	0.11	-16.39	0.44	2.59	-0.06	-0.41	0.31	0.75	-0.23	-0.01	0.61	0.07	1.47	0.00	1.05	0.02	
A3	-0.99	101.56	23.82	76.88	119.99	29.69	-1.61	1.99	-44.20	1.18	0.11	-16.35	0.37	2.68	-0.06	-0.47	0.31	0.80	-0.22	-0.01	0.56	0.04	1.51	0.00	1.03	0.02	
Average	-1.04	101.69	23.68	76.36	130.17	31.54	-1.55	2.03	-43.06	1.20	0.11	-16.36	0.41	2.62	-0.05	-0.44	0.31	0.78	-0.21	-0.01	0.58	0.04	1.49	0.00	1.06	0.02	
A3-B 2nd	-	82.81	20.22	76.34	124.71	9.20	-	-0.18	-	1.20	0.11	-	0.34	2.62	-	-	0.27	0.74	-	-	0.06	0.04	1.33	0.00	0.82	0.02	
BLANK	2.68	58.24	17.29	193.18	41.06	537.49	-0.12	-0.11	11.35	0.01	0.01	8.53	0.97	133.00	0.25	0.05	0.65	0.06	-0.31	-0.68	0.33	0.02	2.44	-0.23	15.23	-0.01	
BLANK	2.79	56.82	6.08	168.54	49.78	137.99	0.08	-0.04	-0.55	0.44	-0.25	13.90	1.50	132.31	0.12	-0.02	0.32	0.06	0.08	-0.76	0.21	0.92	2.74	-0.26	6.19	-0.03	
Average	2.73	57.53	11.69	180.86	45.42	337.74	-0.02	-0.08	5.40	0.22	-0.12	11.21	1.23	132.65	0.19	0.01	0.48	0.06	-0.12	-0.72	0.27	0.47	2.59	-0.24	10.71	-0.02	
A3	1.71	286.24	59.13	703.25	322.07	424.73	0.78	1.71	73.67	2.42	-0.01	37.65	1.51	477.17	0.71	6.19	20.82	2.55	13.67	-0.50	28.18	72.81	127.95	-0.24	10.51	0.09	
A3	2.01	291.71	63.65	751.46	330.74	583.85	0.80	1.81	84.45	2.57	0.07	36.93	2.13	485.35	0.78	6.54	20.67	2.57	14.55	-0.27	28.43	72.74	124.27	-0.17	10.49	0.11	
Average	1.86	288.98	61.39	727.36	326.40	504.29	0.79	1.76	79.06	2.50	0.03	37.29	1.82	481.26	0.74	6.36	20.74	2.56	14.11	-0.39	28.30	72.77	126.11	-0.20	10.50	0.10	
A3-B-3rd dig	-0.87	231.45	49.70	546.50	280.98	166.55	0.79	1.76	73.66	2.28	0.15	26.08	0.59	348.61	0.56	6.35	20.26	2.50	14.23	-	28.03	72.30	123.53	-	-0.21	0.10	
BLANK	0.17	5.67	0.88	0.22	-7.90	-11.95	11.56	4.23	-56.56	-0.07	-0.04	-0.02	0.32	-1.58	0.00	-0.26	-0.05		-0.13	-0.10	0.40	-0.06	0.02	-0.04	-0.37	0.00	
BLANK	0.13	7.01	1.07	0.37	-4.76	-13.15	12.20	4.60	-56.62	-0.07	-0.04	0.01	0.29	-1.41	-0.01	-0.19	-0.04		-0.18	-0.11	0.41	-0.06	0.06	-0.04	-0.40	0.00	
Average	0.15	6.34	0.98	0.30	-6.33	-12.55	11.88	4.41	-	-	-	-0.01	0.30	-1.49	0.00	-0.22	-0.04		-0.15	-0.10	0.41	-0.06	0.04	-0.04	-0.39	0.00	
A4	0.58	43.99	6.68	5.42	16.70	27.84	12.80	5.12	-56.78	-0.04	-0.04	0.12	1.58	0.79	0.00	-0.34	0.09		-0.11	-0.10	0.12	0.02	0.23	-0.04	-0.50	0.01	
A4	1.24	52.17	7.39	6.11	20.67	35.37	13.76	5.36	-57.82	0.00	-0.04	0.16	1.83	1.22	0.00	-0.26	0.10		-0.17	-0.09	0.15	-0.04	0.28	-0.04	-0.43	0.01	
Average	0.91	48.08	7.03	5.77	18.69	31.60	13.28	5.24	-57.30	-0.02	-0.04	0.14	1.70	1.00	0.00	-0.30	0.09		-0.14	-0.09	0.13	-0.01	0.26	-0.04	-0.47	0.01	
A4-B 1st	0.76	41.74	6.06	5.47	18.69	31.60	1.40	0.83	-	-	-	0.14	1.40	1.00	0.00	-	0.09		-	-	-0.27	-	0.22	-	-	0.01	
BLANK	2.68	58.24	17.29	193.18	41.06	537.49	-0.12	-0.11	11.35	0.01	0.01	8.53	0.97	133.00	0.25	0.05	0.65	0.06	-0.31	-0.68	0.33	0.02	2.44	-0.23	15.23	-0.01	
BLANK	2.79	56.82	6.08	168.54	49.78	137.99	0.08	-0.04	-0.55	0.44	-0.25	13.90	1.50	132.31	0.12	-0.02	0.32	0.06	0.08	-0.76	0.21	0.92	2.74	-0.26	6.19	-0.03	
Average	2.73	57.53	11.69	180.86	45.42	337.74	-0.02	-0.08	5.40	0.22	-0.12	11.21	1.23	132.65	0.19	0.01	0.48	0.06	-0.12	-0.72	0.27	0.47	2.59	-0.24	10.71	-0.02	
A4	1.24	279.87	32.38	438.45	182.60	388.71	2.57	0.45	89.83	1.60	0.18	45.18	1.54	610.99	0.24	0.14	1.24	1.74	0.33	0.09	2.32	3.19	20.49	-0.19	3.69	0.35	
A4	1.06	269.56	21.37	332.75	178.31	125.60	2.31	0.30	87.74	1.48	0.10	47.14	1.44	616.77	0.21	0.17	0.70	1.71	0.24	-0.09	2.32	3.48	19.83	-0.24	3.12	0.34	
Average	1.15	274.72	26.87	385.60	180.46	257.15	2.44	0.38	88.78	1.54	0.14	46.16	1.49	613.88	0.22	0.15	0.97	1.72	0.28	0.00	2.32	3.34	20.16	-0.21	3.41	0.34	
A4-B 2nd dig	-1.58	217.19	15.18	204.74	135.04	-80.58	2.46	0.45	83.38	1.32	0.26	34.95	0.25	481.23	0.04	0.14	0.49	1.66	0.28	-	2.05	2.87	17.58	-	-7.30	0.34	
BLANK	0.38	34.87	9.40	1.09	2.49	52.58	18.20	65.49	-6.96	0.05	0.01	-0.04	0.33	4.04	0.05	-0.24	0.11	0.04	-0.13	-0.01	0.53	0.09	0.07	0.00	0.13	0.00	6.95
BLANK	0.46	34.10	9.05	0.96	1.95	41.32	17.69	63.79	-7.11	0.03	0.00	0.01	0.36	3.76	0.05	-0.25	0.10	0.03	-0.12	0.01	0.49	0.01	0.09	0.00	0.11	0.00	6.85
Average	0.42	34.48	9.23	1.03	2.22	46.95	17.94	64.64	-7.03	0.04	0.01	-0.01	0.35	3.90	0.05	-0.24	0.11	0.04	-0.12	0.00	0.51	0.05	0.08	0.00	0.12	0.00	6.90
A5	2.27	38.00	150.97	231.89	72.43	247.28	21.14	65.96	-2.56	0.38	0.25	1.99	0.79	3.47	0.11	-0.21	1.87	0.31	-0.06	-0.01	0.50	0.11	2.41	0.00	1.20	0.08	7.23
A5	2.10	37.66	152.77	233.40	68.11	249.32	20.34	62.86	-0.85	0.40	0.25	2.04	0.78	3.37	0.08	-0.20	1.88	0.31	-0.16	-0.01	0.51	0.04	2.42	0.00	1.02	0.08	6.69
A5	2.60	38.06	152.05	233.31	70.15	254.85	20.66	63.65	-3.34	0.38	0.25	1.88	0.74	3.37	0.07	-0.19	1.88	0.31	-0.05	0.00	0.50	0.07	2.35	0.00	1.01	0.08	6.83
Average	2.32	37.91	151.93	232.87	70.23	250.48	20.71	64.16	-2.25	0.39	0.25	1.97	0.77	3.41	0.08	-0.20	1.87	0.31	-0.09	-0.01	0.51	0.07	2.39	0.00	1.08	0.08	6.92

	B 10	Na 23	Mg 24	Al 27	K 39	Ca 43	V 51	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 65	Zn 66	As 75	Se 82	Sr 88	Rb 85	Zr 90	Ag 109	Cd 111	Sn 118	Ba 137	Tl 205	Pb 207	U 238	Cr 52
A5-B 1st	1.90	3.42	142.70	231.84	68.01	203.53	2.77	-0.48	-	0.35	0.24	1.97	0.42	-0.49	0.04	-	1.77	0.28	-	-	0.00	0.02	2.31	0.00	0.96	0.08	0.01
BLANK	-1.21	19.03	3.50	0.05	5.17	24.99	-1.79	2.30	-50.58	-0.01	0.00	-17.38	0.06	-0.16	-0.05	-0.40	0.05	0.04	-0.28	-0.02	0.55	-0.03	0.02	0.00	0.41	0.00	
BLANK	-1.45	18.74	3.41	-0.03	5.75	19.70	-1.83	2.11	-50.31	-0.01	0.00	-17.43	0.09	-0.09	-0.09	-0.42	0.05	0.04	-0.26	-0.03	0.50	0.03	0.30	-0.01	0.07	0.00	
Average	-1.33	18.88	3.46	0.01	5.46	22.34	-1.81	2.21	-50.44	-0.01	0.00	-17.41	0.08	-0.13	-0.07	-0.41	0.05	0.04	-0.27	-0.03	0.52	0.00	1.26	0.00	0.24	0.00	
A5 1	0.43	36.21	143.33	203.07	82.81	248.71	1.07	2.18	-39.18	0.38	0.25	-14.37	0.21	1.64	-0.03	-0.44	1.70	0.30	-0.28	-0.01	0.46	-0.05	2.44	0.00	1.03	0.08	
A5	0.34	34.63	138.68	196.06	81.47	244.72	1.04	1.99	-39.49	0.38	0.24	-15.23	0.16	1.42	-0.02	-0.35	1.77	0.30	-0.16	0.00	0.49	0.06	2.30	0.00	0.79	0.07	
A5	0.26	33.88	137.42	193.80	81.15	230.10	1.12	2.32	-39.04	0.37	0.24	-15.20	0.31	1.64	-0.04	-0.45	1.71	0.29	-0.21	0.00	0.45	-0.03	2.29	0.00	0.78	0.07	
Average	0.34	34.91	139.81	197.64	81.81	241.17	1.08	2.16	-39.24	0.37	0.24	-14.93	0.22	1.56	-0.03	-0.41	1.73	0.30	-0.22	0.00	0.46	-0.01	2.34	0.00	0.87	0.07	
A5-B 2nd	0.34	16.03	136.36	197.63	76.35	218.83	2.88	-0.05	-	0.37	0.24	-	0.15	1.56	-	-	1.68	0.26	-	0.00	-0.06	-0.01	1.09	0.00	0.63	0.07	
BLANK	0.17	5.67	0.88	0.22	-7.90	-11.95	11.56	4.23	-56.56	-0.07	-0.04	-0.02	0.32	-1.58	0.00	-0.26	-0.05		-0.13	-0.10	0.40	-0.06	0.02	-0.04	-0.37	0.00	
BLANK	0.13	7.01	1.07	0.37	-4.76	-13.15	12.20	4.60	-56.62	-0.07	-0.04	0.01	0.29	-1.41	-0.01	-0.19	-0.04		-0.18	-0.11	0.41	-0.06	0.06	-0.04	-0.40	0.00	
Average	0.15	6.34	0.98	0.30	-6.33	-12.55	11.88	4.41	-56.59	-0.07	-0.04	-0.01	0.30	-1.49	0.00	-0.22	-0.04		-0.15	-0.10	0.41	-0.06	0.04	-0.04	-0.39	0.00	
A5	0.52	30.81	22.60	19.90	31.35	212.53	13.04	4.87	-51.52	0.65	0.10	0.58	0.84	13.49	0.05	-0.34	0.49		-0.10	-0.10	0.16	-0.04	8.38	-0.04	-0.03	0.01	
A5	0.54	32.68	23.61	20.35	36.32	219.58	13.27	5.08	-49.30	0.66	0.10	0.60	0.82	13.46	0.06	-0.29	0.48		-0.13	-0.09	0.16	-0.06	8.36	-0.04	-0.02	0.01	
Average	0.53	31.75	23.11	20.12	33.84	216.06	13.16	4.97	-50.41	0.65	0.10	0.59	0.83	13.48	0.06	-0.32	0.48		-0.12	-0.10	0.16	-0.05	8.37	-0.04	-0.02	0.01	
A5-B 3rd	0.38	25.41	22.13	19.83	33.84	216.06	1.28	0.56	-	0.65	0.10	0.59	0.52	13.48	0.06	-	0.48		-	-	-0.25	-	8.33	-	-	0.01	
BLANK	2.68	58.24	17.29	193.18	41.06	537.49	-0.12	-0.11	11.35	0.01	0.01	8.53	0.97	133.00	0.25	0.05	0.65	0.06	-0.31	-0.68	0.33	0.02	2.44	-0.23	15.23	-0.01	
BLANK	2.79	56.82	6.08	168.54	49.78	137.99	0.08	-0.04	-0.55	0.44	-0.25	13.90	1.50	132.31	0.12	-0.02	0.32	0.06	0.08	-0.76	0.21	0.92	2.74	-0.26	6.19	-0.03	
Average	2.73	57.53	11.69	180.86	45.42	337.74	-0.02	-0.08	5.40	0.22	-0.12	11.21	1.23	132.65	0.19	0.01	0.48	0.06	-0.12	-0.72	0.27	0.47	2.59	-0.24	10.71	-0.02	
A5	4.04	429.24	527.74	4385.33	243.62	4130.06	4.01	0.61	230.32	2.42	1.48	43.59	2.63	563.48	0.38	0.48	17.09	0.97	0.92	1.48	5.02	1.98	63.59	-0.17	12.67	0.18	
A5	3.90	430.73	537.52	4382.49	256.61	3243.55	4.28	0.64	224.70	2.23	1.60	48.66	3.01	612.08	0.38	0.60	16.00	0.95	0.91	1.11	5.57	1.87	65.00	-0.25	12.33	0.14	
Average	3.97	429.98	532.63	4383.91	250.12	3686.80	4.15	0.63	227.51	2.32	1.54	46.13	2.82	587.78	0.38	0.54	16.54	0.96	0.92	1.30	5.29	1.92	64.29	-0.21	12.50	0.16	
SA5-B 4th dig	1.24	372.45	520.94	4203.05	204.70	3349.06	4.15	0.63	222.11	2.10	1.54	34.92	1.58	455.13	0.19	0.53	16.06	0.90	0.92	1.30	5.02	1.45	61.71	-	1.79	0.16	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.06		-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.02		-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17	-19.57	11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.04		-0.02	0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	
A5	0.67	13.78	2.63	5.32	-14.59	24.53	9.06	3.26	-44.16	0.06	0.03	0.25	-1.65	-0.96	-0.07	-0.13	0.06		0.01	0.04	0.06	-0.26	1.68	-0.01	0.19	0.00	
A5	0.84	15.15	2.70	5.10	-13.00	29.63	9.36	3.26	-45.06	0.06	0.03	0.04	-1.51	-1.14	-0.08	-0.24	0.06		0.01	0.03	0.07	-0.22	1.64	-0.01	0.13	0.00	
Average	0.75	14.46	2.67	5.21	-13.79	27.08	9.21	3.26	-44.61	0.06	0.03	0.15	-1.58	-1.05	-0.08	-0.19	0.06		0.01	0.04	0.07	-0.24	1.66	-0.01	0.16	0.00	
SA5-B 5th	-0.03	-5.27	-0.01	5.04	-	15.46	0.05	-0.04	-	0.06	0.03	0.15	-	-	-	-	0.02		0.01	0.02	-0.01	-	1.63	-	0.07	0.00	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.06		-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.02		-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17	-19.57	11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.04		-0.02	0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	
A6	6.43	153.66	11.17	85.87	78.76	24615.90	9.20	4.88	-38.50	0.92	0.01	0.31	-0.99	7.46	0.59	0.03	3025.06		9.37	-0.01	3.10	-0.22	163.03	-0.01	1.26	0.09	
A6	6.30	157.24	11.03	83.50	77.32	23517.89	9.29	4.91	-38.23	0.87	0.01	0.26	-0.60	7.92	0.53	0.00	2964.85		9.58	-0.02	2.96	-0.19	162.88	-0.01	1.25	0.09	
Average	6.36	155.45	11.10	84.69	78.04	24066.90	9.25	4.90	-38.37	0.90	0.01	0.29	-0.79	7.69	0.56	0.01	2994.96		9.47	-0.01	3.03	-0.20	162.96	-0.01	1.26	0.09	
SA6-B 1st	5.58	135.72	8.43	84.52	97.61	24055.27	0.08	1.60	-	0.90	0.01	0.29	-	7.69	0.56	0.01	2994.91		9.47	-0.01	2.95	-	162.93	0.00	1.17	0.09	
BLANK	0.17	5.67	0.88	0.22	-7.90	-11.95	11.56	4.23	-56.56	-0.07	-0.04	-0.02	0.32	-1.58	0.00	-0.26	-0.05		-0.13	-0.10	0.40	-0.06	0.02	-0.04	-0.37	0.00	
BLANK	0.13	7.01	1.07	0.37	-4.76	-13.15	12.20	4.60	-56.62	-0.07	-0.04	0.01	0.29	-1.41	-0.01	-0.19	-0.04		-0.18	-0.11	0.41	-0.06	0.06	-0.04	-0.40	0.00	
Average	0.15	6.34	0.98	0.30	-6.33	-12.55	11.88	4.41	-56.59	-0.07	-0.04	-0.01	0.30	-1.49	0.00	-0.22	-0.04		-0.15	-0.10	0.41	-0.06	0.04	-0.04	-0.39	0.00	
A7	3.04	42.91	5.12	4.35	2.65	37.44	12.91	5.44	-57.40	-0.06	-0.04	0.01	0.21	-0.32	0.20	-0.34	0.23		-0.09	-0.09	0.13	-0.05	1.19	-0.04	-0.53	0.00	
A7	3.34	46.79	5.16	3.99	7.52	42.42	12.53	5.21	-56.17	-0.07	-0.04	0.00	0.29	-0.27	0.17	-0.33	0.22		-0.09	-0.09	0.12	-0.07	1.12	-0.04	-0.52	0.00	
Average	3.19	44.85	5.14	4.17	5.08	39.93	12.72	5.33	-56.79	-0.06	-0.04	0.00	0.25	-0.29	0.19	-0.33	0.23		-0.09	-0.09	0.12	-0.06	1.16	-0.04	-0.52	0.00	
SA7-B 1st	3.05	38.51	4.16	3.88	5.08	39.93	0.84	0.91	-	-	-	0.00	-0.06	-	0.19	-	0.23		-	-	-0.28	-	1.11	-	-	0.00	
BLANK	0.17	5.67	0.88	0.22	-7.90	-11.95	11.56	4.23	-56.56	-0.07	-0.04	-0.02	0.32	-1.58	0.00	-0.26	-0.05		-0.13	-0.10	0.40	-0.06	0.02	-0.04	-0.37	0.00	
BLANK	0.13	7.01	1.07	0.37	-4.76	-13.15	12.20	4.60	-56.62	-0.07	-0.04	0.01	0.29	-1.41	-0.01	-0.19	-0.04		-0.18	-0.11	0.41	-0.06	0.06	-0.04	-0.40	0.00	
Average	0.15	6.34	0.98	0.30	-6.33	-12.55	11.88	4.41	-56.59	-0.07	-0.04	-0.01	0.30	-1.49	0.00	-0.22	-0.04		-0.15	-0.10	0.41	-0.06	0.04	-0.04	-0.39	0.00	
A8	0.48	26.20	2.04	14.81	16.22	2243.73	12.03	5.31	-55.99	0.08	2.64	0.09	0.70	-0.30	-0.06	-0.39	158.26		0.71	-0.10	0.28	-0.04	9.14	-0.04	-0.37	0.03	
A8	1.22	24.92	1.90	14.82	14.76	2239.33	12.01	5.37	-54.17	0.07	2.72	0.10	0.65	-0.71	-0.02	-0.26	155.04		0.70	-0.09	0.24	-0.08	9.14	-0.04	-0.41	0.03	
Average	0.85	25.56	1.97	14.82	15.49	2241.53	12.02	5.34	-55.08	0.07	2.68	0.10	0.68	-0.51	-0.04	-0.32	156.65		0.70	-0.09	0.26	-0.06	9.14	-0.04	-0.39	0.03	
SA8-B 1st	0.71	19.22	0.99	14.52	15.49	2241.53	0.14	0.93	-	0.07	2.68	0.10	0.37	-	-	-	156.65		0.70	-	-0.15	-	9.10	-	-	0.03	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.06		-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.02		-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17	-19.57	11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.04		-0.02	0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	

	B 10	Na 23	Mg 24	Al 27	K 39	Ca 43	V 51	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 65	Zn 66	As 75	Se 82	Sr 88	Rb 85	Zr 90	Ag 109	Cd 111	Sn 118	Ba 137	Tl 205	Pb 207	U 238	Cr 52
A8	0.82	10.70	1.84	13.29	-25.92	118.31	10.63	3.75	-46.09	0.03	1.12	-0.04	-2.05	-0.69	-0.08	-0.26	7.67		0.04	-0.02	0.08	-0.27	3.69	-0.01	0.05	0.18	
A8	1.05	11.77	1.88	13.36	-24.03	111.44	10.82	3.80	-46.38	0.03	1.09	-0.11	-2.05	-0.69	-0.09	-0.20	7.57		0.14	-0.02	0.08	-0.20	3.63	-0.01	0.04	0.17	
Average	0.94	11.24	1.86	13.32	-24.98	114.87	10.73	3.78	-46.23	0.03	1.11	-0.07	-2.05	-0.69	-0.08	-0.23	7.62		0.09	-0.02	0.08	-0.23	3.66	-0.01	0.05	0.17	
SA8-B 2nd	0.16	-8.49	-0.81	13.15	-	103.25	1.56	0.48	-	0.03	1.11	-	-	-	-	-	7.58		0.09	-	0.01	-	3.63	0.00	-0.04	0.18	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.06		-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.02		-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17	-19.57	11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.04		-0.02	0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	
A9	5.29	3583.95	185.44	2.93	325.04	1090.38	6.23	2.19	-39.53	0.14	0.01	0.31	1.35	-2.33	-0.05	-0.20	5.25		0.05	-0.10	0.07	-0.02	0.88	-0.01	0.21	0.03	
A9	4.34	3641.92	179.64	2.85	357.05	1075.13	6.32	2.20	-35.04	0.16	0.01	0.27	0.93	-0.51	-0.04	-0.20	5.08		0.10	-0.07	0.10	-0.03	0.93	0.03	0.24	0.03	
Average	4.81	3612.93	182.54	2.89	341.04	1082.75	6.28	2.20	-37.28	0.15	0.01	0.29	1.14	-1.42	-0.05	-0.20	5.17		0.08	-0.08	0.09	-0.03	0.90	0.01	0.23	0.03	
SA9-B 1st	4.03	3593.20	179.87	2.72	360.61	1071.13	-2.89	-1.10	6.57	0.15	0.02	0.31	2.84	1.64	0.05	0.05	5.12		0.10	-0.10	0.01	0.24	0.87	0.02	0.14	0.03	
BLANK	-1.21	19.03	3.50	0.05	5.17	24.99	-1.79	2.30	-50.58	-0.01	0.00	-17.38	0.06	-0.16	-0.05	-0.40	0.05	0.04	-0.28	-0.02	0.55	-0.03	0.02	0.00	0.41	0.00	
BLANK	-1.45	18.74	3.41	-0.03	5.75	19.70	-1.83	2.11	-50.31	-0.01	0.00	-17.43	0.09	-0.09	-0.09	-0.42	0.05	0.04	-0.26	-0.03	0.50	0.03	0.30	-0.01	0.07	0.00	
Average	-1.33	18.88	3.46	0.01	5.46	22.34	-1.81	2.21	-50.44	-0.01	0.00	-17.41	0.08	-0.13	-0.07	-0.41	0.05	0.04	-0.27	-0.03	0.52	0.00	0.16	0.00	0.24	0.00	
A10	-1.02	23.21	4.21	2.33	5.07	41.37	-1.30	3.38	-41.25	0.04	0.10	-17.00	-0.27	0.97	0.02	-0.32	0.06	0.05	-0.96	-0.02	0.53	-0.27	0.05	0.00	8.33	0.00	
A10	-1.57	20.62	3.88	2.03	5.67	24.62	-1.29	2.77	-42.29	0.03	0.08	-17.70	-0.34	0.89	0.08	-0.33	0.05	0.04	-0.99	-0.01	0.45	-0.28	0.05	0.00	6.80	0.00	
A10	-1.50	23.15	4.41	2.36	3.82	23.33	-1.38	4.01	-42.57	0.04	0.11	-17.52	-0.27	0.91	0.07	-0.33	0.06	0.05	-0.91	-0.01	0.57	-0.28	0.06	0.00	8.59	0.00	
Average	-1.36	21.92	4.17	2.24	4.85	32.99	-1.30	3.39	-41.77	0.04	0.10	-17.41	-0.31	0.93	0.06	-0.33	0.05	0.05	-0.95	-0.01	0.52	-0.28	0.05	0.00	7.56	0.00	
SA10-B	<DL	3.03	0.71	2.23	-0.60	10.65	0.51	1.18	8.67	0.05	0.10	0.00	-0.38	1.06	0.13	0.08	0.01	0.01	-0.68	0.01	-0.01	-0.28	-0.12	0.00	7.32	0.00	
BLANK	0.17	5.67	0.88	0.22	-7.90	-11.95	11.56	4.23	-56.56	-0.07	-0.04	-0.02	0.32	-1.58	0.00	-0.26	-0.05		-0.13	-0.10	0.40	-0.06	0.02	-0.04	-0.37	0.00	
BLANK	0.13	7.01	1.07	0.37	-4.76	-13.15	12.20	4.60	-56.62	-0.07	-0.04	0.01	0.29	-1.41	-0.01	-0.19	-0.04		-0.18	-0.11	0.41	-0.06	0.06	-0.04	-0.40	0.00	
Average	0.15	6.34	0.98	0.30	-6.33	-12.55	11.88	4.41	-56.59	-0.07	-0.04	-0.01	0.30	-1.49	0.00	-0.22	-0.04		-0.15	-0.10	0.41	-0.06	0.04	-0.04	-0.39	0.00	
A10	2.81	127.95	18.80	1.73	25.27	84.51	12.81	4.75	-55.62	-0.04	-0.04	0.04	0.45	-1.27	-0.02	-0.33	0.25		-0.13	-0.10	0.14	-0.07	0.21	-0.04	-0.52	0.00	
A10	2.58	123.60	18.24	1.78	17.44	71.67	12.93	4.64	-56.60	-0.05	-0.04	0.08	0.44	-1.24	-0.03	-0.32	0.25		-0.09	-0.09	0.12	-0.03	0.21	-0.04	-0.50	0.00	
Average	2.69	125.78	2.00	1.75	21.36	78.09	12.87	4.70	-56.11	2.00	-0.04	0.06	2.00	-1.26	-0.03	-0.33	0.25		-0.11	2.00	0.13	2.00	0.21	-0.04	-0.51	0.00	
SA10-B	2.55	119.44	1.02	1.46	27.69	90.64	0.99	0.28	0.48	2.07	0.00	0.07	1.70	0.24	-0.02	-0.10	0.29		0.05	2.10	-0.28	2.06	0.17	0.00	-0.13	0.00	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.06		-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.02		-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17	-19.57	11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.04		-0.02	0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	
A10	4.94	3486.93	190.39	3.22	498.84	1162.77	6.28	2.35	-37.83	0.23	0.03	1.33	2.69	3.79	-0.08	-0.16	5.20		0.12	0.00	0.18	-0.07	0.99	-0.01	0.63	0.03	
A10	4.74	3406.70	176.51	2.19	334.54	1155.25	6.34	2.18	-39.56	0.13	0.00	0.14	-0.47	-1.64	-0.05	-0.24	5.12		0.16	-0.10	0.01	-0.01	0.92	-0.01	0.16	0.03	
Average	4.84	3446.81	183.45	2.70	416.69	1159.01	6.31	2.27	-38.70	0.18	0.02	0.73	1.11	1.07	-0.07	-0.20	5.16		0.14	-0.05	0.10	-0.04	0.95	-0.01	0.39	0.03	
SA10-B	4.06	3427.08	180.78	2.53	436.26	1147.39	-2.85	-1.03	5.16	0.18	0.03	0.76	2.82	4.13	0.03	0.05	5.12		0.16	-0.07	0.02	0.23	0.92	0.00	0.31	0.03	
BLANK	-1.21	19.03	3.50	0.05	5.17	24.99	-1.79	2.30	-50.58	-0.01	0.00	-17.38	0.06	-0.16	-0.05	-0.40	0.05	0.04	-0.28	-0.02	0.55	-0.03	0.02	0.00	0.41	0.00	
BLANK	-1.45	18.74	3.41	-0.03	5.75	19.70	-1.83	2.11	-50.31	-0.01	0.00	-17.43	0.09	-0.09	-0.09	-0.42	0.05	0.04	-0.26	-0.03	0.50	0.03	0.30	-0.01	0.07	0.00	
Average	-1.33	18.88	3.46	0.01	5.46	22.34	-1.81	2.21	-50.44	-0.01	0.00	-17.41	0.08	-0.13	-0.07	-0.41	0.05	0.04	-0.27	-0.03	0.52	0.00	0.16	0.00	0.24	0.00	
A11	-1.78	99.14	5.15	62.48	120.83	53.96	-1.22	2.11	-41.71	0.86	0.03	-15.61	0.27	6.18	0.18	-0.31	0.29	1.07	-0.94	-0.01	0.44	-0.31	3.15	0.00	0.83	0.03	
A11	-1.99	98.16	4.95	61.32	119.51	69.58	-1.31	1.71	-40.37	0.82	0.03	-15.49	0.44	6.46	0.19	-0.33	0.29	1.08	-0.92	-0.02	0.44	-0.21	3.17	0.00	0.82	0.02	
A11	-1.88	99.16	5.08	61.99	120.07	63.06	-1.31	1.71	-41.77	0.84	0.03	-15.53	0.40	6.73	0.16	-0.29	0.31	1.11	-0.97	-0.02	0.40	-0.28	3.13	0.00	0.82	0.03	
Average	-1.88	98.82	5.06	61.93	120.14	62.20	-1.28	1.84	-41.28	0.84	0.03	-15.54	0.37	6.46	0.18	-0.31	0.30	1.09	-0.94	-0.02	0.43	-0.26	3.15	0.00	0.82	0.03	
SA11-B	-	79.93	1.61	61.92	114.68	39.86	-	-0.36	-	0.84	0.03	-	0.29	6.46	0.18	-	0.25	1.05	-	-	-0.09	-0.26	2.99	0.01	0.58	0.03	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.06		-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.02		-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17	-19.57	11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.04		-0.02	0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	
A11	4.98	3573.29	185.88	3.93	333.06	1135.06	6.15	2.26	-37.48	0.15	0.00	0.12	0.30	-0.71	-0.08	-0.27	5.30		0.16	-0.10	0.01	-0.05	1.15	0.00	0.06	0.03	
A11	4.94	3449.36	180.36	3.57	346.94	1140.67	5.97	1.94	-38.58	0.15	0.00	0.76	1.59	0.02	-0.04	-0.23	5.28		0.15	-0.07	0.01	-0.08	1.21	-0.01	0.12	0.03	
Average	4.96	1796.51	183.12	3.75	340.00	1137.86	6.06	2.10	-40.66	0.15	0.00	0.44	-0.70	-0.35	-0.09	-0.25	5.29		0.15	-0.08	0.01	-0.06	1.18	0.00	0.09	0.03	

	B 10	Na 23	Mg 24	Al 27	K 39	Ca 43	V 51	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 65	Zn 66	As 75	Se 82	Sr 88	Rb 85	Zr 90	Ag 109	Cd 111	Sn 118	Ba 137	Tl 205	Pb 207	U 238	Cr 52
SA11-B	4.18	1776.78	180.45	3.58	340.00	1126.24	-3.10	-1.20	-	0.15	0.00	0.44	-	-	-	-	5.25		-	-	-0.06	-	1.14	0.00	0.00	0.03	
BLANK	-1.21	19.03	3.50	0.05	5.17	24.99	-1.79	2.30	-50.58	-0.01	0.00	-17.38	0.06	-0.16	-0.05	-0.40	0.05	0.04	-0.28	-0.02	0.55	-0.03	0.02	0.00	0.41	0.00	
BLANK	-1.45	18.74	3.41	-0.03	5.75	19.70	-1.83	2.11	-50.31	-0.01	0.00	-17.43	0.09	-0.09	-0.09	-0.42	0.05	0.04	-0.26	-0.03	0.50	0.03	0.30	-0.01	0.07	0.00	
Average	-1.33	18.88	3.46	0.01	5.46	22.34	-1.81	2.21	-50.44	-0.01	0.00	-17.41	0.08	-0.13	-0.07	-0.41	0.05	0.04	-0.27	-0.03	0.52	0.00	0.16	0.00	0.24	0.00	
B1	61.01	139.33	252.16	260.83	31.70	7683.34	-1.65	2.62	106.15	3.62	0.57	-16.48	2.83	16.41	0.59	-0.38	5.51	0.24	-0.25	-0.03	0.55	0.09	0.51	0.00	971.58	0.32	
B1	56.44	130.32	237.36	244.52	31.54	7324.56	-1.69	1.82	96.08	3.37	0.53	-16.74	2.32	15.36	0.58	-0.43	5.29	0.22	-0.27	-0.02	0.46	0.02	0.49	0.00	897.82	0.28	
B1	62.03	139.78	253.52	262.18	33.14	7820.94	-1.74	2.18	106.91	3.67	0.62	-16.80	2.82	16.76	0.63	-0.45	5.67	0.24	-0.27	-0.02	0.54	0.04	0.57	0.00	948.58	0.31	
Average	59.83	136.48	247.68	255.84	32.12	7609.61	-1.69	2.20	103.05	3.55	0.57	-16.68	2.66	16.18	0.60	-0.42	5.49	0.23	-0.26	-0.02	0.52	0.05	0.52	0.00	939.33	0.30	
SB1-B 1st	59.43	117.59	244.23	254.18	32.27	7585.04	-1.71	2.07	102.01	3.53	0.57	-16.74	2.60	16.10	0.67	-0.01	5.44	0.23	0.01	0.00	-0.01	0.04	0.36	0.00	928.58	0.30	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.06		-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.02		-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17	-19.57	11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.04		-0.02	0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	
B1	85.56	113.98	9.60	58.13	37.59	11982.29	10.53	3.87	-41.84	9.43	0.06	0.16	0.21	-1.08	4.48	-0.24	73.14		0.43	0.04	0.09	-0.20	0.69	0.00	368.09	1.09	
B1	89.08	117.80	9.77	57.03	38.57	12183.91	10.72	3.60	-41.49	9.35	0.04	0.18	-0.35	-1.38	4.39	-0.15	70.99		0.25	0.01	0.09	-0.21	0.63	0.00	386.97	1.17	
Average	87.32	115.89	9.68	57.58	38.08	12083.10	10.62	3.74	-41.67	9.39	0.05	0.17	-0.07	-1.23	4.44	-0.19	72.06		0.34	0.02	0.09	-0.20	0.66	0.00	377.53	1.13	
SB1-B 2nd	86.54	96.16	7.01	57.41	57.65	12071.48	1.46	0.44	2.19	9.39	0.06	0.19	1.63	1.83	4.53	0.06	72.02		0.36	0.01	0.01	0.06	0.63	0.01	377.45	1.13	
BLANK	0.38	34.87	9.40	1.09	2.49	52.58	18.20	65.49	-6.96	0.05	0.01	-0.04	0.33	4.04	0.05	-0.24	0.11	0.04	-0.13	-0.01	0.53	0.09	0.07	0.00	0.13	0.00	6.95
BLANK	0.46	34.10	9.05	0.96	1.95	41.32	17.69	63.79	-7.11	0.03	0.00	0.01	0.36	3.76	0.05	-0.25	0.10	0.03	-0.12	0.01	0.49	0.01	0.09	0.00	0.11	0.00	6.85
Average	0.42	34.48	9.23	1.03	2.22	46.95	17.94	64.64	-7.03	0.04	0.01	-0.01	0.35	3.90	0.05	-0.24	0.11	0.04	-0.12	0.00	0.51	0.05	0.08	0.00	0.12	0.00	6.90
B2	327.92	327.63	358.34	702.22	248.61	12249.71	18.89	72.40	95.93	6.21	18.74	1.51	12.72	124.46	0.68	-0.20	10.13	2.24	-0.12	-0.01	0.64	0.21	105.80	0.01	3312.53	0.61	12.14
B2	327.65	322.21	352.15	705.75	247.36	12298.56	17.96	69.39	93.82	6.26	18.40	1.55	12.87	123.33	0.68	-0.15	10.09	2.27	-0.12	0.00	0.60	0.13	102.74	0.02	3274.82	0.61	11.90
B2	334.44	334.78	371.06	730.67	250.98	12600.15	19.04	73.01	97.11	6.45	19.28	1.72	13.23	128.87	0.74	-0.23	10.04	2.25	-0.14	0.01	0.64	0.11	104.98	0.02	3390.03	0.62	12.57
Average	330.00	328.20	360.52	712.88	248.98	12382.80	18.63	71.60	95.62	6.31	18.80	1.59	12.94	125.55	0.70	-0.19	10.08	2.25	-0.13	0.00	0.63	0.15	104.51	0.01	3325.79	0.61	12.20
SB2-B 1st	329.59	293.72	351.29	711.85	246.76	12335.85	0.69	6.96	102.66	6.27	18.80	1.61	12.60	121.65	0.65	0.05	9.98	2.22	0.00	0.00	0.11	0.10	104.43	0.01	3325.67	0.61	5.30
BLANK	-1.21	19.03	3.50	0.05	5.17	24.99	-1.79	2.30	-50.58	-0.01	0.00	-17.38	0.06	-0.16	-0.05	-0.40	0.05	0.04	-0.28	-0.02	0.55	-0.03	0.02	0.00	0.41	0.00	
BLANK	-1.45	18.74	3.41	-0.03	5.75	19.70	-1.83	2.11	-50.31	-0.01	0.00	-17.43	0.09	-0.09	-0.09	-0.42	0.05	0.04	-0.26	-0.03	0.50	0.03	0.30	-0.01	0.07	0.00	
Average	-1.33	18.88	3.46	0.01	5.46	22.34	-1.81	2.21	-50.44	-0.01	0.00	-17.41	0.08	-0.13	-0.07	-0.41	0.05	0.04	-0.27	-0.03	0.52	0.00	0.16	0.00	0.24	0.00	
B2	303.19	327.91	338.08	652.80	277.85	12471.45	-1.70	7.35	107.21	6.15	19.83	-15.58	12.51	121.08	0.61	-0.39	9.77	2.27	-0.26	-0.02	0.64	0.13	106.11	0.01	3139.52	0.63	
B2	311.34	324.00	339.74	639.98	271.60	12200.90	-1.72	6.94	109.00	6.05	19.66	-15.76	12.58	120.28	0.58	-0.40	9.51	2.21	-0.25	-0.02	0.55	0.15	104.25	0.01	3095.81	0.62	
Average	307.27	325.96	338.91	646.39	274.72	12336.18	-1.71	7.15	108.10	6.10	19.75	-15.67	12.55	120.68	0.60	-0.39	9.64	2.24	-0.25	-0.02	0.59	0.14	105.18	0.01	3117.66	0.63	
SB2-B 2nd	307.27	307.07	335.45	646.38	269.27	12313.83	0.10	4.94	158.55	6.11	19.75	1.73	12.47	120.81	0.67	0.02	9.59	2.20	0.02	0.01	0.07	0.14	105.01	0.02	3117.42	0.63	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.06		-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.02		-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17	-19.57	11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.04		-0.02	0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	
B2	347.86	340.93	278.95	754.62	306.04	9816.01	8.77	27.70	67.50	4.68	28.85	1.44	10.71	215.52	0.56	-0.30	9.17		-0.24	-0.02	0.23	-0.07	438.22	0.00	3459.41	0.50	
B2	342.67	323.90	264.02	750.29	289.07	9510.63	7.75	26.54	64.73	4.42	28.44	1.31	10.57	213.45	0.56	-0.25	9.48		-0.14	-0.03	0.22	-0.06	453.02	0.00	3532.50	0.50	
Average	345.27	332.41	271.48	752.45	297.56	9663.32	8.26	27.12	66.12	4.55	28.65	1.37	10.64	214.49	0.56	-0.27	9.32		-0.19	-0.02	0.22	-0.06	445.62	0.00	3495.95	0.50	
SB2-B 3rd	344.49	312.68	268.81	752.28	317.13	9651.70	-0.90	23.82	109.97	4.55	28.66	1.39	12.34	217.55	0.65	-0.02	9.28		-0.17	-0.04	0.15	0.21	445.59	0.01	3495.87	0.50	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.06		-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.02		-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17	-19.57	11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.04		-0.02	0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	
B5	4.11	393.78	17.69	263.40	253.90	653.45	9.88	2.54	-38.41	0.55	0.88	0.32	-0.15	1.93	0.21	-0.17	4.01		-0.15	-0.07	0.10	-0.06	1.25	-0.01	11.61	0.06	
B5	3.80	437.01	18.72	289.28	269.30	724.18	11.44	2.97	-39.51	0.60	0.94	0.44	-0.24	2.00	0.25	-0.26	4.37		-0.18	-0.07	0.10	-0.05	1.43	-0.01	12.87	0.07	
Average	3.96	415.40	18.20	276.34	261.60	688.82	10.66	2.76	-38.96	0.57	0.91	0.38	-0.20	1.96	0.23	-0.21	4.19		-0.16	-0.07	0.10	-0.05	1.34	-0.01	12.24	0.07	
SB5-B 1st	3.18	395.67	15.53	276.17	281.17	677.19	1.50	-0.54	4.90	0.58	0.92	0.40	1.51	5.02	0.32	0.04	4.15		-0.14	-0.08	0.02	0.21	1.31	0.00	12.15	0.07	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.06		-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.02		-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17	-19.57	11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.04		-0.02	0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	
B6	6.19	3187.20	165.87	2.52	320.01	1185.76	5.78	2.06	-35.59	0.14	0.00	0.18	-0.52	-1.87	0.11	-0.13	4.92		-0.04	-0.12	0.02	-0.05	0.91	-0.01	2.08	0.03	
B6	6.10	3301.55	178.70	2.53	323.14	1160.14	5.83	2.31	-36.67	0.14	0.00	0.07	-0.61	-2.03	0.04	-0.22	4.91		0.17	-0.12	0.00	-0.11	0.82	-0.01	2.08	0.03	
Average	6.14	3244.37	172.29	2.52	321.58	1172.95	5.81	2.19	-36.13	0.14	0.00	0.12	-0.57	-1.95	0.08	-0.18	4.91		0.07	-0.12	0.01	-0.08	0.86	-0.01	2.08	0.03	

	B 10	Na 23	Mg 24	Al 27	K 39	Ca 43	V 51	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 65	Zn 66	As 75	Se 82	Sr 88	Rb 85	Zr 90	Ag 109	Cd 111	Sn 118	Ba 137	Tl 205	Pb 207	U 238	Cr 52
SB6-B 1st	5.36	3224.64	169.62	2.35	341.14	1161.33	-3.36	-1.11	7.72	0.14	0.01	0.14	1.14	1.11	0.17	0.07	4.87		0.09	-0.13	-0.07	0.19	0.83	0.00	2.00	0.03	
BLANK	0.38	34.87	9.40	1.09	2.49	52.58	18.20	6.95	-6.96	0.05	0.01	-0.04	0.33	4.04	0.05	-0.24	0.11	0.04	-0.13	-0.01	0.53	0.09	0.07	0.00	0.13	0.00	65.49
BLANK	0.46	34.10	9.05	0.96	1.95	41.32	17.69	6.85	-7.11	0.03	0.00	0.01	0.36	3.76	0.05	-0.25	0.10	0.03	-0.12	0.01	0.49	0.01	0.09	0.00	0.11	0.00	63.79
Average	0.42	34.48	9.23	1.03	2.22	46.95	17.94	6.90	-7.03	0.04	0.01	-0.01	0.35	3.90	0.05	-0.24	0.11	0.04	-0.12	0.00	0.51	0.05	0.08	0.00	0.12	0.00	64.64
C1	105.72	496.58	58.46	444.01	176.63	770.66	23.01	7.26	7.11	0.83	19.41	1.52	2.41	19.72	0.55	-0.16	1.39	0.83	-0.01	0.02	0.51	0.16	5.27	0.00	559.76	0.06	66.43
C1	110.80	532.18	62.62	477.86	191.34	818.86	24.65	7.49	3.63	0.91	20.99	1.56	2.62	20.88	0.65	-0.24	1.46	0.88	-0.03	0.02	0.55	0.10	5.56	0.00	594.90	0.06	70.50
C1	111.82	527.18	62.47	476.15	190.55	825.90	24.55	7.65	4.85	0.88	20.67	1.60	2.71	20.63	0.61	-0.19	1.42	0.84	-0.05	0.01	0.53	0.09	5.53	0.00	581.63	0.06	70.34
Average	109.45	518.65	61.18	466.01	186.17	805.14	24.07	7.47	5.20	0.87	20.36	1.56	2.58	20.41	0.60	-0.20	1.42	0.85	-0.03	0.01	0.53	0.11	5.45	0.00	578.77	0.06	69.09
SC1-B	109.03	484.16	51.95	464.98	183.95	758.19	6.13	0.56	12.23	0.83	20.35	1.57	2.23	16.51	0.56	0.04	1.31	0.81	0.10	0.01	0.02	0.07	5.37		578.64	0.06	4.45
BLANK	-1.21	19.03	3.50	0.05	5.17	24.99	-1.79	2.30	-50.58	-0.01	0.00	-17.38	0.06	-0.16	-0.05	-0.40	0.05	0.04	-0.28	-0.02	0.55	-0.03	0.02	0.00	0.41	0.00	
BLANK	-1.45	18.74	3.41	-0.03	5.75	19.70	-1.83	2.11	-50.31	-0.01	0.00	-17.43	0.09	-0.09	-0.09	-0.42	0.05	0.04	-0.26	-0.03	0.50	0.03	0.30	-0.01	0.07	0.00	
Average	-1.33	18.88	3.46	0.01	5.46	22.34	-1.81	2.21	-50.44	-0.01	0.00	-17.41	0.08	-0.13	-0.07	-0.41	0.05	0.04	-0.27	-0.03	0.52	0.00	0.16	0.00	0.24	0.00	
C1	92.84	496.26	57.00	402.72	203.39	789.11	2.93	1.73	-32.09	0.80	20.92	-15.55	2.02	18.54	0.44	-0.40	1.31	0.79	-0.24	-0.02	0.48	0.04	5.42	0.00	538.27	0.06	
C1	94.66	514.33	57.93	415.30	209.51	791.17	3.29	1.64	-33.19	0.85	21.65	-15.65	2.12	19.00	0.45	-0.45	1.39	0.81	-0.22	0.00	0.46	0.05	5.72	0.00	550.23	0.06	
C1	96.91	517.41	57.73	414.08	212.25	789.94	3.14	1.86	-32.58	0.83	21.16	-15.66	2.06	18.68	0.42	-0.42	1.34	0.83	-0.17	-0.01	0.45	0.03	5.43	0.00	545.31	0.06	
Average	94.80	509.33	57.47	410.70	206.45	790.07	3.12	1.69	-32.62	0.82	21.24	-15.62	2.07	18.74	0.44	-0.43	1.35	0.81	-0.21	-0.01	0.46	0.04	5.57	0.00	544.60	0.06	
SC1-B	94.08	490.45	54.01	410.69	200.99	767.73	4.92	-0.52	17.83	0.84	21.25	1.79	2.00	18.87	0.51	-0.01	1.30	0.77	0.06	0.02	-0.06	0.04	5.41	0.00	544.36	0.06	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.00	0.06	-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.00	0.02	-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17	-19.57	11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.00	0.04	-0.02	0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	
C2	6.97	3252.05	185.84	12.69	421.43	1499.14	5.75	2.07	-12.81	1.75	0.47	0.57	2.04	329.89	-0.08	-0.25	0.00	5.82	0.21	-0.10	0.07	-0.02	1.93	-0.01	14.88	0.02	
C2	6.68	3245.42	190.16	12.86	412.15	1527.89	5.83	2.16	-14.74	1.80	0.50	0.51	1.48	362.67	-0.08	-0.25	0.00	6.15	0.24	-0.09	0.08	-0.03	2.06	-0.01	15.13	0.03	
Average	6.82	3248.74	188.00	12.77	416.79	1513.52	5.79	2.12	-13.77	1.77	0.49	0.54	1.76	346.28	-0.08	-0.25	0.00	5.99	0.22	-0.09	0.07	-0.02	1.99	-0.01	15.01	0.02	
SC2-B	6.04	3229.01	185.32	12.60	436.36	1501.89	-3.37	-1.18	30.08	1.78	0.49	0.56	3.46	349.34	0.02	0.00	0.00	5.94	0.24	-0.11	0.00	0.24	1.96	0.00	14.92	0.03	
BLANK	-1.21	19.03	3.50	0.05	5.17	24.99	-1.79	2.30	-50.58	-0.01	0.00	-17.38	0.06	-0.16	-0.05	-0.40	0.05	0.04	-0.28	-0.02	0.55	-0.03	0.02	0.00	0.41	0.00	
BLANK	-1.45	18.74	3.41	-0.03	5.75	19.70	-1.83	2.11	-50.31	-0.01	0.00	-17.43	0.09	-0.09	-0.09	-0.42	0.05	0.04	-0.26	-0.03	0.50	0.03	0.30	-0.01	0.07	0.00	
Average	-1.33	18.88	3.46	0.01	5.46	22.34	-1.81	2.21	-50.44	-0.01	0.00	-17.41	0.08	-0.13	-0.07	-0.41	0.05	0.04	-0.27	-0.03	0.52	0.00	0.16	0.00	0.24	0.00	
C3	20.33	1143.29	242.87	774.87	1094.66	1294.56	43.38	3.53	-15.41	2.25	0.13	-5.77	0.39	3.61	0.38	-0.29	2.18	2.29	-0.52	-0.03	0.58	-0.21	2.20	0.00	46.15	0.08	
C3	20.58	1208.94	249.39	802.69	1113.03	1275.53	45.34	3.57	-16.57	2.35	0.13	-4.89	0.45	3.56	0.34	-0.35	2.29	2.34	-0.58	-0.03	0.57	-0.28	2.25	0.00	47.93	0.08	
C3	16.74	940.87	191.17	624.18	912.96	987.26	33.73	1.90	-23.62	1.75	0.10	-8.21	0.19	2.26	0.29	-0.33	1.74	1.88	-0.61	-0.03	0.38	-0.29	1.68	0.00	35.57	0.07	
Average	19.22	1097.70	227.81	733.91	1040.22	1185.78	40.82	3.00	-18.53	2.12	0.12	-6.29	0.35	3.14	0.34	-0.32	2.07	2.17	-0.57	-0.03	0.51	-0.26	2.04	0.00	43.22	0.08	
SC3-B	19.22	1078.82	224.36	733.90	1034.76	1163.44	20.22	20.22	31.91	2.13	0.12	11.12	0.27	3.27	0.41	0.09	21.22	21.22	21.22	0.00	-0.02	-0.26	1.88	0.01	42.97	22.22	
BLANK	-1.21	19.03	3.50	0.05	5.17	24.99	-1.79	2.30	-50.58	-0.01	0.00	-17.38	0.06	-0.16	-0.05	-0.40	0.05	0.04	-0.28	-0.02	0.55	-0.03	0.02	0.00	0.41	0.00	
BLANK	-1.45	18.74	3.41	-0.03	5.75	19.70	-1.83	2.11	-50.31	-0.01	0.00	-17.43	0.09	-0.09	-0.09	-0.42	0.05	0.04	-0.26	-0.03	0.50	0.03	0.30	-0.01	0.07	0.00	
Average	-1.33	18.88	3.46	0.01	5.46	22.34	-1.81	2.21	-50.44	-0.01	0.00	-17.41	0.08	-0.13	-0.07	-0.41	0.05	0.04	-0.27	-0.03	0.52	0.00	0.16	0.00	0.24	0.00	
C4	1.23	472.67	15.79	209.39	158.51	56.92	5.36	3.51	-32.69	0.20	0.83	-16.68	0.89	1.07	0.05	-0.36	0.55	0.41	-0.88	-0.01	0.53	-0.31	6.75	0.00	3.26	0.07	
C4	0.88	479.75	15.82	213.55	160.95	55.34	5.56	3.69	-28.72	0.21	0.83	-16.99	0.81	1.18	0.04	-0.39	0.54	0.42	-0.93	0.00	0.47	-0.32	6.65	0.00	3.32	0.07	
C4	1.90	493.08	16.46	218.53	164.80	49.77	5.69	3.57	-31.27	0.21	0.86	-16.77	0.93	1.28	0.07	-0.33	0.56	0.43	-0.97	-0.01	0.55	-0.22	7.00	0.00	3.53	0.08	
Average	1.34	481.83	16.02	213.82	161.42	54.01	5.54		-30.89	0.20	0.84	-16.81	0.88	1.18	0.05	-0.36	0.55	0.42	-0.92	0.00	0.52	-0.28	6.80	0.00	3.37	0.07	
SC4-B	1.34	462.95	12.57	213.81	155.96	31.67	3.34	-2.21	19.55	0.22	0.84	4.34	0.80	5.34	0.13	0.05	5.34	5.34	5.34	0.02	-0.01	6.34		0.00	3.13	7.34	
BLANK	0.38	34.87	9.40	1.09	2.49	52.58	18.20	65.49	-6.96	0.05	0.01	-0.04	0.33	4.04	0.05	-0.24	0.11	0.04	-0.13	-0.01	0.53	0.09	0.07	0.00	0.13	0.00	6.95
BLANK	0.46	34.10	9.05	0.96	1.95	41.32	17.69	63.79	-7.11	0.03	0.00	0.01	0.36	3.76	0.05	-0.25	0.10	0.03	-0.12	0.01	0.49	0.01	0.09	0.00	0.11	0.00	6.85
Average	0.42	34.48	9.23	1.03	2.22	46.95	17.94	64.64	-7.03	0.04	0.01	-0.01	0.35	3.90	0.05	-0.24	0.11	0.04	-0.12	0.00	0.51	0.05	0.08	0.00	0.12	0.00	6.90
C5	4.45	725.70	86.93	634.23	473.80	163.67	30.49	61.20	0.99	0.72	3.06	0.39	1.53	7.32	0.14	-0.24	11.37	0.96	0.01	0.00	0.45	0.00	8.34	0.00	6.36	0.18	7.32
C5	4.87	713.98	84.62	620.81	461.15	155.67	33.15	64.42	1.89	0.71	2.91	0.42	1.68	7.69	0.14	-0.12	10.55	0.92	-0.08	0.00	0.49	0.08	8.23	0.00	7.65	0.20	7.05
C5	4.47	703.11	85.24	618.73	461.86	155.03	30.59	61.59	1.74	0.71	2.95	0.33	1.50	7.86	0.14	-0.17	10.73	0.93	-0.09	-0.01	0.45	0.03	8.25	0.00	5.97	0.17	6.74
Average	4.59	714.26	85.60	624.59	465.60	158.12	31.41	62.40	1.54	0.71	2.98	0.38	1.57	7.62	0.14	-0.18	10.89	0.93	-0.06	0.00	0.46	0.03	8.27	0.00	6.66	0.18	7.04
SC5-B	4.18	679.78	76.37	623.56	463.38	111.17	13.47	-2.24	8.57	0.67	2.97	0.39	1.23	3.72	0.09	0.07	10.78	0.90	0.07	0.00	-0.05	-0.01	8.19	0.00	6.54	0.18	0.14
BLANK	-1.21	19.03	3.50	0.05	5.17	24.99	-1.79	2.30	-50.58	-0.01	0.00	-17.38	0.06	-0.16	-0.05	-0.40	0.05	0.04	-0.28	-0.02	0.55	-0.03	0.02	0.00	0.41	0.00	
BLANK	-1.45	18.74	3.41	-0.03	5.75	19.70	-1.83	2.11	-50.31	-0.01	0.00	-17.43	0.09	-0.09	-0.09	-0.42	0.05	0.04	-0.26	-0.03	0.50	0.03	0.30	-0.01	0.07	0.00	
Average	-1.33	18.88	3.46	0.01	5.46	22.34	-1.81	2.21	-50.44	-0.01	0.00	-17.41	0.08	-0.13	-0.07	-0.41	0.05	0.04	-0.27	-0.03	0.52	0.00	0.16	0.00	0.24	0.00	
C5	1.17	454.61	48.50	385.38	309.57	97.17	9.44	3.60	-37.58	0.49	1.88	-16.24	0.69	4.20	0.04	-0.34	7.72	0.50	-0.79	0.00	0.42	-0.23	6.25	0.00	17.34	0.12	
C5	2.10	472.82	50.85	398.36	323.76	88.66	9.66	3.40	-36.22	0.50	1.98	-16.25	0.61	4.29	0.08	-0.29	7.80	0.50	-0.85	0.01	0.41	-0.30	6.44	0.00	17.78	0.13	
C5	2.33	472.30	50.40	398.78	319.16	93.20	9.55	2.95	-36.18	0.50	1.96	-16.28	0.75	4.23	0.10	-0.32	7.88	0.50	-0.87	-0.01	0.40	-0.32	6.57	0.00	18.10	0.13	
Average	1.87	466.58	49.92	394.17	317.49	93.01	9.55	3.32	-36.66	0.49	1.94	-16.26	0.68	4.24	0.07	-0.32	7.80	0.50	-0.84	0.00	0.41	-0.28	6.42	0.00	17.74	0.13	

	B 10	Na 23	Mg 24	Al 27	K 39	Ca 43	V 51	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 65	Zn 66	As 75	Se 82	Sr 88	Rb 85	Zr 90	Ag 109	Cd 111	Sn 118	Ba 137	Tl 205	Pb 207	U 238	Cr 52
SC5-B	1.87	447.69	46.46	394.16	312.04	70.66	3.87	1.11	13.79	0.51	1.94	4.87	0.61	4.37	0.14	0.09	5.87	5.87	5.87	0.03	-0.11	6.87	6.26	0.00	17.50	7.87	
BLANK	0.17	5.67	0.88	0.22	-7.90	-11.95	11.56	4.23	-56.56	-0.07	-0.04	-0.02	0.32	-1.58	0.00	-0.26	-0.05		-0.13	-0.10	0.40	-0.06	0.02	-0.04	-0.37	0.00	
BLANK	0.13	7.01	1.07	0.37	-4.76	-13.15	12.20	4.60	-56.62	-0.07	-0.04	0.01	0.29	-1.41	-0.01	-0.19	-0.04		-0.18	-0.11	0.41	-0.06	0.06	-0.04	-0.40	0.00	
Average	0.15	6.34	0.98	0.30	-6.33	-12.55	11.88	4.41	-56.59	-0.07	-0.04	-0.01	0.30	-1.49	0.00	-0.22	-0.04		-0.15	-0.10	0.41	-0.06	0.04	-0.04	-0.39	0.00	
C5	7.91	1306.92	94.50	70.69	410.15	235.70	15.03	5.65	-42.62	0.81	0.44	0.39	4.35	7.15	0.07	-0.27	4.71		-0.06	0.03	0.53	-0.03	8.48	-0.04	99.92	0.01	
C5	8.03	1319.75	97.36	72.84	421.05	246.21	15.33	5.72	-43.29	0.86	0.44	0.40	4.42	7.68	0.04	-0.29	4.72		-0.09	0.03	0.54	-0.09	8.62	-0.04	101.42	0.01	
Average	7.97	1313.33	95.93	71.77	415.60	240.96	15.18	5.69	-42.95	0.83	0.44	0.40	4.38	7.41	0.06	-0.28	4.71		-0.08	0.03	0.54	-0.06	8.55	-0.04	100.67	0.01	
SC5-B	7.82	1306.99	94.95	71.47	421.93	253.51	3.30	1.27	13.64	0.90	0.48	0.41	4.08	8.91	0.06	-0.06	4.76		0.08	0.13	0.13	0.00	8.51	0.00	101.05	0.01	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.06		-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.02		-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17	-19.57	11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.04		-0.02	0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	
C5	6.54	813.71	23.14	101.77	422.42	131.39	13.12	3.29	-36.05	0.40	0.49	0.23	-1.18	6.86	-0.07	-0.22	3.44		0.04	0.05	0.08	-0.25	3.36	-0.01	34.30	0.03	
C5	6.35	788.35	22.31	100.57	419.04	150.14	13.25	3.48	-37.65	0.41	0.48	0.23	-0.88	5.89	-0.05	-0.16	3.28		0.06	0.05	0.12	-0.25	3.31	-0.01	32.04	0.02	
Average	6.45	801.03	22.72	101.17	420.73	140.77	13.19	3.39	-36.85	0.41	0.49	0.23	-1.03	6.38	-0.06	-0.19	3.36		0.05	0.05	0.10	-0.25	3.34	-0.01	33.17	0.03	
SC5-B	5.67	19.73	20.05	101.00	440.30	129.14	4.02	0.09	7.00	0.41	0.50	0.25	0.68	9.44	0.04	0.06	3.32		0.07	0.04	0.03	0.02	3.30	0.00	33.08	0.03	
BLANK	0.38	34.87	9.40	1.09	2.49	52.58	18.20	65.49	-6.96	0.05	0.01	-0.04	0.33	4.04	0.05	-0.24	0.11	0.04	-0.13	-0.01	0.53	0.09	0.07	0.00	0.13	0.00	6.95
BLANK	0.46	34.10	9.05	0.96	1.95	41.32	17.69	63.79	-7.11	0.03	0.00	0.01	0.36	3.76	0.05	-0.25	0.10	0.03	-0.12	0.01	0.49	0.01	0.09	0.00	0.11	0.00	6.85
Average	0.42	34.48	9.23	1.03	2.22	46.95	17.94	64.64	-7.03	0.04	0.01	-0.01	0.35	3.90	0.05	-0.24	0.11	0.04	-0.12	0.00	0.51	0.05	0.08	0.00	0.12	0.00	6.90
C6	5.09	427.12	53.76	249.59	131.92	74.31	20.89	61.74	21.95	2.65	2.11	12.02	4.94	11.59	0.13	-0.24	0.54	0.57	-0.12	-0.01	0.50	0.07	2.34	0.00	70.12	0.11	6.39
C6	5.37	447.95	54.66	256.31	141.20	76.09	21.30	63.21	22.18	2.70	2.10	11.45	4.86	11.28	0.15	-0.24	0.52	0.57	-0.07	0.01	0.55	0.05	2.26	0.00	71.23	0.11	6.80
Average	5.23	437.54	54.21	252.95	136.56	75.20	21.10	62.48	22.06	2.68	2.10	11.73	4.90	11.44	0.14	-0.24	0.53	0.57	-0.09	0.00	0.53	0.06	2.30	0.00	70.67	0.11	6.59
SC6-B	4.81	403.05	44.98	251.92	134.34	28.25	3.15	-2.16	29.10	2.64	2.10	11.75	4.55	7.53	0.09	0.01	0.42	0.54	0.03	0.00	0.02	0.01	2.22	0.00	70.55	0.11	-0.31
BLANK	-1.21	19.03	3.50	0.05	5.17	24.99	-1.79	2.30	-50.58	-0.01	0.00	-17.38	0.06	-0.16	-0.05	-0.40	0.05	0.04	-0.28	-0.02	0.55	-0.03	0.02	0.00	0.41	0.00	
BLANK	-1.45	18.74	3.41	-0.03	5.75	19.70	-1.83	2.11	-50.31	-0.01	0.00	-17.43	0.09	-0.09	-0.09	-0.42	0.05	0.04	-0.26	-0.03	0.50	0.03	0.30	-0.01	0.07	0.00	
Average	-1.33	18.88	3.46	0.01	5.46	22.34	-1.81	2.21	-50.44	-0.01	0.00	-17.41	0.08	-0.13	-0.07	-0.41	0.05	0.04	-0.27	-0.03	0.52	0.00	0.16	0.00	0.24	0.00	
C6	10.07	748.04	74.28	426.91	223.32	95.16	11.17	1.51	8.10	5.28	3.98	-15.03	2.35	4.93	0.12	-0.44	0.69	0.69	-0.15	-0.01	0.52	0.09	3.07	0.00	151.15	0.28	
C6	10.94	763.50	75.78	429.20	221.02	94.39	11.29	1.55	9.08	5.36	4.00	-15.42	2.22	5.04	0.10	-0.40	0.68	0.69	-0.20	-0.02	0.49	0.00	3.06	0.00	153.12	0.29	
Average	10.50	755.77	75.03	428.06	222.17	94.77	11.23	1.53	8.59	5.32	3.99	-15.22	2.28	4.98	0.11	-0.42	0.69	0.69	-0.17	-0.01	0.51	0.04	3.06	0.00	152.13	0.28	
SC6-B	10.50	736.88	71.57	11.50	12.50	12.50	12.50	12.50	13.50	13.50	13.50	2.18	2.21	14.50	0.18	15.50	0.64	15.50	0.10	0.02	-0.01	16.50	2.90	0.00	17.50	0.28	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.06		-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.02		-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17	-19.57	11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.04		-0.02	0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	
C6	11.80	735.43	42.43	501.99	186.67	36.97	14.84	3.22	-2.42	3.08	3.67	0.50	1.17	0.58	0.03	-0.23	0.57		-0.01	0.01	0.11	-0.22	3.87	-0.01	113.32	0.10	
C6	11.50	745.65	42.83	499.57	184.66	44.49	14.49	3.37	-1.75	3.05	3.59	0.55	1.08	0.62	0.01	-0.24	0.55		0.00	-0.01	0.08	-0.23	3.90	0.00	113.90	0.12	
Average	11.65	740.54	42.63	500.78	185.67	40.73	14.66	3.29	-2.08	3.07	3.63	0.52	1.12	0.60	0.02	-0.24	0.56		0.00	0.00	0.09	-0.23	3.88	-0.01	113.61	0.11	
SC6-B	10.87	720.81	39.96	500.61	205.23	29.11	5.50	-0.01	41.77	3.07	3.64	0.55	2.83	3.66	0.12	0.01	0.52		0.02	-0.01	0.02	0.04	3.85	0.00	113.52	0.11	
BLANK	0.38	34.87	9.40	1.09	2.49	52.58	18.20	65.49	-6.96	0.05	0.01	-0.04	0.33	4.04	0.05	-0.24	0.11	0.04	-0.13	-0.01	0.53	0.09	0.07	0.00	0.13	0.00	6.95
BLANK	0.46	34.10	9.05	0.96	1.95	41.32	17.69	63.79	-7.11	0.03	0.00	0.01	0.36	3.76	0.05	-0.25	0.10	0.03	-0.12	0.01	0.49	0.01	0.09	0.00	0.11	0.00	6.85
Average	0.42	34.48	9.23	1.03	2.22	46.95	17.94	64.64	-7.03	0.04	0.01	-0.01	0.35	3.90	0.05	-0.24	0.11	0.04	-0.12	0.00	0.51	0.05	0.08	0.00	0.12	0.00	6.90
C7	3.16	713.47	70.34	594.20	435.29	157.39	30.16	68.47	33.59	1.34	2.37	18.35	2.29	10.66	0.42	-0.19	9.90	0.83	-0.08	0.02	0.54	0.10	11.22	0.00	137.84	0.15	7.45
C7	3.36	713.35	69.31	587.71	423.38	157.90	29.40	66.56	31.72	1.31	2.34	18.64	2.33	10.99	0.42	-0.24	9.47	0.80	-0.09	0.02	0.55	0.13	10.72	0.00	137.76	0.15	7.23
Average	3.26	713.41	69.82	590.96	429.33	157.64	29.78	67.51	32.66	1.32	2.35	18.49	2.31	10.82	0.42	-0.22	9.68	0.82	-0.09	0.02	0.54	0.11	10.97	0.00	137.80	0.15	7.34
SC7-B	2.84	678.93	60.59	589.93	427.11	110.69	11.84	2.87	39.69	1.28	2.35	18.51	1.96	6.92	0.37	0.03	9.58	0.78	0.04	0.02	0.03	0.07	10.89	0.00	137.68	0.14	0.44
BLANK	-1.21	19.03	3.50	0.05	5.17	24.99	-1.79	2.30	-50.58	-0.01	0.00	-17.38	0.06	-0.16	-0.05	-0.40	0.05	0.04	-0.28	-0.02	0.55	-0.03	0.02	0.00	0.41	0.00	
BLANK	-1.45	18.74	3.41	-0.03	5.75	19.70	-1.83	2.11	-50.31	-0.01	0.00	-17.43	0.09	-0.09	-0.09	-0.42	0.05	0.04	-0.26	-0.03	0.50	0.03	0.30	-0.01	0.07	0.00	
Average	-1.33	18.88	3.46	0.01	5.46	22.34	-1.81	2.21	-50.44	-0.01	0.00	-17.41	0.08	-0.13	-0.07	-0.41	0.05	0.04	-0.27	-0.03	0.52	0.00	0.16	0.00	0.24	0.00	
C7	-0.70	436.92	39.99	359.56	283.55	96.63	6.26	4.24	-37.12	0.44	1.49	-16.13	1.06	4.95	0.30	-0.21	8.37	0.40	-0.73	0.00	0.43	-0.27	5.79	0.00	35.00	0.08	
C7	-0.01	429.38	40.92	366.76	278.20	102.25	5.55	1.63	-37.29	0.47	1.54	-16.36	1.24	4.79	0.32	-0.28	8.47	0.41	-0.83	-0.01	0.46	-0.27	5.92	0.00	34.28	0.09	
C7	-0.56	437.29	41.05	368.53	283.48	100.20	5.80	1.56	-37.15	0.45	1.54	-16.33	1.08	5.00	0.31	-0.32	8.35	0.41	-0.93	-0.01	0.43	-0.30	5.89	0.00	35.95	0.08	
Average	-0.42	434.53	40.45	364.95	281.74	99.69	5.87	2.48	-37.19	0.45	1.53	-16.27	1.13	4.91	0.31	-0.27	8.40	0.41	-0.83	-0.01	0.44	-0.27	5.87	0.00	34.64	0.09	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.06		-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.02		-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17	-19.57	11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.04		-0.02	0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	
C7	3.56	1380.97	132.23	947.81	683.24	222.60	29.55	3.38	-27.59	1.25	4.04	0.78	1.08	3.84	0.72	-0.20	23.71		0.08	0.05	0.17	-0.21	15.25	0.00	189.75	0.23	
C7	3.97	1283.46	121.90	894.88	642.71	212.14	26.99	3.33	-27.96	1.18	3.72	0.66	0.84	5.66	0.71	-0.21	21.82		0.02	0.04	0.17	-0.22	14.42	0.00	181.36	0.21	
Average	3.76	1332.21	127.07	921.35	662.97	217.37	28.27	3.35	-27.77	1.21	3.88	0.72	0.96	4.75	0.71	-0.20	22.77		0.05	0.05	0.17	-0.21	14.83	0.00	185.55	0.22	
SC7-B	2.98	1312.48	124.40	921.18	682.54	205.75	19.11	0.06	<DL	1.22	3.88	0.72	0.96	4.75	0.81	0.05	22.73		0.07	0.03	0.09	0.05	14.80	0.00	185.47	0.22	
BLANK	1.14	29.11	4.09	0.33	-20.14	16.08	9.35	3.44	-43.50	0.00	-0.01	-0.06	-1.63	-3.22	-0.11	-0.27	0.06		-0.03	0.01	0.06	-0.29	0.03	-0.01	0.06	0.00	
BLANK	0.43	10.35	1.25	0.01	-19.00	7.17	8.98	3.16	-44.21	-0.01	-0.01	0.02	-1.78	-2.90	-0.08	-0.24	0.02		-0.01	0.02	0.09	-0.25	0.04	-0.01	0.11	0.00	
Average	0.78	19.73	2.67	0.17	-19.57	11.62	9.16	3.30	-43.85	0.00	-0.01	-0.02	-1.70	-3.06	-0.10	-0.25	0.04		-0.02	0.01	0.08	-0.27	0.03	-0.01	0.09	0.00	
C8	63.91	11193.59	262.53	1424.28	4223.66	529.17	37.08	4.28	145.11	54.28	13.73	1.12	2.31	10.96	0.09	-0.15	5.59		0.08	0.21	0.22	-0.23	18.82	0.01	963.48	0.68	
C8	67.19	11038.61	260.70	1429.24	4249.59	481.42	36.61	4.36	139.55	53.93	13.73	1.27	2.40	10.02	0.06	-0.21	5.49		0.02	0.22	0.22	-0.22	19.21	0.02	988.56	0.70	
Average	65.55	11116.10	261.61	1426.76	4236.62	505.29	36.85	4.32	142.33	54.11	13.73	1.20	2.35	10.49	0.07	-0.18	5.54		0.05	0.22	0.22	-0.23	19.02	0.02	976.02	0.69	
SC8-B	64.77	11096.37	258.94	1426.59	4256.19	493.67	27.68	1.02	186.18	54.11	13.74	1.22	4.06	13.55	0.17	0.07	5.50		0.07	0.20	0.14	0.04	18.99	0.02	975.93	0.69	

Orange juice leach test calculations

	B 10	Na 23	Mg 24	Al 27	K 39	Ca 43	V 51	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 65	Zn 66	As 75	Se 82	Sr 88	Rb 85	Ag 109	Cd 111	Sn 118	Ba 137	Tl 205	Pb 207	U 238
Blank 1	79.08	1231.87	7581.96	2.69	**HIGH**	7286.88	0.35	3.11	31.37	21.49	0.12	0.62	15.97	13.02	0.17	0.23	31.49	137.65	0.07	0.00	-0.05	18.74	0.01	-0.06	0.00
Blank 2	80.28	1260.04	7649.85	3.40	**HIGH**	7367.62	0.14	2.66	29.96	21.96	0.14	0.99	17.66	39.75	0.03	0.01	33.77	141.43	0.05	0.13	0.54	19.96	0.02	-0.06	0.00
Average	79.68	1245.96	7615.90	3.04	**HIGH**	7327.25	0.25	2.88	30.67	21.73	0.13	0.80	16.81	26.38	0.10	0.12	32.63	139.54	0.06	0.06	0.24	19.35	0.01	-0.06	0.00
Orange A3	86.08	1396.94	8548.86	3.31	**HIGH**	8084.61	-0.03	2.33	37.38	24.32	0.14	0.80	19.11	15.54	0.09	0.02	35.95	147.92	0.04	0.01	-0.06	21.61	0.01	-0.09	0.00
Orange A3	90.13	1299.65	8100.72	3.14	**HIGH**	7813.81	-0.15	1.86	35.73	23.73	0.15	0.78	18.39	15.17	0.11	0.17	34.91	144.34	0.06	0.01	-0.06	20.84	0.01	-0.11	0.00
Average	88.11	1348.30	8324.79	3.22	**HIGH**	7949.21	-0.09	2.09	36.55	24.02	0.14	0.79	18.75	15.35	0.10	0.09	35.43	146.13	0.05	0.01	-0.06	21.23	0.01	-0.10	0.00
SB-A3-1	8.42	102.34	708.89	0.18	**HIGH**	621.96	<DL	-0.79	5.89	2.30	0.01	-0.01	1.94	-11.03	0.00	-0.03	2.79	6.59	-0.01	-0.06	-0.31	1.88	0.00	-0.04	0.00
Orange A7	94.22	1395.63	8775.23	3.44	**HIGH**	8290.85	-0.32	1.84	37.44	25.67	0.14	0.81	19.13	16.20	0.09	0.08	36.31	150.94	0.05	0.01	-0.09	22.69	0.01	-0.12	0.00
Orange A7	89.10	1305.54	8433.56	3.08	**HIGH**	7940.50	-0.33	1.53	36.51	24.30	0.14	0.76	18.78	13.84	0.15	-0.04	34.33	143.60	0.05	0.00	-0.09	21.04	0.01	-0.12	0.00
Average	91.66	1350.59	8604.40	3.26	**HIGH**	8115.68	-0.33	1.69	36.98	24.98	0.14	0.79	18.95	15.02	0.12	0.02	35.32	147.27	0.05	0.01	-0.09	21.86	0.01	-0.12	0.00
SB-A7	11.98	104.63	988.49	0.22	**HIGH**	788.43	<DL	-1.20	6.31	3.25	0.01	-0.02	2.14	-11.36	0.02	-0.10	2.69	7.73	-0.01	-0.06	-0.33	2.52	0.00	-0.06	0.00
Orange A9	100.13	1489.72	9323.70	3.85	**HIGH**	8951.97	-0.16	2.28	44.52	27.54	0.19	0.97	21.06	17.66	0.18	0.17	38.95	160.52	0.04	0.02	-0.07	23.64	0.02	-0.08	0.00
Orange A9	86.30	1309.97	8312.27	3.08	**HIGH**	7817.05	-0.24	1.71	35.35	24.24	0.15	0.81	18.30	15.09	-0.04	0.03	34.03	146.46	0.04	0.01	-0.08	21.12	0.01	-0.08	0.00
Average	93.21	1399.85	8817.99	3.47	**HIGH**	8384.51	-0.20	2.00	39.94	25.89	0.17	0.89	19.68	16.38	0.07	0.10	36.49	153.49	0.04	0.02	-0.07	22.38	0.01	-0.08	0.00
SB-A9	13.53	153.89	1202.08	0.42	**HIGH**	1057.26	<DL	-0.89	9.27	4.16	0.04	0.09	2.86	-10.01	-0.03	-0.02	3.86	13.95	-0.02	-0.05	-0.32	3.03	0.00	-0.02	0.00
Orange A10	95.89	1433.19	8895.20	3.47	**HIGH**	8423.09	-0.41	1.45	39.20	26.68	0.16	0.98	20.51	26.86	0.17	0.22	37.78	153.19	0.05	0.00	-0.09	23.28	0.01	-0.09	0.00
Orange A10	101.49	1464.18	9461.80	3.70	**HIGH**	8915.60	-0.47	1.12	41.89	28.11	0.17	0.99	21.32	28.38	0.15	0.12	39.65	167.35	0.03	0.02	-0.10	24.99	0.01	-0.10	0.00
Average	98.69	1448.68	9178.50	3.59	**HIGH**	8669.34	-0.44	1.28	40.55	27.40	0.17	0.98	20.91	27.62	0.16	0.17	38.72	160.27	0.04	0.01	-0.09	24.13	0.01	-0.09	0.00
SB-A10	19.01	202.73	1562.59	0.54	**HIGH**	1342.09	<DL	-1.60	9.88	5.67	0.03	0.18	4.10	1.24	0.06	0.05	6.09	20.73	-0.02	-0.05	-0.34	4.79	0.00	-0.03	0.00
Orange A11	87.22	1266.46	7993.75	3.41	**HIGH**	7586.50	-0.39	1.12	35.12	23.36	0.15	0.91	18.34	21.18	0.07	0.08	34.47	143.66	0.04	0.01	-0.01	20.95	0.01	-0.09	0.00
Orange A11	93.07	1330.84	8606.28	3.54	**HIGH**	8138.51	-0.41	1.47	36.52	24.91	0.16	0.82	19.88	19.22	0.12	0.15	35.97	148.45	0.04	0.03	-0.10	22.43	0.01	-0.09	0.00
Average	90.15	1298.65	8300.02	3.48	**HIGH**	7862.50	-0.40	1.29	35.82	24.13	0.15	0.86	19.11	20.20	0.09	0.12	35.22	146.05	0.04	0.02	-0.06	21.69	0.01	-0.09	0.00
SB-A11	10.46	52.69	684.11	0.43	**HIGH**	535.25	<DL	-1.59	5.15	2.40	0.02	0.06	2.30	-6.18	0.00	-0.01	2.59	6.51	-0.02	-0.05	-0.30	2.35	0.00	-0.03	0.00
Orange B6	87.72	1271.05	8152.35	3.05	**HIGH**	7801.90	-0.54	0.89	33.90	23.95	0.15	0.81	18.74	16.49	0.08	0.14	34.00	141.88	0.05	0.01	-0.10	21.13	0.01	0.08	0.00
Orange B6	86.47	1282.52	8171.02	2.92	**HIGH**	7820.17	-0.56	0.56	34.68	24.09	0.14	0.77	17.93	12.87	0.05	-0.01	34.82	146.99	0.04	0.00	-0.07	21.47	0.01	0.04	0.00
Average	87.09	1276.79	8161.69	2.98	**HIGH**	7811.03	-0.55	0.73	34.29	24.02	0.15	0.79	18.33	14.68	0.06	0.06	34.41	144.43	0.04	0.01	-0.08	21.30	0.01	0.06	0.00
SB-B6	7.41	30.83	545.78	-0.06	**HIGH**	483.78	<DL	-2.16	3.62	2.30	0.01	-0.01	1.52	-11.70	-0.03	-0.06	1.78	4.89	-0.02	-0.06	-0.33	1.95	0.00	0.11	0.00
Orange C1	98.92	1403.10	9194.33	7.38	**HIGH**	8809.81	-0.62	0.79	42.41	25.91	0.46	1.00	20.95	62.69	0.10	-0.14	37.69	153.31	0.05	0.01	0.32	23.42	0.01	4.51	0.00
Orange C1	103.10	1457.61	9402.19	7.95	**HIGH**	9150.75	-0.66	0.76	45.53	26.92	0.47	1.11	21.51	65.96	0.05	0.07	40.26	165.34	0.05	0.02	0.35	24.72	0.01	4.79	0.00
Average	101.01	1430.36	9298.26	7.67	**HIGH**	8980.28	-0.64	0.78	43.97	26.42	0.47	1.06	21.23	64.33	0.08	-0.04	38.98	159.33	0.05	0.01	0.34	24.07	0.01	4.65	0.00
SB-C1	21.32	184.40	1682.35	4.62	**HIGH**	1653.03	<DL	-2.11	13.30	4.69	0.34	0.25	4.42	37.94	-0.02	-0.16	6.34	19.78	-0.01	-0.05	0.09	4.72	0.00	4.70	0.00
Orange C2	88.17	1275.28	8347.89	3.10	**HIGH**	7834.12	-0.60	0.53	32.03	23.93	0.15	0.79	18.91	13.73	0.05	0.09	34.30	142.94	0.04	0.00	-0.09	20.82	0.01	-0.07	0.00
Orange C2	89.77	1311.98	8548.88	3.42	**HIGH**	8105.23	-0.63	0.63	36.35	24.66	0.14	0.79	18.96	15.73	0.07	-0.02	35.26	149.74	0.04	-0.01	-0.08	21.21	0.01	-0.08	0.00
Average	88.97	1293.63	8448.39	3.26	**HIGH**	7969.67	-0.62	0.58	34.19	24.30	0.15	0.79	18.94	14.73	0.06	0.03	34.78	146.34	0.04	0.00	-0.09	21.01	0.01	-0.08	0.00
SB-C2	9.28	47.67	832.48	0.21	**HIGH**	642.43	<DL	-2.31	3.52	2.57	0.02	-0.02	2.12	-11.66	-0.04	-0.09	2.14	6.79	-0.02	-0.07	-0.33	1.67	0.00	-0.02	0.00
Orange C8	100.64	1434.84	9626.37	4.01	**HIGH**	8875.27	-0.71	0.70	41.03	27.73	0.17	0.93	21.68	15.53	0.11	0.10	39.96	165.58	0.03	0.00	-0.09	24.19	0.01	0.39	0.00
Orange C8	96.14	1334.21	8826.64	3.72	**HIGH**	8449.62	-0.75	0.07	37.48	25.66	0.15	0.84	20.02	14.60	0.07	0.07	36.99	151.39	0.03	0.02	-0.09	22.23	0.01	0.35	0.00
Average	98.39	1384.52	9226.50	3.87	**HIGH**	8662.44	-0.73	0.38	39.25	26.69	0.16	0.88	20.85	15.07	0.09	0.08	38.48	158.49	0.03	0.01	-0.09	23.21	0.01	0.37	0.00
SB-C8	18.71	138.57	1610.60	0.82	**HIGH**	1335.19	-0.98	-2.50	8.59	4.97	0.03	0.08	4.04	-11.32	-0.01	-0.04	5.85	18.94	-0.03	-0.05	-0.33	3.86	0.00	0.43	0.00
Blank 1	0.04	91.01	172.86	5.92	3091.11	193.65	-0.41	0.00	-2.02	0.43	0.01	0.66	2.48	3.73	-0.04	0.01	0.89	3.06	0.02	0.02	0.05	0.60	0.00	-0.04	-0.01
Blank 2	0.16	92.05	179.52	5.84	3177.27	196.75	-0.62	-0.60	-4.68	0.40	0.02	0.66	2.36	3.57	0.06	0.02	0.86	2.88	0.03	0.02	0.00	0.58	0.00	-0.07	-0.01
Average	0.10	91.53	176.19	5.88	3134.19	195.20	-0.51	-0.30	-3.35	0.41	0.01	0.66	2.42	3.65	0.01	0.01	0.87	2.97	0.03	0.02	0.02	0.59	0.00	-0.06	-0.01

	B 10	Na 23	Mg 24	Al 27	K 39	Ca 43	V 51	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 65	Zn 66	As 75	Se 82	Sr 88	Rb 85	Ag 109	Cd 111	Sn 118	Ba 137	Tl 205	Pb 207	U 238
Orange A3	0.56	93.09	160.37	4.25	2743.17	165.05	-1.22	-2.93	-5.37	0.30	0.01	0.73	2.16	2.69	-0.08	-0.07	0.76	2.59	0.02	0.04	-0.03	0.52	0.00	-0.04	-0.01
Orange A3	-0.12	87.49	156.30	4.08	2693.29	171.35	-1.25	-2.96	-7.06	0.29	0.02	0.62	1.96	2.32	-0.02	-0.08	0.80	2.63	0.02	0.01	-0.03	0.51	0.00	-0.07	-0.01
Average	0.22	90.29	158.34	4.16	2718.23	168.20	-1.24	-2.95	-6.21	0.30	0.02	0.67	2.06	2.51	-0.05	-0.08	0.78	2.61	0.02	0.02	-0.03	0.51	0.00	-0.05	-0.01
SB-A3-1	0.13	-1.24	-17.85	-1.72	-415.96	-27.00	-0.73	-2.65	-2.87	-0.12	0.00	0.01	-0.36	-1.14	-0.06	-0.09	-0.09	-0.36	-0.01	0.00	-0.05	-0.08	0.00	0.00	0.00
Orange A7	0.57	90.03	179.80	3.10	3213.44	198.67	-0.89	-1.46	-5.70	0.40	0.01	0.62	1.83	2.70	-0.08	-0.07	0.88	3.11	0.03	0.03	-0.02	0.58	0.00	-0.10	-0.01
Orange A7	0.80	91.52	187.85	3.55	3159.39	200.86	-0.91	-1.70	-7.82	0.39	0.01	0.56	2.03	2.74	-0.08	-0.06	0.90	3.02	0.02	0.02	-0.03	0.55	0.00	-0.08	-0.01
Average	0.69	90.77	183.83	3.32	3186.42	199.76	-0.90	-1.58	-6.76	0.39	0.01	0.59	1.93	2.72	-0.08	-0.07	0.89	3.07	0.03	0.03	-0.03	0.56	0.00	-0.09	-0.01
SB-A7	0.59	-0.75	7.64	-2.56	52.23	4.56	-0.39	-1.28	-3.41	-0.02	0.00	-0.07	-0.49	-0.93	-0.09	-0.08	0.02	0.10	0.00	0.01	-0.05	-0.03	0.00	-0.04	0.00
Orange A9	0.07	82.88	162.88	1.12	2797.76	171.60	-1.24	-2.67	-6.72	0.32	0.01	0.52	1.82	2.08	-0.08	-0.07	0.83	2.74	0.03	0.02	-0.04	0.55	0.00	-0.10	-0.01
Orange A9	0.09	86.28	171.04	1.58	2959.38	173.71	-1.23	-2.61	-2.74	0.34	0.01	0.55	1.82	2.21	-0.07	-0.11	0.79	2.72	0.02	0.02	-0.03	0.53	0.00	0.02	-0.01
Average	0.08	84.58	166.96	1.35	2878.57	172.65	-1.24	-2.64	-4.73	0.33	0.01	0.53	1.82	2.14	-0.07	-0.09	0.81	2.73	0.02	0.02	-0.03	0.54	0.00	-0.04	-0.01
SB-A9	-0.02	-6.95	-9.23	-4.53	-255.61	-22.55	-0.73	-2.34	-1.38	-0.08	0.00	-0.13	-0.60	-1.51	-0.08	-0.11	-0.07	-0.24	0.00	0.00	-0.05	-0.05	0.00	0.01	0.00
Orange A10	-0.09	87.86	169.03	1.04	2846.86	198.34	-1.17	-2.61	-6.42	0.33	0.01	0.62	2.24	2.46	0.01	-0.09	0.82	2.70	0.08	0.04	-0.04	0.55	0.00	-0.08	-0.01
Orange A10	0.15	92.08	173.40	1.02	2913.61	181.05	-1.20	-2.65	-6.39	0.34	0.01	0.57	2.29	2.52	-0.02	-0.02	0.84	2.84	0.03	0.04	-0.03	0.52	0.00	-0.08	-0.01
Average	0.03	89.97	171.21	1.03	2880.23	189.70	-1.18	-2.63	-6.41	0.33	0.01	0.59	2.27	2.49	0.00	-0.05	0.83	2.77	0.06	0.04	-0.04	0.54	0.00	-0.08	-0.01
SB-A10	-0.07	-1.56	-4.98	-4.85	-253.95	-5.50	-0.67	-2.33	-3.06	-0.08	0.00	-0.07	-0.15	-1.16	-0.01	-0.06	-0.05	-0.20	0.03	0.02	-0.06	-0.05	0.00	-0.02	0.00
Orange A11	0.25	90.74	167.33	6.92	2905.98	182.92	-1.30	-2.84	-5.99	0.41	0.01	1.27	1.92	2.82	0.00	-0.04	0.85	2.82	0.02	0.02	-0.03	0.49	0.00	-0.08	-0.01
Orange A11	0.62	93.64	173.88	8.17	2986.85	189.68	-1.29	-2.83	-5.93	0.35	0.01	0.81	1.89	2.70	0.05	-0.06	0.84	2.75	0.02	0.03	-0.05	0.53	0.00	-0.08	-0.01
Average	0.43	92.19	170.60	7.54	2946.41	186.30	-1.30	-2.84	-5.96	0.38	0.01	1.04	1.90	2.76	0.02	-0.05	0.85	2.79	0.02	0.02	-0.04	0.51	0.00	-0.08	-0.01
SB-A11	0.34	0.66	-5.59	1.66	-187.77	-8.90	-0.78	-2.54	-2.61	-0.03	0.00	0.38	-0.52	-0.89	0.02	-0.06	-0.03	-0.18	-0.01	0.01	-0.06	-0.09	0.00	-0.02	0.00
Orange B6	0.51	90.46	171.26	3.37	3041.74	181.14	-0.91	-1.70	-4.27	0.36	0.02	0.58	1.95	2.44	-0.12	-0.18	0.82	2.80	0.02	0.00	-0.03	0.55	0.00	-0.05	-0.01
Orange B6	0.49	91.22	170.04	3.22	2974.92	184.59	-1.03	-2.23	-6.07	0.35	0.01	0.64	1.87	2.65	-0.12	-0.14	0.87	2.76	0.03	0.01	-0.02	0.57	0.00	-0.10	-0.01
Average	0.50	90.84	170.65	3.30	3008.33	182.87	-0.97	-1.96	-5.17	0.36	0.01	0.61	1.91	2.54	-0.12	-0.16	0.84	2.78	0.03	0.01	-0.03	0.56	0.00	-0.08	-0.01
SB-B6	0.40	-0.69	-5.54	-2.58	-125.85	-12.33	-0.46	-1.66	-1.82	-0.06	0.00	-0.05	-0.51	-1.11	-0.13	-0.17	-0.03	-0.19	0.00	-0.01	-0.05	-0.03	0.00	-0.02	0.00
Orange C1	0.36	93.81	181.11	3.92	3208.71	207.88	-0.66	-1.09	-5.52	0.41	0.02	0.63	2.11	3.18	-0.05	-0.01	0.91	2.99	0.02	0.02	0.02	0.53	0.00	0.19	-0.01
Orange C1	0.17	89.77	178.89	4.03	3192.43	192.39	-0.81	-1.39	-5.38	0.42	0.02	0.61	2.18	3.47	-0.04	0.03	0.89	3.02	0.02	0.03	0.01	0.58	0.00	0.14	-0.01
Average	0.26	91.79	180.00	3.97	3200.57	200.14	-0.74	-1.24	-5.45	0.41	0.02	0.62	2.14	3.33	-0.04	0.01	0.90	3.01	0.02	0.02	0.01	0.56	0.00	0.17	-0.01
SB-C1	0.17	0.26	3.81	-1.91	66.38	4.94	-0.23	-0.94	-2.10	0.00	0.00	-0.05	-0.27	-0.32	-0.05	0.00	0.03	0.04	-0.01	0.01	-0.01	-0.04	0.00	0.22	0.00
Orange C2	0.18	89.78	169.06	7.05	2842.57	180.46	-1.10	-2.24	-3.53	0.34	0.01	0.61	1.79	2.54	-0.07	-0.04	0.82	2.82	0.03	0.00	-0.05	0.50	0.00	-0.09	-0.01
Orange C2	0.02	90.27	164.94	6.82	2912.65	185.18	-1.14	-2.21	-6.27	0.36	0.01	0.59	1.82	2.42	-0.04	-0.09	0.84	2.83	0.04	0.03	-0.03	0.52	0.00	-0.06	-0.01
Average	0.10	90.02	167.00	6.94	2877.61	182.82	-1.12	-2.23	-4.90	0.35	0.01	0.60	1.81	2.48	-0.06	-0.07	0.83	2.82	0.03	0.02	-0.04	0.51	0.00	-0.08	-0.01
SB-C2	0.00	-1.51	-9.19	1.06	-256.58	-12.38	-0.61	-1.93	-1.55	-0.06	0.00	-0.07	-0.61	-1.18	-0.07	-0.08	-0.05	-0.15	0.01	0.00	-0.06	-0.08	0.00	-0.02	0.00
Orange C8	0.09	90.98	178.45	1.71	3209.40	191.36	-1.10	-2.14	-7.19	0.40	0.01	0.71	2.21	2.47	-0.05	-0.01	0.87	3.01	0.03	0.02	-0.03	0.60	0.00	-0.03	-0.01
Orange C8	0.10	92.55	185.93	1.84	3205.64	185.07	-1.11	-2.33	-6.13	0.41	0.01	0.60	2.11	2.31	-0.10	-0.02	0.88	3.07	0.03	0.03	-0.01	0.58	0.00	-0.05	-0.01
Average	0.10	91.76	182.19	1.78	3207.52	188.22	-1.11	-2.24	-6.66	0.41	0.01	0.66	2.16	2.39	-0.07	-0.01	0.88	3.04	0.03	0.03	-0.02	0.59	0.00	-0.04	-0.01
SB-C8	0.00	0.24	6.00	-4.10	73.33	-6.98	-0.59	-1.94	-3.31	-0.01	0.00	0.00	-0.26	-1.26	-0.08	-0.02	0.00	0.07	0.00	0.01	-0.04	0.00	0.00	0.02	0.00
Blank 1	5.95	2097.79	581.41	56.47	12217.76	4641.73	0.12	0.64	-65.72	63.32	0.00	1.10	6.51	28.60	0.11	0.17	4.58	33.79	-0.15	0.07	-0.06	1.53	-0.05	0.08	-0.01
Blank2	2.95	1823.20	601.08	45.14	13294.06	4539.53	0.13	0.62	-64.69	59.21	0.01	1.37	4.93	21.69	-0.07	0.02	3.61	37.92	-0.15	0.03	0.00	1.11	-0.05	0.27	-0.01
Average	4.45	1960.50	591.24	50.80	12755.91	4590.63	0.12	0.63	-65.21	61.27	0.00	1.24	5.72	25.15	0.02	0.09	4.09	35.86	-0.15	0.05	-0.03	1.32	-0.05	0.17	-0.01

	B 10	Na 23	Mg 24	Al 27	K 39	Ca 43	V 51	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 65	Zn 66	As 75	Se 82	Sr 88	Rb 85	Ag 109	Cd 111	Sn 118	Ba 137	Tl 205	Pb 207	U 238
Hot Lemon Tea leaching test calculation																									
Blank 1	5.95	2097.79	581.41	56.47	12217.76	4641.73	0.12	0.64	-65.72	63.32	0.00	1.10	6.51	28.60	0.11	0.17	4.58	33.79	-0.15	0.07	-0.06	1.53	-0.05	0.08	-0.01
Blank2	2.95	1823.20	601.08	45.14	13294.06	4539.53	0.13	0.62	-64.69	59.21	0.01	1.37	4.93	21.69	-0.07	0.02	3.61	37.92	-0.15	0.03	0.00	1.11	-0.05	0.27	-0.01
Average	4.45	1960.50	591.24	50.80	12755.91	4590.63	0.12	0.63	-65.21	61.27	0.00	1.24	5.72	25.15	0.02	0.09	4.09	35.86	-0.15	0.05	-0.03	1.32	-0.05	0.17	-0.01
A3	2.10	1335.36	488.77	54.96	10244.91	4174.93	0.08	0.43	-61.23	44.43	-0.04	0.84	2.83	19.49	0.09	-0.01	2.88	26.78	-0.18	0.01	-0.07	1.84	-0.07	-0.03	-0.02
A3	1.78	1394.90	475.65	52.41	10160.61	4631.87	0.06	0.41	-64.12	51.09	-0.05	0.69	1.70	20.80	0.02	0.21	1.92	26.48	-0.18	0.04	-0.06	0.92	-0.07	-0.12	-0.02
Average	1.94	1365.13	482.21	53.69	10202.76	4403.40	0.07	0.42	-62.67	47.76	-0.04	0.77	2.26	20.14	0.06	0.10	2.40	26.63	-0.18	0.02	-0.07	1.38	-0.07	-0.08	-0.02
SB-A3	-2.51	-595.37	-109.03	2.89	-2553.15	-187.23	-0.06	-0.63	-	-13.51	-	-0.47	-3.46	-5.01	0.04	0.01	-1.69	-9.23	-	-0.03	-0.04	0.06	-0.02	-0.25	-0.01
A7	1.96	1797.73	683.12	29.76	12627.65	5273.73	0.10	0.57	-63.38	124.48	-0.03	0.80	2.76	45.69	0.10	0.24	3.05	31.91	-0.17	0.03	-0.15	2.61	-0.06	-0.05	-0.01
A7	2.39	1841.64	678.71	29.91	12833.02	5167.62	0.10	0.54	-67.69	137.14	-0.02	0.78	2.44	28.16	-0.07	0.18	3.18	31.75	-0.18	0.01	-0.03	2.73	-0.06	-0.09	-0.02
Average	2.17	1819.68	680.92	29.83	12730.34	5220.67	0.10	0.55	-65.53	130.81	-0.02	0.79	2.60	36.93	0.01	0.21	3.11	31.83	-0.17	0.02	-0.09	2.67	-0.06	-0.07	-0.01
SB-A7	-2.28	-140.82	89.67	-20.97	-25.57	630.04	-0.03	-0.08	-0.33	69.55	-0.03	-0.45	-3.12	11.78	-0.01	0.11	-0.98	-4.03	-0.03	-0.03	-0.06	1.35	-0.01	-0.24	-0.01
A9	2.15	1401.33	500.48	54.10	10334.34	4433.01	0.09	0.57	-65.56	44.97	-0.05	0.85	1.91	14.31	0.09	0.07	2.04	28.00	-0.16	0.04	-0.04	0.77	-0.06	-0.12	-0.01
A9	2.15	1451.71	531.12	52.43	10663.56	4760.73	0.16	0.68	-61.91	52.73	0.04	0.85	1.90	20.12	0.14	0.05	2.30	28.66	-0.06	0.15	-0.04	1.10	-0.01	-0.09	0.00
Average	2.15	1426.52	515.80	53.27	10498.95	4596.87	0.12	0.63	-63.74	48.85	0.00	0.85	1.91	17.21	0.12	0.06	2.17	28.33	-0.11	0.09	-0.04	0.93	-0.04	-0.11	-0.01
SB-A9	-2.30	-533.98	-75.44	2.46	-2256.96	6.24	0.00	-0.01	1.47	-12.42	-0.01	-0.39	-3.81	-7.93	0.10	-0.03	-1.92	-7.53	0.04	0.04	-0.01	-0.39	0.01	-0.28	0.00
A10	2.60	1146.12	754.39	127.70	15644.15	3336.74	0.16	0.80	-60.47	122.39	0.03	1.72	4.24	22.51	-0.01	-0.07	2.11	44.35	-0.15	0.31	-0.03	1.10	-0.04	0.49	0.00
A10	1.99	1186.19	757.39	115.31	15240.18	3419.46	0.22	0.92	-58.44	108.32	0.04	1.66	4.92	24.76	0.16	0.24	2.27	47.43	-0.11	0.28	0.01	1.20	-0.01	0.53	0.00
Average	2.29	1166.15	755.89	121.50	15442.17	3378.10	0.19	0.86	-59.46	115.35	0.04	1.69	4.58	23.63	0.07	0.08	2.19	45.89	-0.13	0.29	-0.01	1.15	-0.02	0.51	0.00
SB-A10	-2.16	-794.34	164.65	70.70	2686.26	-1212.53	0.07	0.23	-	54.09	0.03	0.45	-1.14	-1.51	0.05	-0.01	-1.90	10.03	-	0.24	-	-0.17	0.02	0.34	0.01
A11	2.04	2025.04	602.96	15.66	11420.79	6050.53	0.18	0.66	-59.67	35.65	-0.05	0.51	1.59	24.08	0.12	0.19	2.61	27.26	-0.16	0.04	0.00	1.08	-0.06	-0.08	-0.01
A11	1.70	2055.73	627.61	18.56	11577.13	6044.71	0.22	0.87	-61.43	48.62	-0.03	0.45	1.78	27.08	0.21	0.16	2.72	27.43	-0.13	0.06	-0.06	1.11	-0.05	0.08	0.00
Average	1.87	2040.38	615.28	17.11	11498.96	6047.62	0.20	0.76	-60.55	42.14	-0.04	0.48	1.68	25.58	0.17	0.17	2.67	27.35	-0.15	0.05	-0.03	1.10	-0.05	0.00	-0.01
SB-A11	-2.58	79.89	24.04	-33.69	-1256.95	1456.99	0.08	0.13	-	-19.13	-0.04	-0.76	-4.04	0.43	0.15	0.08	-1.43	-8.51	0.00	0.00	0.00	-0.22	-0.01	-0.17	0.00
B6	3.31	1117.86	544.47	53.04	9351.23	3521.85	0.26	0.86	-60.17	69.41	-0.03	0.99	3.43	17.40	0.00	0.06	3.02	28.14	-0.18	0.01	-0.04	0.91	-0.06	0.10	-0.01
B6	3.57	1155.97	498.09	56.21	9575.93	3098.51	0.22	0.82	-61.47	67.04	-0.04	0.93	2.05	18.87	0.06	0.11	3.25	27.71	-0.19	0.03	-0.09	0.98	-0.06	0.41	-0.01
Average	3.44	1136.92	521.28	54.62	9463.58	3310.18	0.24	0.84	-60.82	68.23	-0.03	0.96	2.74	18.14	0.03	0.08	3.13	27.93	-0.19	0.02	-0.07	0.95	-0.06	0.25	-0.01
SB-B6	-1.01	-823.58	-69.97	3.82	-3292.33	-1280.45	0.12	0.21	-	6.96	-0.04	-0.28	-2.98	-7.01	0.01	-0.01	-0.96	-7.93	-	-0.03	-	-0.38	-	0.08	0
C1	3.00	4542.89	1591.64	75.48	28443.17	12826.58	0.46	1.65	-50.00	97.70	0.19	1.56	3.93	59.80	0.24	0.61	6.31	73.16	-0.05	0.10	0.07	1.98	0.00	1.62	0.02
C1	3.73	4466.85	1495.29	73.63	28335.58	12197.69	0.39	1.64	-56.89	94.56	0.21	1.65	3.65	57.68	0.24	0.43	6.03	72.38	-0.03	0.12	0.10	1.69	0.02	1.68	0.01
Average	3.36	4504.87	1543.47	74.56	28389.37	12512.13	0.43	1.64	-53.44	96.13	0.20	1.60	3.79	58.74	0.24	0.52	6.17	72.77	-0.04	0.11	0.09	1.84	0.01	1.65	0.01
SB-C1	-1.09	2544.38	952.22	23.75	15633.46	7921.50	0.30	1.01	-	34.86	0.20	0.37	-1.93	33.59	0.22	0.43	2.07	36.91	-	0.06	0.11	0.52	0.06	1.48	0.02
C2	3.08	4349.24	1168.56	49.99	25289.52	13309.07	0.10	0.74	-66.89	78.41	-0.04	1.09	2.64	51.84	0.27	0.54	5.45	59.84	-0.20	0.04	-0.13	1.81	-0.06	-0.11	-0.02
C2	3.16	4743.88	1228.44	50.13	27139.08	13928.89	0.13	0.90	-62.76	79.68	-0.03	1.36	3.60	66.45	0.25	0.57	5.16	62.13	-0.19	0.07	0.04	1.80	-0.06	-0.04	-0.02
Average	3.12	4546.56	1198.50	50.06	26214.30	13618.98	0.11	0.82	-64.83	79.05	-0.03	1.23	3.12	59.15	0.26	0.56	5.31	60.99	-0.19	0.05	-0.04	1.81	-0.06	-0.08	-0.02
SB-C2	-1.33	2586.07	607.26	-0.74	13458.39	9028.35	-0.01	0.19	-	17.78	-0.03	-0.01	-2.60	34.00	0.24	0.46	1.21	25.13	-	0.00	-	0.49	-	-0.08	-

	B 10	Na 23	Mg 24	Al 27	K 39	Ca 43	V 51	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 65	Zn 66	As 75	Se 82	Sr 88	Rb 85	Ag 109	Cd 111	Sn 118	Ba 137	Tl 205	Pb 207	U 238
Hot black tea leaching calculations																									
Blank	9.98	443.45	839.09	8.09	11770.56	2615.62	0.21	0.47	-39.93	61.63	0.05	0.93	1.60	11.23	0.06	-0.08	22.06	12.72	-0.15	0.01	-0.11	16.79	-0.06	-0.02	-0.01
Blank	12.15	546.13	1092.93	13.49	15294.38	3518.22	0.23	0.44	-31.03	80.05	0.06	1.29	2.29	13.05	0.11	0.01	29.93	16.19	-0.19	-0.01	-0.03	23.77	-0.07	-0.05	-0.01
Average	11.07	494.79	966.01	10.79	13532.47	3066.92	0.22	0.45	-35.48	70.84	0.05	1.11	1.94	12.14	0.08	-0.03	25.99	14.46	-0.17	0.00	-0.07	20.28	-0.06	-0.03	-0.01
A3	3.83	418.51	363.53	3.00	3616.52	894.22	-0.43	-1.39	-37.14	24.91	0.08	0.42	2.35	6.22	0.12	-0.07	8.72	4.98	-1.69	0.02	-1.22	6.56	0.00	0.26	-0.01
A3	3.80	421.24	383.17	2.23	3775.87	966.43	-0.43	-1.30	-34.74	24.93	0.06	0.46	2.67	5.94	0.12	-0.03	8.32	4.80	-1.68	0.04	-1.13	7.03	0.00	0.16	-0.02
Average	3.81	419.87	373.35	2.61	3696.19	930.32	-0.43	-1.35	-35.94	24.92	0.07	0.44	2.51	6.08	0.12	-0.05	8.52	4.89	-1.69	0.03	-1.17	6.79	0.00	0.21	-0.02
SB-A3	-7.26	-74.91	-592.66	-8.18	-9836.27	-2136.60	-	-	-	-45.92	0.02	-0.67	0.56	-6.06	0.04	-	-17.47	-9.56	-	0.03	-	-13.49	0.00	0.21	0.00
A7	9.69	517.62	779.55	6.96	9157.62	2067.51	-0.19	-0.80	14.81	49.32	0.10	2.39	2.18	8.87	0.16	0.03	18.77	11.07	-1.66	0.08	-1.14	15.47	0.00	0.23	-0.01
A7	7.88	424.22	730.82	4.29	8486.67	1852.95	-0.20	-0.96	-22.74	43.63	0.08	0.86	1.54	7.63	0.25	0.03	16.10	8.97	-1.69	0.05	-1.26	12.93	0.01	0.08	-0.01
Average	8.78	470.92	755.19	5.63	8822.14	1960.23	-0.20	-0.88	-3.97	46.48	0.09	1.62	1.86	8.25	0.20	0.03	17.44	10.02	-1.68	0.06	-1.20	14.20	0.01	0.15	-0.01
SB-A7	-2.28	-23.87	-210.83	-5.16	-4710.32	-1106.69	-	-	-	-24.36	0.04	0.52	-0.09	-3.88	0.12	0.00	-8.56	-4.43	-	0.06	-	-6.08	0.01	0.15	0
A9	4.59	493.29	417.78	2.28	4631.40	1062.66	-0.30	-1.06	-31.86	26.39	0.07	0.65	3.17	6.07	0.18	0.00	9.67	5.58	-1.66	0.07	-1.21	7.68	0.02	0.10	-0.01
A9	3.74	455.40	377.07	19.37	3998.75	901.32	-0.35	-1.26	-39.83	24.88	0.06	0.39	6.22	5.32	0.08	0.09	9.50	5.48	-1.68	0.05	-1.24	6.76	0.00	0.11	-0.01
Average	4.17	474.35	397.42	10.83	4315.07	981.99	-0.33	-1.16	-35.85	25.64	0.07	0.52	4.70	5.70	0.13	0.04	9.58	5.53	-1.67	0.06	-1.23	7.22	0.01	0.11	-0.01
SB-A9	-6.90	-20.44	-568.59	0.04	-9217.39	-2084.93	-	-	-	-45.20	0.01	-0.59	2.75	-6.44	0.05	0.04	-16.41	-8.93		0.06	-	-13.06	0.01	0.11	0
A10	16.97	758.06	1677.21	11.11	17485.43	4343.05	-0.21	-1.07	10.76	106.73	0.21	1.82	4.54	15.57	0.15	0.00	36.22	21.25	-1.69	0.09	-1.20	32.49	0.01	0.13	-0.01
A10	16.22	743.27	1713.90	11.65	18284.15	4651.16	-0.20	-1.14	11.58	113.79	0.22	1.75	3.12	15.57	0.12	0.09	37.35	21.85	-1.68	0.05	-1.11	35.24	0.01	0.12	-0.01
Average	16.60	750.67	1695.56	11.38	17884.79	4497.10	-0.20	-1.11	11.17	110.26	0.21	1.79	3.83	15.57	0.14	0.04	36.78	21.55	-1.68	0.07	-1.15	33.86	0.01	0.13	-0.01
SB-A10	5.53	255.88	729.54	0.60	4352.33	1430.18	-	-	11.17	39.42	1.73	0.68	13.62	3.43	-0.04	0.04	10.79	7.09	-	0.07	-	13.58	0.01	0.13	0
A11	13.51	1649.22	1340.24	7.05	14360.35	3323.81	0.12	0.01	-22.30	83.37	0.28	1.37	1.98	12.96	0.06	0.31	28.40	19.28	-1.35	0.21	-1.19	21.65	0.11	0.11	0.02
A11	13.44	1632.21	1361.46	6.58	15016.51	3452.76	-0.16	-0.57	-19.88	91.41	0.17	1.50	2.55	13.24	0.21	0.13	27.77	18.84	-1.68	0.05	-1.23	20.89	0.01	0.11	-0.01
Average	13.47	1640.71	1350.85	6.81	14688.43	3388.28	-0.02	-0.28	-21.09	87.39	0.22	1.43	2.26	13.10	0.13	0.22	28.08	19.06	-1.51	0.13	-1.21	21.27	0.06	0.11	0.01
SB-A11	2.41	1145.93	384.84	-3.98	1155.97	321.36	-	-	-	16.55	0.17	0.33	0.32	0.97	0.05	0.22	2.09	4.61	-	0.13	-	0.99	0.06	0.11	0.01
B6	5.74	631.42	525.52	2.95	5695.78	1292.60	-0.27	-1.19	-30.83	34.79	0.22	0.96	3.74	6.89	0.27	0.23	12.06	7.98	-1.23	0.21	-1.20	9.91	0.09	1.40	0.01
B6	5.60	622.07	513.87	3.36	5431.97	1264.69	-0.38	-1.31	-16.07	34.95	0.07	0.59	3.51	16.55	0.15	-0.02	10.95	7.27	-1.69	0.04	-1.28	8.96	0.00	1.43	-0.01
Average	5.67	626.74	519.69	3.15	5563.88	1278.64	-0.32	-1.25	-23.45	34.87	0.15	0.78	3.62	11.72	0.21	0.11	11.50	7.63	-1.46	0.12	-1.24	9.43	0.04	1.41	0.00
SB-B6	-5.39	131.96	-446.32	-7.64	-7968.59	-1788.28	-	-	-	-35.96	0.09	-0.33	1.68	-0.42	0.13	0.11	-14.49	-6.83	-	0.12	-	-10.85	0.04	1.41	0.00
C1	3.00	4542.89	1591.64	75.48	28443.17	12826.58	0.46	1.65	-50.00	97.70	0.19	1.56	3.93	59.80	0.24	0.61	6.31	73.16	-0.05	0.10	0.07	1.98	0.00	1.62	0.02
C1	3.73	4466.85	1495.29	73.63	28335.58	12197.69	0.39	1.64	-56.89	94.56	0.21	1.65	3.65	57.68	0.24	0.43	6.03	72.38	-0.03	0.12	0.10	1.69	0.02	1.68	0.01
Average	3.36	4504.87	1543.47	74.56	28389.37	12512.13	0.43	1.64	-53.44	96.13	0.20	1.60	3.79	58.74	0.24	0.52	6.17	72.77	-0.04	0.11	0.09	1.84	0.01	1.65	0.01
SB-C1	-7.70	4010.09	577.45	63.77	14856.91	9445.21	0.21	1.19	-17.96	25.29	0.15	0.50	1.85	46.60	0.16	0.52	-19.82	58.31	-	0.12	0.09	-18.44	0.01	1.65	0.01
C2	15.18	1448.29	1319.85	15.26	17094.01	4060.08	0.15	0.35	-37.12	105.45	0.46	1.27	5.78	185.77	0.04	-0.05	34.11	21.34	-0.18	0.02	0.33	24.81	-0.06	8.72	-0.01
C2	14.08	1463.85	1285.86	14.29	16634.23	3980.15	0.16	0.43	-33.87	109.23	0.33	1.30	5.93	202.54	0.00	-0.05	32.89	20.78	-0.18	0.02	0.26	24.37	-0.06	10.79	-0.01
Average	14.63	1456.07	1302.86	14.77	16864.12	4020.11	0.15	0.39	-35.50	107.34	0.39	1.29	5.85	194.15	0.02	-0.05	33.50	21.06	-0.18	0.02	0.30	24.59	-0.06	9.76	-0.01
SB-C2	3.56	961.29	336.85	3.98	3331.66	953.19	-0.06	-0.07	-	36.50	0.34	0.18	3.91	182.01	-0.06	-	7.50	6.61	-	0.02	0.3	4.31		9.76	-

	B 10	Na 23	Mg 24	Al 27	K 39	Ca 43	V 51	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 65	Zn 66	As 75	Se 82	Sr 88	Rb 85	Ag 109	Cd 111	Sn 118	Ba 137	Tl 205	Pb 207	U 238
Hot Water Leaching Calculation																									
BLANK	1.62	19.57	100.82	3.29	1584.04	161.16	0.11		-35.15	0.31	0.00	0.20	1.96	6.36	-0.06	-0.12	1.44	1.49	-0.18	1.37	-0.07	1.15	-0.02	0.04	-0.02
BLANK	2.14	23.59	127.27	2.70	2057.26	177.51	0.08		-33.81	0.37	0.01	0.15	2.14	13.56	-0.03	-0.03	1.50	1.93	-0.22	4.32	-0.06	1.18	-0.02	0.04	-0.02
Average	1.88	21.58	114.05	3.00	1820.65	169.34	0.10		-34.48	0.34	0.00	0.17	2.05	9.96	-0.04	-0.08	1.47	1.71	-0.20	2.84	-0.07	1.16	-0.02	0.04	-0.02
A31 1	0.91	23.40	59.85	4.05	903.10	102.62	0.06		-36.44	0.19	0.01	0.24	1.88	26.50	-0.05	0.01	0.86	0.90	-0.22	9.75	-0.06	0.84	-0.02	0.11	-0.02
A3 1 2	0.76	20.82	58.74	7.15	881.79	109.83	0.07		-36.90	0.19	0.02	0.22	1.82	25.33	-0.06	-0.15	0.88	0.86	-0.21	9.50	-0.08	0.86	-0.02	0.08	-0.02
Average	0.83	22.11	59.30	5.60	892.44	106.22	0.06		-36.67	0.19	0.02	0.23	1.85	25.92	-0.06	-0.07	0.87	0.88	-0.22	9.63	-0.07	0.85	-0.02	0.09	-0.02
SB-A3	-1.05	0.53	-54.75	2.60	-928.20	-63.11	-0.03		-	-0.15	0.01	0.06	-0.20	15.96	-	-	-0.60	-0.84	-	6.78	-	-0.31	-	0.06	-
A7 1	1.43	30.65	116.17	5.74	1897.65	183.11	0.04		-36.26	0.38	0.00	0.43	3.39	4.17	-0.06	-0.16	1.48	1.81	-0.21	0.20	-0.06	1.86	-0.02	0.14	-0.02
A7 2	1.69	32.35	114.69	6.12	1847.47	173.44	0.04		-38.01	0.37	0.00	0.48	3.39	4.31	0.03	-0.03	1.44	1.71	-0.21	0.19	-0.07	1.98	-0.02	0.13	-0.02
Average	1.56	31.50	115.43	5.93	1872.56	178.27	0.04		-37.13	0.38	0.00	0.45	3.39	4.24	-0.01	-0.10	1.46	1.76	-0.21	0.19	-0.07	1.92	-0.02	0.14	-0.02
SB-A7	-0.32	9.92	1.38	2.93	51.92	8.94	-0.06		-	0.04	0	0.22	1.34	-5.72	-	-	-0.01	0.05	-	-2.65	-	0.75	-	0.10	-
A9 1	1.04	22.53	110.04	2.37	1785.94	167.10	0.21		-29.31	0.34	0.00	0.13	2.24	6.31	-0.06	-0.11	1.33	1.69	-0.22	1.31	-0.03	1.03	-0.02	0.04	-0.01
A9 2	0.92	21.56	109.34	4.20	1769.64	160.84	0.16		-20.79	0.33	0.00	0.16	2.29	6.51	-0.03	-0.10	1.32	1.66	-0.23	1.28	0.04	0.95	-0.02	0.04	-0.01
Average	0.98	22.04	109.69	3.29	1777.79	163.97	0.19		-25.05	0.33	0.00	0.15	2.26	6.41	-0.04	-0.11	1.33	1.68	-0.22	1.30	0.00	0.99	-0.02	0.04	-0.01
SB-A9	-0.91	0.46	-4.35	0.29	-42.86	-5.37	0.09		-	-0.01	0	-0.03	0.21	-3.55	-	-	-0.14	-0.04	-	-1.55	0	-0.17	-	0.00	-
A10	0.85	31.69	93.95	3.71	1442.70	137.80	0.06		-36.68	0.27	0.01	0.41	2.46	7.90	-0.06	-0.05	1.19	1.36	-0.19	1.93	-0.07	1.51	-0.02	0.17	-0.02
A10	1.10	38.10	92.83	8.34	1436.78	159.24	0.05		-37.80	0.30	0.01	0.45	2.51	8.07	-0.01	-0.13	1.22	1.36	-0.19	1.85	-0.07	1.49	-0.02	0.25	-0.02
Average	0.98	34.89	93.39	6.02	1439.74	148.52	0.06		-37.24	0.28	0.01	0.43	2.48	7.99	-0.03	-0.09	1.21	1.36	-0.19	1.89	-0.07	1.50	-0.02	0.21	-0.02
SB-A10	-0.91	13.31	-20.66	3.02	-380.91	-20.82	-0.04		-	-0.06	0.01	0.26	0.44	-1.97	-	-	-0.27	-0.35	-	-0.96	-	0.34	0.00	0.17	0.00
A11	1.13	36.51	68.76	6.42	1037.17	125.94	0.07		-35.85	0.21	0.00	0.26	3.43	3.13	-0.02	-0.02	0.92	1.06	-0.23	0.22	-0.07	0.89	-0.02	0.13	-0.02
A11	1.07	31.51	69.43	7.82	1040.56	117.68	0.08		-35.37	0.22	0.00	0.29	3.58	3.77	-0.17	-0.07	0.92	1.03	-0.22	0.21	-0.07	0.84	-0.02	0.16	-0.02
Average	1.10	34.01	69.10	7.12	1038.87	121.81	0.07		-35.61	0.21	0.00	0.28	3.50	3.45	-0.10	-0.05	0.92	1.04	-0.23	0.21	-0.07	0.86	-0.02	0.15	-0.02
SB-A11	-0.78	12.43	-44.95	4.12	-781.78	-47.53	-0.02		-	-0.13	0.00	0.10	1.46	-6.51	-	-	-0.55	-0.67	-	-2.63	-	-0.30		0.11	-
B6	0.61	22.11	101.51	3.53	1607.96	148.25	0.13		-33.04	0.32	0.00	0.20	2.03	10.59	0.00	-0.03	1.31	1.57	-0.24	3.17	-0.05	1.07	-0.02	0.11	-0.02
B6	0.81	21.80	99.54	4.16	1613.22	149.80	0.13		-33.18	0.33	0.00	0.22	1.97	10.53	-0.01	0.01	1.32	1.53	-0.25	3.13	-0.04	1.07	-0.02	0.07	-0.02
Average	0.71	21.96	100.53	3.84	1610.59	149.02	0.13		-33.11	0.33	0.00	0.21	2.00	10.56	-0.01	-0.01	1.32	1.55	-0.24	3.15	-0.04	1.07	-0.02	0.09	-0.02
SB-B6	-1.17	0.38	-13.52	-0.21	-210.05	-20.31	0.04		-	-0.02	0	0.04	-0.05	0.60	-	-	-0.15	-0.16	-	0.30	-	-0.09	-	0.05	-
C1	1.38	29.99	82.76	4.35	1286.62	149.36	0.33		-17.21	0.32	0.01	0.44	2.65	3.86	0.05	0.04	1.15	1.21	-0.23	0.18	0.02	8.07	-0.02	1.30	-0.01
C1	0.73	28.79	77.73	6.18	1223.57	139.84	0.25		-27.26	0.27	0.00	0.41	2.44	3.74	-0.07	-0.06	1.13	1.18	-0.22	0.23	0.01	7.53	-0.02	1.13	-0.01
Average	1.06	29.39	80.25	5.27	1255.09	144.60	0.29		-22.23	0.29	0.01	0.42	2.55	3.80	-0.01	-0.01	1.14	1.19	-0.23	0.20	0.01	7.80	-0.02	1.21	-0.01
SB-C1	-0.83	7.81	-33.80	2.27	-565.55	-24.74	0.19		-	-0.05	0.00	0.25	0.50	-6.16	-	-	-0.33	-0.52	-	-2.64	0.01	6.63	-	1.17	-
C2 2	0.82	28.79	89.79	3.19	1370.18	132.79	0.04		-37.92	0.29	0.00	0.26	2.02	3.06	-0.03	-0.09	1.35	1.34	-0.23	0.25	-0.06	1.09	-0.02	0.12	-0.02
C2 1	1.18	27.94	88.91	3.72	1380.02	143.22	0.05		-36.83	0.30	0.00	0.28	2.05	3.06	-0.08	-0.18	1.31	1.30	-0.23	0.22	-0.06	1.02	-0.02	0.15	-0.02
Average	1.00	28.37	89.35	3.46	1375.10	138.01	0.05		-37.37	0.30	0.00	0.27	2.03	3.06	-0.05	-0.14	1.33	1.32	-0.23	0.23	-0.06	1.06	-0.02	0.14	-0.02
SB-C2	-0.89	6.79	-24.70	0.46	-445.54	-31.33	-0.05		-	-0.05	0	0.10	-0.01	-6.90	-	-	-0.14	-0.39	-	-2.61	-	-0.11	-	0.10	-

	B 10	Na 23	Mg 24	Al 27	K 39	Ca 43	V 51	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 65	Zn 66	As 75	Se 82	Sr 88	Rb 85	Ag 109	Cd 111	Sn 118	Ba 137	Tl 205	Pb 207	U 238
Coca Cola leaching calculation																									
Blank	4.33	2910.55	120.81	1.70	5.02	949.68	0.13		-39.43	-0.04	0.00	0.15	0.29	-0.26	-0.03	-0.19	4.35	0.01	-0.26	0.01	-0.09	0.70	-0.02	0.00	0.00
Blank	4.13	2869.84	119.26	1.80	47.58	896.18	0.12		-41.37	-0.05	-0.01	0.08	0.19	-0.20	0.05	-0.10	4.41	0.08	-0.26	0.01	-0.08	0.81	-0.02	-0.03	0.00
Average	4.23	2890.19	120.04	1.75	26.30	922.93	0.12		-40.40	-0.04	0.00	0.12	0.24	-0.23	0.01	-0.14	4.38	0.04	-0.26	0.01	-0.08	0.75	-0.02	-0.02	0.00
A3	4.03	3062.01	141.92	2.60	123.04	895.19	-1.03		-33.44	-0.01	0.02	0.13	0.29	0.03	0.10	-0.30	3.99	0.31	0.02	0.02	-0.34	0.82	0.00	-0.09	0.01
A3	4.45	3198.54	139.79	2.63	40.48	941.00	-1.04		-32.90	-0.01	0.02	0.16	0.28	-0.32	0.05	-0.37	4.33	0.31	0.03	0.02	-0.33	0.85	0.00	-0.06	0.01
Average	4.24	3130.28	140.85	2.62	81.76	918.10	-1.04		-33.17	-0.01	0.02	0.15	0.29	-0.14	0.07	-0.33	4.16	0.31	0.02	0.02	-0.34	0.83	0.00	-0.07	0.01
SB-A3	0.01	240.09	20.82	0.86	55.46	-4.83	-		-	-	0.02	0.03	0.05	-	0.06	-0.19	-0.22	0.26	0.02	0.01	-	0.08	0.00	-	0.01
A7	4.84	3227.21	131.68	3.97	33.43	945.71	-1.11		-35.19	-0.06	0.02	0.46	0.59	-0.21	0.10	-0.32	4.22	0.12	0.03	-0.01	-0.33	0.76	0.00	0.02	0.00
A7	3.89	3045.73	138.44	4.74	26.03	924.31	-1.16		-37.70	-0.04	0.01	0.15	0.26	-0.37	0.07	-0.41	4.35	0.21	0.02	0.01	-0.34	0.77	0.00	-0.09	0.01
Average	4.36	3136.47	135.06	4.35	29.73	935.01	-1.13		-36.44	-0.05	0.01	0.30	0.42	-0.29	0.08	-0.36	4.28	0.16	0.02	0.00	-0.33	0.77	0.00	-0.03	0.01
SB-A7	0.13	246.28	15.03	2.60	3.43	12.08	-		-	-	0.01	0.18	0.18	-	0.07	-	-0.10	0.12	0.02	0		0.01	0	-	0.01
A9	4.48	2979.18	127.48	3.22	41.16	939.63	-0.57		-27.06	0.00	0.02	0.76	0.40	0.25	0.10	-0.18	4.29	0.08	0.02	0.01	-0.30	0.74	0.00	-0.05	0.01
A9	4.20	2885.24	118.24	2.45	6.52	898.32	-0.74		-28.77	-0.06	0.01	0.16	0.31	-0.21	0.02	-0.36	4.10	0.05	0.03	0.00	-0.33	0.74	0.00	-0.06	0.00
Average	4.34	2932.21	122.86	2.84	23.84	918.97	-0.66		-27.91	-0.03	0.02	0.46	0.36	0.02	0.06	-0.27	4.20	0.06	0.02	0.01	-0.31	0.74	0.00	-0.06	0.01
SB-A9	0.11	42.02	2.82	1.09	-2.46	-3.96	-		-	-	0.02	0.35	0.12	0.02	0.05	-	-0.18	0.02	0.02	0	-	-0.02	0	-	0.01
A10	4.88	3130.62	131.18	2.57	6.96	946.20	-1.06		-33.98	-0.05	0.01	0.23	0.36	-0.26	0.03	-0.42	4.17	0.03	0.02	0.01	-0.34	1.01	0.00	-0.02	0.01
A10	4.05	3236.60	134.58	2.65	32.32	952.25	-1.05		-36.61	-0.04	0.01	0.17	0.35	-0.31	0.05	-0.36	4.30	0.11	0.01	0.02	-0.33	0.71	0.00	-0.05	0.01
Average	4.46	3183.61	132.88	2.61	19.64	949.22	-1.05		-35.30	-0.05	0.01	0.20	0.35	-0.29	0.04	-0.39	4.24	0.07	0.02	0.02	-0.34	0.86	0.00	-0.03	0.01
SB-A10	0.23	293.42	12.84	0.86	-6.66	26.29	-		-	-	0.01	0.08	0.12	-	0.03	-	-0.14	0.03	0.02	0.01	-	0.11	0	-	0.01
A11	4.64	3082.24	125.80	3.91	28.73	947.13	-0.99		-32.42	-0.07	0.01	0.38	0.39	-0.31	0.07	-0.21	4.13	0.07	0.01	0.01	-0.33	0.94	0.00	-0.04	0.00
A11	4.47	3048.39	125.18	3.05	20.94	907.70	-0.99		-33.02	-0.07	0.01	0.07	0.24	-0.34	0.09	-0.25	4.10	0.05	0.02	0.00	-0.33	0.93	0.00	-0.07	0.00
Average	4.56	3065.31	125.49	3.48	24.84	927.42	-0.99		-32.72	-0.07	0.01	0.23	0.32	-0.33	0.08	-0.23	4.11	0.06	0.02	0.01	-0.33	0.94	0.00	-0.05	0.00
SB-A11	0.33	175.12	5.45	1.73	-1.46	4.49	-		-	-	0.01	0.11	0.08	-	0.07	-	-0.27	0.01	0.02	0.00	-	0.18	0	-	0
B6	4.08	3051.84	125.53	2.35	11.89	986.94	-0.84		-30.71	-0.05	0.01	0.15	0.26	-0.26	0.09	-0.26	4.12	0.05	0.04	0.01	-0.34	0.75	0.00	0.84	0.00
B6	5.30	3087.24	128.08	3.75	5.65	1021.32	-0.85		-30.21	-0.04	0.02	0.22	0.40	-0.28	0.19	-0.25	4.18	0.02	0.02	0.00	-0.32	0.77	0.00	0.87	0.00
Average	4.69	3069.54	126.81	3.05	8.77	1004.13	-0.85		-30.46	-0.05	0.01	0.18	0.33	-0.27	0.14	-0.25	4.15	0.03	0.03	0.01	-0.33	0.76	0.00	0.86	0.00
SB-B6	0.46	179.35	6.77	1.30	-17.53	81.20	-		-	-	0.02	0.07	0.09	-	0.13	-	-0.23	-0.01	0.03	0	-	0.01	0	0.86	0
C1	4.51	3174.69	141.55	7.95	48.27	964.33	-0.74		-28.38	0.56	0.01	0.17	0.88	-0.10	0.03	-0.23	4.44	0.21	0.01	0.01	-0.34	0.82	0.00	1.76	0.01
C1	4.69	2911.45	126.43	7.14	34.39	930.64	-0.83		-28.81	0.63	0.02	0.40	1.08	-0.25	0.02	-0.34	4.21	0.10	0.04	0.02	-0.34	0.93	0.00	1.51	0.01
Average	4.60	3043.07	133.99	7.54	41.33	947.49	-0.79		-28.60	0.60	0.01	0.28	0.98	-0.17	0.03	-0.28	4.33	0.15	0.02	0.01	-0.34	0.87	0.00	1.64	0.01
SB-C1	0.37	152.88	13.95	5.79	15.02	24.56	-0.91		-	0.60	0.01	0.16	0.74	-	0.01	-	-0.06	0.11	0.02	0.00	-	0.12	0.00	1.64	0.01
C2	5.70	2982.08	159.60	10.71	132.91	1397.82	-0.30		-14.32	1.15	0.45	0.27	0.95	260.57	0.10	-0.29	5.32	0.55	0.01	0.02	-0.26	1.86	0.00	6.38	0.00
C2	5.76	2982.84	159.82	11.00	114.62	1318.94	-0.53		-16.08	1.02	0.44	0.33	1.06	249.38	0.04	-0.29	5.04	0.75	0.01	0.03	-0.27	1.60	0.00	6.16	0.00
Average	5.73	2982.46	159.71	10.85	123.76	1358.38	-0.42		-15.20	1.09	0.45	0.30	1.01	254.97	0.07	-0.29	5.18	0.65	0.01	0.02	-0.27	1.73	0.00	6.27	0.00
SB-C2	1.50	92.27	39.67	9.10	97.46	435.45	-		-	1.09	0.45	0.18	0.77	259.97	0.05	-	0.80	0.61	0.01	0.01	-	0.98	0	6.27	0

	B 10	Na 23	Mg 24	Al 27	K 39	Ca 43	V 51	Cr 53	Fe 54	Mn 55	Co 59	Ni 60	Cu 65	Zn 66	As 75	Se 82	Sr 88	Rb 85	Ag 109	Cd 111	Sn 118	Ba 137	Tl 205	Pb 207	U 238
Cold water leaching calculation																									
Blank	0.55	14.05	1.81	-0.16	26.55	109.50	-0.01	0.13	-22.69	0.16	0.00	0.12	0.32	-1.04	0.01	-0.12	0.10	-0.53	-0.02	0.03	-0.07	0.02	-0.01	0.09	0.00
Blank	0.32	13.90	1.82	-0.19	26.88	118.03	0.04	-0.01	-20.98	0.16	0.00	0.10	0.34	-1.52	-0.06	-0.12	0.09	-1.02	-0.02	0.03	-0.07	0.03	-0.01	0.08	0.00
Average	0.44	13.97	1.82	-0.18	26.71	113.76	0.01	0.06	-21.83	0.16	0.00	0.11	0.33	-1.28	-0.02	-0.12	0.10	-0.77	-0.02	0.03	-0.07	0.03	-0.01	0.08	0.00
C6	14.64	1274.91	172.25	0.20	303.18	876.11	0.11	0.22	-21.32	0.84	0.00	0.29	1.91	10.14	0.10	-0.16	2.94	-0.18	-0.03	0.15	-0.01	1.12	-0.01	1.98	0.00
C6	14.37	1236.40	171.43	0.27	307.71	907.16	0.12	0.20	-20.24	0.85	0.01	0.24	1.86	11.61	0.04	-0.22	2.92	-0.21	-0.04	0.12	-0.01	1.09	-0.01	0.08	0.00
Average	2.00	1255.66	171.84	0.23	305.44	2.00	0.12	0.21	-20.78	0.84	2.00	0.27	1.89	10.88	0.07	2.00	2.93	-0.20	-0.04	0.13	2.00	1.11	-0.01	1.03	0.00
Blank-C6	1.57	1241.68	170.02	0.23	278.73	ND	0.11	1.23	ND	0.69	2.00	2.23	1.55	10.88	0.07	2.00	2.84	ND	ND	0.11	2.00	1.08	ND	5.23	0.00
A7	15.83	1282.76	174.45	0.38	361.39	883.80	0.08	0.14	-21.05	0.15	0.04	0.37	2.09	9.40	0.05	-0.16	2.89	-0.57	-0.03	0.14	-0.07	1.24	-0.01	0.24	0.00
A7	15.93	1234.26	168.70	0.27	345.76	872.38	0.11	0.19	-22.83	0.10	0.04	0.36	2.05	8.90	0.12	-0.16	2.93	-0.38	-0.02	0.12	-0.03	1.27	-0.01	0.18	0.00
Average	15.88	1258.51	171.58	0.33	353.58	878.09	0.09	0.16	-21.94	0.12	0.04	0.36	2.07	9.15	0.09	-0.16	2.91	-0.47	-0.03	0.13	-0.05	1.25	-0.01	0.21	0.00
Blank-A7	15.45	1244.53	169.76	0.33	326.86	764.32	0.08	0.10	ND	-0.04	0.04	0.25	1.74	9.15	0.09	ND	2.81	ND	ND	0.10	ND	1.23	ND	0.13	0.00
B3	15.62	1266.36	176.19	0.28	339.82	896.75	0.06	0.21	-21.11	0.17	0.01	0.42	2.30	8.17	0.00	-0.19	2.78	-0.96	-0.04	0.15	-0.13	1.43	-0.01	0.13	0.00
B3	14.15	1290.44	181.00	0.32	331.08	900.24	0.09	0.16	-19.54	0.13	0.01	0.41	2.36	6.63	0.13	-0.26	2.80	-0.52	-0.05	0.11	-0.03	1.43	-0.01	0.14	0.00
Average	14.89	1278.40	178.60	0.30	335.45	898.49	0.08	0.18	-20.32	0.15	0.01	0.41	2.33	7.40	0.06	-0.23	2.79	-0.74	-0.04	0.13	-0.08	1.43	-0.01	0.13	0.00
Blank -B3	14.45	1264.43	176.78	0.30	308.73	784.73	0.07	0.12	ND	-0.01	0.01	0.30	2.00	7.40	0.06	ND	2.70	ND	ND	0.10	ND	1.40	0.00	0.05	0.00
C1	20.14	1340.72	168.92	0.73	521.91	822.92	0.09	0.22	-21.55	0.17	0.04	0.72	3.04	14.28	0.05	-0.16	2.57	-0.46	-0.05	0.20	-0.06	1.06	-0.01	0.31	0.00
C1	18.07	1398.36	174.87	0.81	540.89	806.74	0.11	0.15	-21.02	0.16	0.04	0.64	3.16	18.38	0.07	-0.19	2.59	-0.28	-0.05	0.25	-0.04	1.03	-0.01	0.32	0.00
Average	19.10	1369.54	171.89	0.81	531.40	814.83	0.10	0.18	-21.28	0.16	0.04	0.68	3.10	16.33	0.06	-0.17	2.58	-0.37	-0.05	0.23	-0.05	1.04	-0.01	0.31	0.00
Blank- C1	18.67	1355.57	170.08	0.99	504.69	701.07	0.09	0.12	ND	0.01	0.05	0.56	2.77	16.33	0.06	ND	2.48	ND	ND	0.20	ND	1.02	ND	0.23	0.00
A3-1	0.22	21.81	2.24	-0.16	31.22	24.28	0.03	0.04	-22.57	0.03	0.01	0.05	0.90	-0.02	-0.05	-0.27	0.05	-0.81	-0.03	0.05	-0.08	0.35	-0.01	0.11	0.00
A3-1	0.65	21.42	2.27	-0.07	31.67	29.68	0.01	0.03	-19.82	0.02	0.01	0.11	0.93	-0.08	-0.05	-0.29	0.06	-0.79	-0.03	0.03	-0.07	0.19	-0.01	0.10	0.00
Average	0.44	21.62	2.26	-0.12	31.45	26.98	0.02	0.03	-21.20	0.02	0.01	0.08	0.91	-0.05	-0.05	-0.28	0.06	-0.80	-0.03	0.04	-0.07	0.27	-0.01	0.11	0.00
Blank -A3-1	0.00	7.64	0.44	ND	4.73	-86.78	0.01	-0.03	ND	-0.13	0.01	-0.03	0.58	ND	ND	ND	-0.04	ND	ND	0.01	ND	0.24	ND	0.02	0.00