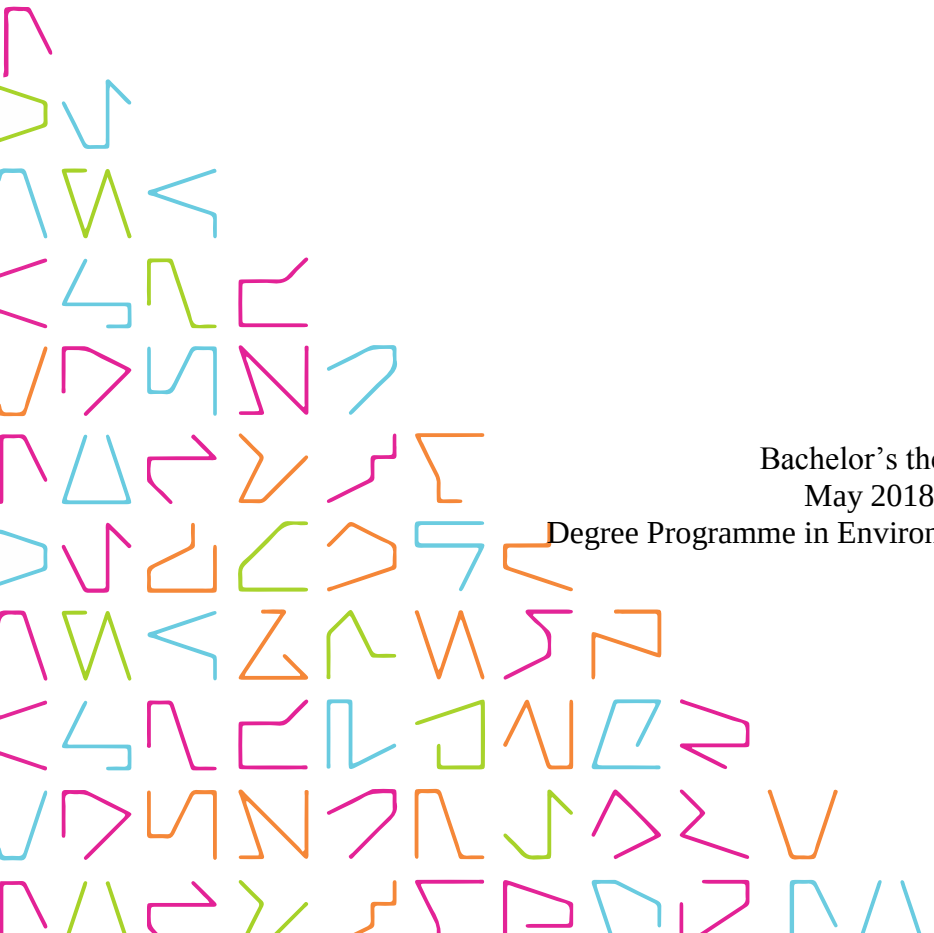
TAMPERE UNIVERSITY
OF APPLIED SCIENCES

HBCD IN INSULATION MATERIALS

XRF in Preliminary Detection

Inka Honkala



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ABSTRACT

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HBCD in Insulation Materials - XRF in Preliminary Detection

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Due to a new amendment to a piece of legislation on persistent organic pollutants, consistent methods are needed to properly detect, process and dispose of a newly added substance, hexabromocyclododecane, which has now been globally banned from use.

Bromine based flame retardants like HBCD have been used increasingly in construction materials since the 1960s to meet fire safety requirements, so it will be widely present in demolition waste in the years to come. HBCD has been used especially in insulating materials such as expanded and extruded plastics, but it could also be present in imported packaging materials of electronics and other products. No samples of packaging materials containing HBCD were found during this study.

Hexabromocyclododecane (HBCD) cannot be visually detected, nor has it been marked or labeled on the products it has been used in. Because chemical laboratory analyses to detect HBCD are time-consuming and the volume of construction waste considerable, a faster on-site method is needed.

An x-ray fluorescence gun can detect bromine from plastics. Because HBCD contains bromine, XRF can be used to estimate whether HBCD could be present, although the results are not conclusive enough to replace more accurate laboratory analyses entirely.

The method described in this thesis work appears to be suitable for identifying materials that have not been treated with any brominated flame retardants, but additional steps need to be taken to tell HBCD apart from other brominated compounds.

Key words: detection method, construction waste, polystyrene, hexabromocyclododecane

CONTENTS

ABBREVIATIONS AND TERMS

Br	bromine
EPS	expanded polystyrene
FR	flame retardant
GC	gas chromatography
HBCD	hexabromocyclododecane
PBDEs	polybrominated diphenyl ethers (flame retardants)
PBT	persistent, bioaccumulative and toxic substance
PolyFR	copolymer of styrene and butadiene, new flame retardant
POP	persistent organic pollutant
SYKE	Finnish Environment Institute
TBBPA	tetrabromobisphenol A (flame retardant)
UNEP	United Nations Environment Programme
XPS	extruded polystyrene
XRF	X-ray fluorescence

1 INTRODUCTION

A decision made by UNEP Stockholm Convention in 2013 listed hexabromocyclododecane as a persistent organic pollutant (POP), and it was subsequently banned globally. (UNEP SC-6/13, 2013)

HBCD has been used as a flame retardant in construction and insulation materials, and continues to exist in buildings approaching their end of life. To assess the implications of the Stockholm Convention decision on how waste insulation materials from demolished buildings are processed and disposed of, two study departments of Tampere University of Applied Sciences formed a preliminary 4-thesis-project with Finnish Environment Institute SYKE.

The goal of the whole project is to provide background information and material for instructions for construction workers, builders and authorities on how to detect, separate and process HBCD from construction waste.

This paper focuses on on-site detection of bromine as an HBCD indicator by using a handheld x-ray fluorescence gun. The goal was not to accurately measure the amount of bromine or HBCD present, but to simply find out whether the presence of HBCD was possible to predict with this method or not.

2 BACKGROUND

2.1 HBCD and Brominated Flame retardants

Hexabromocyclododecane, or HBCD, is a bromine-based flame retardant that has been widely used since the 1960s to reduce the flammability of otherwise flammable materials, particularly insulation materials made of polystyrene.

Polystyrene foam (EPS and XPS) is an affordable and versatile plastic used to insulate buildings to prevent unwanted heat exchange. It is easily shaped into any form it is needed in and resists moisture, but flame retardants such as HBCD have been used to allow buildings to meet fire safety regulations. (Plastics Europe, 2014)

Although HBCD has now been classified as a persistent organic pollutant and banned from use (Ympäristöhallinto, 2018), some other brominated flame retardants, such as HBCD's newer replacement, a butadiene styrene brominated copolymer PolyFR, can still be used. (EPA, 2014; Schlummer et al., 2015)

The difference between the banned brominated flame retardants and the still allowed ones is the way they are used in the polystyrene resin. Many of the banned substances like HBCD and PBDEs are *additive*, while the others (PolyFR and TBBPA) are *reactive.* Reactive flame retardants are covalently bonded with the polystyrene and are therefore less likely to get separated from the insulation material into the environment than the more easily extractable additive ones. (Hyötyläinen, 2002)

2.2 Properties

According to its material safety data sheet (MSDS), HBCD is a persistent, bioaccumulative and toxic substance (PBT) with the molecular formula of $C_{12}H_{18}Br_6$ and molecular weight of 641,73g/mol.

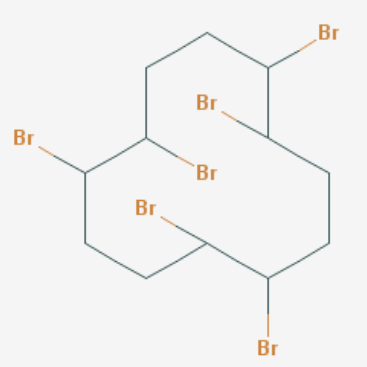

Figure 1. Structural formula of HBCD (PubChem, 2018)

On its own, HBCD is a white powder, but when it is mixed in as an additive with the polystyrene resin, it has no apparent colour or smell and can only be detected through chemical analysis, such as gas chromatography.

HBCD is very toxic to aquatic life with long lasting effects and presents a hazard to humans and animals as an endocrine disrupting chemical. It is toxic to the thyroid and liver, and appears to cause developmental problems in infants. (Papaspyrides & Kiliaris, 2014)

Because of the large volumes of FR treated plastics in construction waste, and because HBCD persists in nature and travels long distances once attached to airborne particles, it is a formidable and long-lasting environmental pollutant. (Ympäristöhallinto, 2018)

While EPS and XPS insulation materials that do not contain HBCD can be readily recycled, any materials treated with HBCD should be disposed of by incineration in a well-functioning waste incineration plant under high temperatures (Plastics Europe, 2014).

2.3 Occurrence

According to SYKE, around 10% of the EPS used in construction is treated with a fire-retardant chemical. (Seppälä, 2016)

Another thesis in this project covers the occurrence of HBCD in buildings in Finland. (Hämäläinen, 2017)

2.4 Detection

Over the course of the project it has become clear that accurate data on where and how frequently HBCD has been used in construction materials are not readily available. Detecting it to be able to process the waste correctly is important – while polystyrene in general is recyclable, any polystyrene that contains HBCD should be handled with appropriate caution and disposed of by incineration.

In a laboratory setting, HBCD can be measured directly using different kinds of gas chromatography (GC) methods. A separate thesis work is to be published on the specific laboratory analyses.

To indicate presence of HBCD quickly and on site, however, an x-ray fluorescent gun (XRF) can be used to measure the amount of bromine in a plastic product or insulation material. Each HBCD molecule has six bromine atoms, which the XRF can pick up on.

If the reliability of an XRF method can be shown, using a handheld XRF-gun for screening waste materials would be faster and more practical than sending samples of all construction waste polystyrene directly to laboratory analyses when use of HBCD is suspected.

3 MATERIALS AND METHOD

3.1 XRF

The device used in both screening and radiation laboratory analysis of this study was a Thermo Scientific Niton XL3t GOLDD handheld XRF analyser. The calibration configuration used was Consumer Goods: Plastics.

FigureX. Niton XL3t GOLDD XRF Analyzer. (ThermoFisher Scientific)

Although the purpose of this thesis was to estimate the presence of HBCD in the collected samples, the device produces an elemental analysis and therefore measures bromine in Br ppm, not HBCD directly.

To analyse the samples measured, and to control the XRF in its table stand remotely, two pieces of compatible computer software were used: NDT 7.2.2. and NDTr 7.1.2.

3.2 Samples

Samples were collected from three separate source categories (A, B and C). Two of the three sets went through an additional screening phase to selectively reduce the amount of material.

There were two initial goals behind the sample selection: to map out what kind of sources HBCD could be found in, and to see how accurately a hand-held XRF analyser could predict its presence in the sample.

To that end, finding samples with bromine was prioritized.

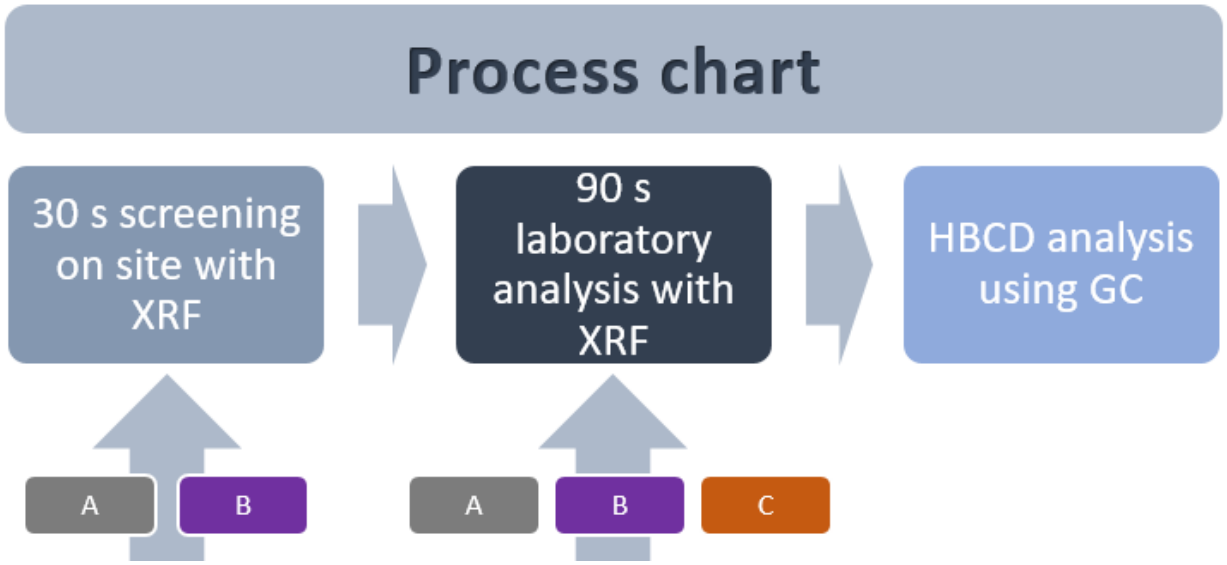

Figure 2. Process flow in this study

The samples were collected and screened, and the selected samples bagged and labelled on site. Some of the samples that were found to contain no bromine in the screening were discarded.

Figure 3. Sample A9. Light blue XPS.

Figure 4. Discarded sample A15. White EPS.

3.2.1 Sample set A

The first set of samples (A) was randomly selected from a local construction waste stream. The collected samples went through the additional screening step on site to determine which samples would be taken to the radiation laboratory for further analysis.

From this source, the intention was to collect samples that appeared to contain bromine in levels high enough to indicate presence of HBCD. The material in the waste stream was mainly construction waste, some from older demolished buildings, so this was considered to be the batch most likely to contain samples treated with HBCD.

Because these samples were collected from a unified waste stream, it is not possible to pinpoint where exactly each individual sample originated from.

3.2.2 Sample set B

The second set (B) consisted of packaging materials of everyday items, furniture and electronic appliances, collected by various people involved with the project, from a variety of different sources.

The intention was to collect information on what kind of packaging materials HBCD might be present in.

These samples were also screened before selection for the laboratory analysis.

3.2.3 Sample set C

The third set (C) was collected from a current local construction and renovation project of an apartment building, and include insulation materials as well as packaging materials for home appliances.

3.3 Screening

To select samples for the laboratory analysis, a quick 30-second XRF screening was done on site to determine which samples would be included in further analysis to avoid collecting only samples with no bromine present in them, or only samples with large amounts of bromine.

Each sample (from sets A and B) was measured for 30 seconds, 10 s with each filter of the handheld XRF. Due to the large amount of available material, most of the samples that appeared completely free of bromine in the screening were discarded. A few were kept to provide a reference point for the analysis.

3.4 Radiation laboratory analysis

The actual analysis of the selected samples was carried out in a radiation laboratory, using a table top stand for the handheld XRF machine.

The duration of each measurement was set to 90 seconds, 30 seconds with each filter. Because the XRF only measures a small area on the surface of the sample during each measurement, each sample was measured three times and the average result calculated from all three.

When possible, the sample was cut in half and one or two of the measurements done from the freshly exposed surface to avoid only measuring the dirtier surface layers that could have been in contact with HBCD or bromine and give a positive reading even if no brominated flame retardants were used in the material itself.

Figure 5. Radiation laboratory equipment setup.

3.5 Comparison

Simultaneously with the radiation laboratory measurements, a parallel testing was conducted in the chemical laboratory using gas chromatography.

It is important to note that unlike the XRF, the chemical analysis directly measures HBCD instead of bromine as an indicator. This means, for instance, that 1000 ppm Br measured with the XRF analyser is not the same result as 1000 ppm HBCD measured with GC.

While the results of the two types of measurements are not directly comparable, the presence or absence of presumed HBCD can be indicated by either method.

The last column in Table 1 (section 4.1.2) shows the preliminary result of the chemical analysis.

4 MEASUREMENT RESULTS

4.1 Results of radiation laboratory analyses

The data from the screening, the actual XRF measurement and the GC measurement done in the chemistry laboratory were collected in one table (Table 1). The errors as they are reported are due to the detection properties of the equipment used.

4.1.1 Errors

The errors of the XRF screening are not presented. The screening was done solely to select samples, not to produce accurate and comparable results. These results are presented in the table only to depict the difference between the 30 second screenings and the actual 90 second measurements.

The average error of three measurements of the 90 second XRF analysis is marked in "Br error (of 3)" column.

The error for the analyses done in the chemistry laboratory is approximately 10%. The full thesis on the GC analysis with its exact error values is yet to be published at this time.

4.1.2 Results

Table 1. Colour coded table of results.

SAMPLE	Description	Br 30s ppm	Br 90s Avg ppm (of 3)	Br Error (of 3)	ppm HBCD, mg/kg
A1	*White EPS*	194	670	59	none
A2	*Pink foam, hard*	2261	2627	110	3200.0
A3	*Grey EPS*	7197	6266	322	none
A4	*Grey EPS*	5759	6682	299	none
A5	*Grey EPS, smaller grainsize*	6513	7415	173	none
A6	*Grey EPS*	0	0	31	none
A7	*White EPS*	724	302	43	none
A8	*Grey EPS, smaller grainsize*	7020	6699	279	-
A9	*Light blue XPS*	10900	9456	298	15000(-25000)
C1	*Yellow XPS*		0	16	none
C13	*Insulation material*		261	42	none
C14	*Underfloor insulation, grey*		50	16	none
C15	*Underfloor insulation, current construction, grey*		7845	290	none
C17	*Underfloor insulation, current construction, grey*		7372	308	none
C18	*Socle EPS, current construction*		3215	171	none
C19	*Underfloor insulation, grey*		7178	279	150-300
C20	*Underfloor insulation, socle*		5902	246	none
C21	*Underfloor insulation,socle, white*		5879	243	none
B1	*Chinese souvenir packaging*	0	0	66	none
B2	*Couch structure packaging*	3467	3265	164	-
B3	*Clock radio packaging*	0	0	22	-
B4	*Packing peanuts, compact*	77	401	75	-
B5	*Packing peanuts, porous*	0	0	33	-
B6	*Packing peanuts, yellow*	89	440	77	-
B7	*Television packaging*	0	0	42	none
C2	*Dishwasher packaging*		179	26	-
C3	*Refridgerator packaging*		0	69	-
C4	*Stove packaging*		33	25	-
C5	*Dishwasher packaging*		0	29	-
C6	*Refridgerator packaging, from Hungary*		0	32	-
C7	*Microwave packaging, from UK*		0	29	-
C8	*Stove packaging, from Germany*		0	32	-
C9	*Induction stove packaging, from Germany*		0	57	-
C10	*Refridgerator packaging*		0	72	-
C11	*Laundry machine packaging*		0	32	-
C12	*Induction stove packaging, from Germany*		0	31	-
C16	*Television packaging, from Hungary*		0	122	-

Red highlights in the table depict samples where HBCD was initially estimated to be present and green highlights samples presumed free of HBCD based on initial assumptions, in cases where both an XRF measurement and a lab measurement have been done for the sample. The samples in the above table have been sorted by type: first waste materials, then construction materials and finally packaging materials.

5 DISCUSSION

5.1 Observations

Based on the data presented in this thesis work, the following observations can be made:

1. HBCD occurs in demolition waste insulation materials in Finland.
2. HBCD was not found in packaging materials in this study.
3. XRF does detect bromine in all samples containing HBCD.
4. XRF does not differentiate HBCD from other bromine-based compounds.

The table of results (4.1) shows that the XRF gave more positive results (bromine detected) than the chemical analysis (HBCD detected), which confirms that the XRF cannot differentiate between HBCD and whatever other chemical compound or flame retardant might have been used.

In this study XRF did, however, produce a result other than zero for all the samples which contained HBCD according to the laboratory analysis. This suggests that the method described in this paper *is* one way of identifying and excluding insulation materials that have not been treated with brominated flame retardants at all.

Although the XRF-measured presence of bromine might indicate use of some brominated flame retardant, it does not detect the molecular structure. In other words, it measures bromine whose presence suggests that a brominated flame retardant has been used, but a further chemical analysis needs be done to identify the specific FR used.

5.2 Accuracy and reliability

The initial assumption was that based on the XRF results, a 'limit value' of Br ppm could be given as a result of this study, to easily tell whether the sample contains HBCD or not based on the amount of bromine in the sample. The laboratory-confirmed results, however, show that HBCD was found in samples with Br ppm ranging from as low as 2600 up to almost 10000. Some samples whose measured results were in the middle of that

range did *not* contain HBCD when measured with gas chromatography, so the idea of such a limit value is not feasible.

One possible reason for the largeness of the range of measured Br ppm is that different kinds of brominated flame retardants and their various derivatives have been used over the years, on insulation materials of varying compositions. (Hyötyläinen, 2002) Differences in the amount of retardant used on the product, as well as in the product material itself, affect the measured XRF results.

It is worth consideration that if the exact amount of Br ppm does not give any additional information or insight, only its presence or absence in the sample is significant, and the results should be considered qualitative estimates instead of quantitative analyses. This reduces the accuracy required from the method, and shorter measurement times might suffice for field measurement purposes in the future. During the measurements done for this thesis, for instance, the XRF quickly showed if the amount of bromine in the sample was below detection limit when none would be found, and did not deviate from that reading over the measurement time.

A related conclusion was drawn in a study done by Washington State Department of Ecology in 2012. While the study focused on PBDEs rather than HBCD, it approached the matter by using XRF to screen for bromine as an indicator of a brominated flame retardant as well. They found that the method has a tendency to give ‘false positives’ - samples with bromine detected in the absence of PBDEs. (Furl et al., 2012)

False positives, however, are not as problematic as ‘false negatives’. Samples that did not contain bromine according to the XRF measurement in the study mentioned above did not contain PBDEs in more accurate and specific laboratory analyses either, so the potential downside in using this method is only in having to send negative samples to be analysed further in the case of a false positive reading.

5.3 Further studies

While the method described in this thesis work seems to accurately indicate the presence or absence of brominated flame retardants in general, it does not offer the means to differentiate between specific banned (HBCD) and currently legal flame retardants. The new alternative to HBCD, PolyFR (Beach et al., 2013), and another popular brominated FR, tetrabromobisphenol A (TBBPA) (EPA, 2014; Lüthje, 2003), also contain bromine and will turn up in measurements using the method described here.

A study on the same topic as this thesis work, published in Germany in 2015, solved this problem by adding an extra step of dissolving a portion of the sample in acetone. The idea behind the extraction step is that both PolyFR and TBBPA are *reactive* retardants and form chemical bonds with the polystyrene, whereas HBCD is *additive* and can be separated from the insulation material when dissolved in an acetone solution. (Schlummer et al., 2015)

A chart of a suggested improved process flow for future studies is depicted in appendix 1. In it, the first XRF measurement is taken directly from the polystyrene sample. If the sample contains no bromine, no brominated flame retardants have been used and the material can be recycled. If, on the other hand, it does contain bromine, an extraction can be done to a portion of the sample. The sample is then dissolved in an acetone-based solution, and the next XRF measurement taken from the extraction solution. If the bromine can now be found in the extraction solution, the sample most likely contains an *additive* retardant such as HBCD. If the bromine remains in the polymer gel after extraction, it is likely to be bound to a *reactive* FR such as PolyFR or TBBPA.

The next proposed course of action is to test the extraction method and its viability as an on-site method by comparing its results to chemical analyses, and creating step-by-step instructions for a suitable field detection method. Due to the commercial availability and relative harmlessness of the materials needed for the extraction, it might be possible to eventually piece together a measurement kit for on-site detection, with solvent measured beforehand, a scale to weigh the polystyrene sample, and suitable containers for dissolving it.

This way, only the samples with bromine measured from the extraction solution would have to be sent to the laboratory for GC analysis.

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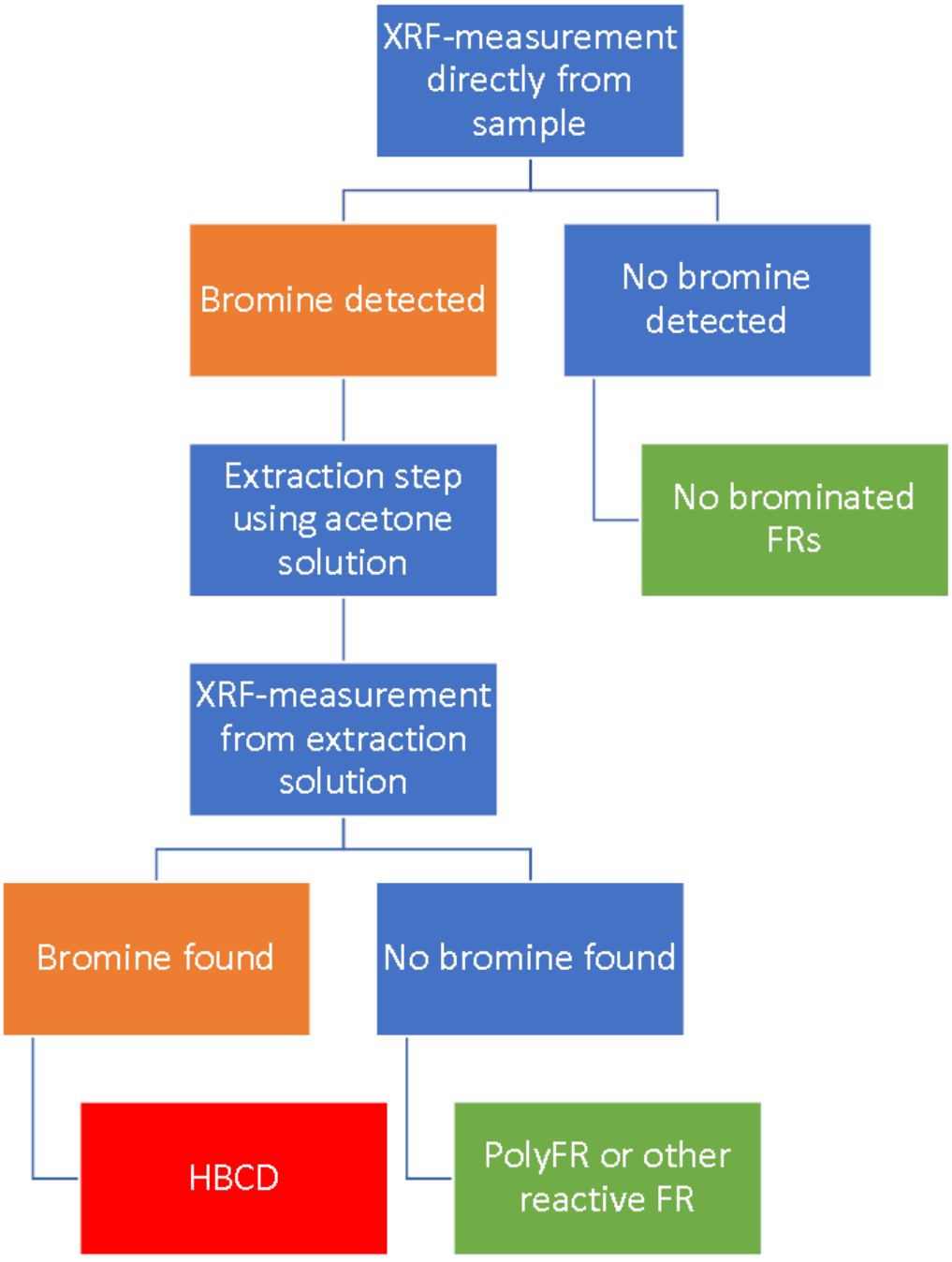
APPENDICES

Appendix 1. Suggested method flow chart with extraction step



Appendix 2. Data from XRF measurement

1

Durati	Units	User Logi	Ba	Ba Error	Sb	Sb Error	Sn	Sn Error	Cd	Cd Error	Bal	Bal Error	Bi	Bi Error	Pb	Pb Error	Br	Br Error	Se	Se Error	As	As Error	Hg
90	ppm	A01-1	976.87	515	< LOD	141.42	< LOD	91.47	< LOD	75.43	997078.56	1188.55	< LOD	42.45	< LOD	33.43	198.07	47.84	< LOD	73.99	< LOD	26.68	< LOD
90	ppm	A01-2	< LOD	517.15	< LOD	101.59	< LOD	65.35	< LOD	52.65	995375.88	816.15	< LOD	40.04	< LOD	32.05	162.2	32.65	< LOD	45.07	< LOD	21.05	< LOD
90	ppm	A01-3	575.85	340.58	< LOD	95.52	< LOD	65.6	< LOD	52.07	997097.25	766.44	< LOD	65.6	< LOD	22.83	1650.63	95.71	< LOD	43.39	< LOD	14.79	< LOD
90	ppm	A03.1	< LOD	262.54	< LOD	53.88	49.93	27.14	< LOD	30.88	975684.19	709.9	< LOD	73.45	< LOD	21.91	2912.35	103.47	< LOD	24.56	< LOD	13.51	< LOD
90	ppm	A03.2	< LOD	342.49	< LOD	68.1	< LOD	49.91	< LOD	37.53	984354.63	718.46	< LOD	83.17	< LOD	30.67	2737.25	117.25	< LOD	31.62	< LOD	18.13	< LOD
90	ppm	A03.3	455.5	244.72	< LOD	72.26	< LOD	50.2	< LOD	41.16	983947.69	808.45	< LOD	80.97	< LOD	39.45	2230.37	109.36	< LOD	35.2	< LOD	24.58	< LOD
90	ppm	A05-1	813.5	323.46	< LOD	99.12	< LOD	68.12	< LOD	53.7	992000.19	767.29	< LOD	142.11	< LOD	42.12	6592.43	309.4	< LOD	51.94	< LOD	20.9	< LOD
90	ppm	A05-2	< LOD	519.24	< LOD	102.37	< LOD	65.72	< LOD	58.11	992799.06	781.23	< LOD	149.26	< LOD	42.48	6363.16	301.13	< LOD	52.14	< LOD	21.4	< LOD
90	ppm	A05-3	946.3	453.01	< LOD	132.31	< LOD	90.73	< LOD	68.08	992423.19	1028.14	< LOD	178.45	< LOD	60.7	5843.87	354.67	< LOD	72.92	< LOD	32.35	< LOD
90	ppm	A06-1	< LOD	461.77	< LOD	94.74	< LOD	65.35	< LOD	52.29	991922	750.64	< LOD	135.56	< LOD	38.47	6882.03	298	< LOD	44.98	< LOD	18.87	< LOD
90	ppm	A06-2	947.79	346.73	< LOD	105.64	< LOD	71.94	< LOD	54.02	991866.75	839.27	< LOD	161.6	< LOD	42.13	6606.62	327.23	< LOD	56.01	< LOD	22.41	< LOD
90	ppm	A06-3	418.24	263.76	< LOD	80.24	< LOD	55.78	< LOD	44.96	989255	729.3	< LOD	123.4	< LOD	35.92	6558.64	270.39	< LOD	43.14	< LOD	18.85	< LOD
90	ppm	A07-1	< LOD	204.84	< LOD	43.13	< LOD	30.04	< LOD	23.87	990940.25	357.17	< LOD	79.02	< LOD	18.35	7656.9	166.9	< LOD	17.87	< LOD	8.58	< LOD
90	ppm	A07-2	< LOD	185.63	< LOD	39.55	< LOD	27.11	< LOD	21.81	990896.63	320.85	< LOD	73.93	< LOD	18.55	7638.24	156.07	< LOD	17.13	< LOD	8.36	< LOD
90	ppm	A07-3	< LOD	276.88	< LOD	58.44	< LOD	38.46	< LOD	31.23	991187.06	476.95	< LOD	100.35	< LOD	27.09	6950.68	197.49	< LOD	25.7	< LOD	12.52	< LOD
90	ppm	A08.1	860.52	418.67	< LOD	115.47	< LOD	82.85	< LOD	64.34	998289.19	1021.85	< LOD	29.78	< LOD	31.25	< LOD	36.35	< LOD	54.66	< LOD	21.04	< LOD
90	ppm	A08.2	717.73	369.68	< LOD	103.26	< LOD	69.03	< LOD	52.64	998092.19	827.66	< LOD	26.35	< LOD	24.14	< LOD	28.45	< LOD	40.53	< LOD	16.71	< LOD
90	ppm	A08.3	< LOD	503.54	< LOD	96.15	< LOD	65.85	< LOD	49.85	998291.88	750.64	< LOD	23.76	< LOD	19.34	< LOD	27.19	< LOD	35.9	< LOD	15.2	< LOD
90	ppm	A09.1	545.65	353.93	< LOD	102.15	< LOD	72.41	< LOD	55.66	998253.19	794.57	< LOD	37.83	< LOD	23.13	423.86	43.06	< LOD	41.14	< LOD	14.4	< LOD
90	ppm	A09.2	< LOD	562.06	< LOD	106.78	< LOD	72.54	< LOD	55.83	998670.63	860.09	< LOD	39.25	< LOD	23.94	275.3	37.29	< LOD	45.32	< LOD	17.17	< LOD
90	ppm	A09.3	798.05	525.31	< LOD	144.16	< LOD	98.9	< LOD	74.02	998262.56	1203.1	< LOD	63.47	< LOD	27.93	207.74	50.12	< LOD	67.74	< LOD	25.41	< LOD
90	ppm	A11-1	< LOD	460.32	< LOD	94.14	< LOD	61.37	< LOD	51.97	992511.38	734.64	< LOD	136.04	< LOD	42.58	6845.38	293.6	< LOD	43.99	< LOD	20.14	< LOD
90	ppm	A11-2	457.44	261.69	< LOD	78.76	< LOD	55.85	< LOD	44.08	992515.69	623.96	< LOD	120.63	< LOD	32.6	6696.91	260.17	< LOD	38.53	< LOD	15.97	< LOD
90	ppm	A11-3	< LOD	449.41	< LOD	89.85	< LOD	63.54	< LOD	49.06	991438.88	724.78	< LOD	132.13	< LOD	36.11	6555.31	284.48	< LOD	45.34	< LOD	18.87	< LOD
90	ppm	A13-1	550.55	204.49	< LOD	63.05	< LOD	43.73	< LOD	35.88	945779.19	1726.01	< LOD	142.39	< LOD	36.54	9299.15	359.67	< LOD	41.23	< LOD	20.19	< LOD
90	ppm	A13-2	332.87	180.82	< LOD	54.62	< LOD	40.64	< LOD	31.91	969730.69	874.89	< LOD	115.22	50.17	25.83	9464.96	291.47	< LOD	30.54	< LOD	18	< LOD
90	ppm	A13-3	299.65	145.64	< LOD	45.36	< LOD	31.54	< LOD	25.08	979795	568.73	< LOD	97.08	< LOD	26.29	9604.41	241.63	< LOD	22.95	< LOD	11.85	< LOD
90	ppm	B01-1	1483.04	521.69	< LOD	139.62	< LOD	94.42	< LOD	75.15	997174.25	1216.36	< LOD	48.58	< LOD	35.49	< LOD	59.24	< LOD	92.79	< LOD	29.41	< LOD
90	ppm	B01-2	1341.08	593.46	< LOD	157.47	< LOD	112.54	< LOD	82.88	996400.94	1398.89	< LOD	39.73	< LOD	32.56	< LOD	72.22	< LOD	97.42	< LOD	26.37	< LOD
90	ppm	B01-3	1593.49	598.53	< LOD	161.19	< LOD	104.07	< LOD	84.76	996824.63	1330.01	< LOD	41.64	< LOD	47.46	< LOD	66.58	< LOD	96.74	< LOD	33.95	< LOD
90	ppm	B04.1	641.39	315.21	< LOD	92.71	< LOD	63.32	< LOD	49.46	993514.88	741.54	< LOD	98.35	< LOD	30.79	3253.32	159.03	< LOD	45.97	< LOD	17.75	< LOD
90	ppm	B04.2	< LOD	521.5	< LOD	106.84	< LOD	69.46	< LOD	57.03	996085.06	799.57	< LOD	98.57	< LOD	37.87	3272.13	165.46	< LOD	46.69	< LOD	20.14	< LOD
90	ppm	B04.3	571.47	355.67	< LOD	104.01	< LOD	68.75	< LOD	53.97	995416.63	809.59	< LOD	101.94	< LOD	33.32	3268.69	167.72	< LOD	47.53	< LOD	19.42	< LOD
90	ppm	B06.1	475.53	288.99	< LOD	83.54	< LOD	57.41	< LOD	43.6	999134.44	675.64	< LOD	24.44	< LOD	17.63	< LOD	20.65	< LOD	28.56	< LOD	12.53	< LOD
90	ppm	B06.2	634.36	291.08	< LOD	83.93	< LOD	56.91	< LOD	45.39	998624.25	682.99	< LOD	22.6	< LOD	17.81	< LOD	22.41	< LOD	31.75	< LOD	14.1	< LOD
90	ppm	B06.3	< LOD	472.54	< LOD	90.83	< LOD	62.28	< LOD	49.23	998825.75	723.66	< LOD	20.65	< LOD	22.35	< LOD	22.55	< LOD	33.33	< LOD	14.32	< LOD
90	ppm	B07.1	1297.77	514.93	< LOD	138.31	< LOD	91.68	< LOD	76.46	994492.56	1144.69	< LOD	69.25	< LOD	38.91	389.36	67.77	< LOD	82.92	< LOD	27.49	< LOD
90	ppm	B07.2	1308.74	513.36	< LOD	141.02	< LOD	97.06	< LOD	77.49	987462	1392.21	< LOD	72.72	< LOD	29.5	< LOD	89.38	< LOD	116.05	< LOD	32.84	< LOD
90	ppm	B07.3	1225.59	483.59	< LOD	131.32	< LOD	86.46	< LOD	70.61	993789.5	1152.71	< LOD	60.15	< LOD	32.26	412.76	68.11	< LOD	83.15	< LOD	28.62	< LOD

Durati	Units	User Logi	Ba	Ba Error	Sb	Sb Error	Sn	Sn Error	Cd	Cd Error	Bal	Bal Error	Bi	Bi Error	Pb	Pb Error	Br	Br Error	Se	Se Error	As	As Error	Hg
90	ppm	B08.1	< LOD	546.53	< LOD	102.38	< LOD	68.22	< LOD	53.55	996156	820.59	< LOD	35.88	< LOD	24.38	< LOD	31.76	< LOD	44.34	< LOD	17.87	< LOD
90	ppm	B08.2	579.24	327.08	< LOD	95.36	< LOD	62.84	< LOD	49.23	997391.44	760.46	< LOD	28.19	< LOD	21.27	< LOD	26	< LOD	37.09	< LOD	16.56	< LOD
90	ppm	B08.3	820.23	418.91	< LOD	120.45	< LOD	75.28	< LOD	63.06	996608.88	977.26	< LOD	35.96	< LOD	22.74	< LOD	42.12	< LOD	58.54	< LOD	19.33	< LOD
90	ppm	B09.1	1362.43	577.94	< LOD	160.94	< LOD	117.52	< LOD	88.01	991471.25	1331.5	< LOD	81.79	< LOD	42.87	366.78	80.15	< LOD	111.55	< LOD	35.57	< LOD
90	ppm	B09.2	982.36	451.97	< LOD	123.29	< LOD	83.66	< LOD	75.78	994784.06	1064.94	< LOD	44.62	< LOD	37.16	503.25	67.2	< LOD	72.08	< LOD	24.55	< LOD
90	ppm	B09.3	1806.07	576.61	< LOD	156.46	< LOD	108.17	< LOD	87.59	994509.44	1340.41	< LOD	77.83	< LOD	53.31	450.34	83.91	< LOD	109.36	< LOD	39.25	< LOD
90	ppm	B10.1	828.53	360.29	< LOD	105.44	< LOD	68.54	< LOD	55.41	997715.13	861.21	< LOD	31.62	< LOD	26.11	< LOD	37.25	< LOD	52.87	< LOD	19.2	< LOD
90	ppm	B10.2	792.18	394.93	< LOD	110.82	< LOD	76.94	< LOD	59.31	997953.75	938.02	< LOD	32.94	< LOD	23.23	< LOD	39.07	< LOD	53.08	< LOD	19.94	< LOD
90	ppm	B10.3	909.71	484.74	< LOD	138.41	< LOD	93.06	< LOD	73.73	998311.88	1118.9	< LOD	38.19	< LOD	28.03	< LOD	49.16	< LOD	72.67	< LOD	25.24	< LOD
90	ppm	C01.1	388.42	256.48	< LOD	75.3	< LOD	48.59	< LOD	40.75	997571.56	583.43	< LOD	19.99	< LOD	14.94	< LOD	16.46	< LOD	22.37	< LOD	11.27	< LOD
90	ppm	C01.2	401.67	264.56	< LOD	79	< LOD	53.77	< LOD	41.35	998184.88	612.66	< LOD	20.56	< LOD	9.91	< LOD	18.31	< LOD	25.65	< LOD	8.78	< LOD
90	ppm	C01.3	< LOD	326.74	< LOD	63.8	< LOD	42.64	< LOD	34.05	998213.13	503.9	< LOD	14.32	< LOD	11.12	< LOD	12.93	< LOD	19	< LOD	8.58	< LOD
90	ppm	C02.1	553.51	293.09	< LOD	85.21	< LOD	55.95	< LOD	45.28	998547.81	670.31	< LOD	32.95	< LOD	18.09	295.12	30.41	< LOD	33.48	< LOD	11.68	< LOD
90	ppm	C02.2	< LOD	454.28	< LOD	87.07	< LOD	59.56	< LOD	47.54	998538.31	718.05	< LOD	28.01	< LOD	16.75	112.91	24.22	< LOD	36.34	< LOD	12.65	< LOD
90	ppm	C02.3	498.24	270.55	< LOD	79.53	< LOD	53.92	< LOD	40.13	998803.69	626.72	< LOD	27.12	< LOD	16.2	130.38	22.23	< LOD	29.21	< LOD	11.47	< LOD
90	ppm	C03.1	569.59	356.04	< LOD	97.29	< LOD	70.58	< LOD	55.48	998864.38	789.12	< LOD	30.13	< LOD	25.51	< LOD	30.05	< LOD	43.34	< LOD	17.68	< LOD
90	ppm	C03.2	2277.11	1113.67	< LOD	303.71	< LOD	187.99	< LOD	145.46	996413.38	2515.77	< LOD	128.04	< LOD	84.08	< LOD	149.75	< LOD	203.25	< LOD	63.55	< LOD
90	ppm	C03.3	666.14	313.69	< LOD	91.58	< LOD	63.49	< LOD	48.12	998645.94	720.29	< LOD	24.41	< LOD	12.33	< LOD	28.02	< LOD	38.23	< LOD	9.6	< LOD
90	ppm	C04.1	518.97	312.62	< LOD	92.26	< LOD	59.5	< LOD	49.2	998134.94	729.09	< LOD	15.98	< LOD	17.23	33.03	19.06	< LOD	37.26	< LOD	13.61	< LOD
90	ppm	C04.2	673.5	304.78	< LOD	88.05	< LOD	58.25	< LOD	47.82	997921.81	702.39	< LOD	29.45	< LOD	20.62	< LOD	28.74	< LOD	35.95	< LOD	14.94	< LOD
90	ppm	C04.3	571.92	306.57	< LOD	89.16	< LOD	62.94	< LOD	47.21	998690.5	711.11	< LOD	25.8	< LOD	19.61	< LOD	26.93	< LOD	37.42	< LOD	13.42	< LOD
90	ppm	C05.1	877.84	306.69	< LOD	89.62	< LOD	58.62	< LOD	45.9	998685.81	671.14	< LOD	19.39	< LOD	16.86	< LOD	23.97	< LOD	34.47	< LOD	12.43	< LOD
90	ppm	C05.2	520.54	305.41	< LOD	87.52	< LOD	59.99	< LOD	45.87	998658.75	722.54	< LOD	26.01	< LOD	14.79	< LOD	25.02	< LOD	33.69	< LOD	12.31	< LOD
90	ppm	C05.3	812.12	427.92	< LOD	117.77	< LOD	78.77	< LOD	62.45	998407.69	955.96	< LOD	33.34	< LOD	19.17	< LOD	39.2	< LOD	54.76	< LOD	20.08	< LOD
90	ppm	C06.1	< LOD	477.53	< LOD	91.73	< LOD	61.28	< LOD	51.16	998909.06	749.2	< LOD	18.62	< LOD	21.72	< LOD	26.31	< LOD	38.49	< LOD	15.29	< LOD
90	ppm	C06.2	< LOD	531.88	< LOD	104.25	< LOD	66.89	< LOD	56.08	998911.56	815.12	< LOD	26.44	< LOD	25.76	< LOD	28.93	< LOD	42.24	< LOD	19.24	< LOD
90	ppm	C06.3	< LOD	650.31	< LOD	125	< LOD	86.52	< LOD	62.89	998503.25	1009.95	< LOD	32.45	< LOD	25.17	< LOD	41.33	< LOD	57.49	< LOD	19.51	< LOD
90	ppm	C07.1	829.6	335.18	< LOD	95.19	< LOD	62.9	< LOD	51.61	998275.06	774.19	< LOD	23.25	< LOD	22.57	< LOD	31.48	< LOD	40.49	< LOD	15.32	< LOD
90	ppm	C07.2	633.23	335.81	< LOD	92.48	< LOD	66.09	< LOD	50.58	998319.5	760.77	< LOD	21.25	< LOD	18.25	< LOD	27.3	< LOD	41.24	< LOD	15.1	< LOD
90	ppm	C07.3	516.73	330.57	< LOD	97.24	< LOD	66.28	< LOD	52.85	998591.44	764.76	< LOD	27.94	< LOD	15.29	< LOD	27.31	< LOD	39.53	< LOD	15.14	< LOD
90	ppm	C08.1	1119.7	400.09	< LOD	110.85	< LOD	75.12	< LOD	56.81	998350.31	899.67	< LOD	29.57	< LOD	17.98	< LOD	38.4	< LOD	55.15	< LOD	15.49	< LOD
90	ppm	C08.2	496.49	309.14	< LOD	86.35	< LOD	58.99	< LOD	45.99	998454.75	737.4	< LOD	28.94	< LOD	19.1	< LOD	26.06	< LOD	37.16	< LOD	14.07	< LOD
90	ppm	C08.3	< LOD	558.24	< LOD	105.79	< LOD	70.69	< LOD	57.02	998828.5	833.73	< LOD	20.06	< LOD	25.41	< LOD	32.22	< LOD	47	< LOD	18.54	< LOD
90	ppm	C09.1	< LOD	531.47	< LOD	100.89	< LOD	70.77	< LOD	57.73	998450.56	842.36	< LOD	28.83	< LOD	16.03	< LOD	29.18	< LOD	40.89	< LOD	12.8	< LOD
90	ppm	C09.2	2266.18	932.74	< LOD	259.2	< LOD	154.34	< LOD	127.85	996322.19	1926.34	< LOD	83.14	< LOD	68.52	< LOD	115.67	< LOD	159.41	< LOD	56.18	< LOD
90	ppm	C09.3	< LOD	504.75	< LOD	96.28	< LOD	65.38	< LOD	51.84	999007.06	764.04	< LOD	27.32	< LOD	18.96	< LOD	26.91	< LOD	40.79	< LOD	14.86	< LOD
90	ppm	C10.1	752.97	354.26	< LOD	98.44	< LOD	63.76	< LOD	51.64	998619.06	835.33	< LOD	27.96	< LOD	26.01	< LOD	30.54	< LOD	44.71	< LOD	19.12	< LOD
90	ppm	C10.2	3057.33	1167.23	< LOD	283.49	< LOD	205.32	< LOD	146.31	996114.63	2428.69	< LOD	108.87	< LOD	89.97	< LOD	156.75	< LOD	232.17	< LOD	66.24	< LOD
90	ppm	C10.3	< LOD	536.87	< LOD	101.17	< LOD	69.02	< LOD	52.87	998091.44	837.95	< LOD	25.26	< LOD	14.8	< LOD	29.81	< LOD	42.47	< LOD	14.3	< LOD

Durati	Units	User Logi	Ba	Ba Error	Sb	Sb Error	Sn	Sn Error	Cd	Cd Error	Bal	Bal Error	Bi	Bi Error	Pb	Pb Error	Br	Br Error	Se	Se Error	As	As Error	Hg
90	ppm	C11.1	689.44	313.48	< LOD	88.71	< LOD	59.93	< LOD	49.23	998830.25	727	< LOD	25.56	< LOD	15.54	< LOD	25.92	< LOD	36.46	< LOD	14.55	< LOD
90	ppm	C11.2	< LOD	706.78	< LOD	137.79	< LOD	94.73	< LOD	70.14	998813.63	1092.63	< LOD	45.76	< LOD	16.2	< LOD	47.13	< LOD	63.45	< LOD	18.38	< LOD
90	ppm	C11.3	< LOD	443.73	< LOD	85.44	< LOD	59.46	< LOD	45.22	998818.69	677.14	< LOD	11.35	< LOD	13.34	< LOD	21.52	< LOD	31.51	< LOD	12.12	< LOD
90	ppm	C12.1	539.6	334.84	< LOD	98.24	< LOD	63.69	< LOD	50.6	998885.5	763.36	< LOD	32.55	< LOD	21.75	< LOD	26.81	< LOD	38.8	< LOD	14.34	< LOD
90	ppm	C12.2	< LOD	479.15	< LOD	92.71	< LOD	61.71	< LOD	48.57	998714.5	740.3	< LOD	22.66	< LOD	22.12	< LOD	26.9	< LOD	37.15	< LOD	14.9	< LOD
90	ppm	C12.3	767.74	409	< LOD	117.14	< LOD	81.34	< LOD	62.68	998603.06	933.67	< LOD	26.83	< LOD	23.42	< LOD	38.45	< LOD	51.81	< LOD	16.95	< LOD
90	ppm	C13.1	794.57	309.66	< LOD	89.56	< LOD	60.96	< LOD	47.39	998427.13	718.15	< LOD	35.08	< LOD	17.23	166.88	27.8	< LOD	35.27	< LOD	13.32	< LOD
90	ppm	C13.2	1131.64	527.72	< LOD	145.01	< LOD	99.23	< LOD	76.29	998354.13	1260.04	< LOD	53.22	< LOD	29.76	< LOD	60.15	< LOD	74.5	< LOD	25.4	< LOD
90	ppm	C13.3	612.67	339.41	< LOD	97.05	< LOD	64.04	< LOD	51.96	998342.31	778.29	< LOD	44.32	< LOD	15.02	355.82	38.15	< LOD	37.97	< LOD	12.76	< LOD
90	ppm	C14.1	< LOD	372.34	< LOD	72.38	< LOD	48.89	< LOD	38.79	998700.44	584.27	< LOD	15.41	< LOD	11.03	< LOD	17.96	< LOD	23.65	< LOD	9.44	< LOD
90	ppm	C14.2	376.47	219.05	< LOD	65.28	< LOD	44.57	< LOD	35.01	998924.13	505.61	< LOD	17.74	< LOD	14.13	24.52	11.31	< LOD	20.01	< LOD	9.21	< LOD
90	ppm	C14.3	477.54	248.97	< LOD	72.76	< LOD	46.67	< LOD	39.15	998166.88	572.42	< LOD	25.16	< LOD	13.53	93.1	17.66	< LOD	23.33	< LOD	9.48	< LOD
90	ppm	C15.1	< LOD	380.97	< LOD	78.18	< LOD	53.69	< LOD	43.13	991288.69	629.71	< LOD	127.74	< LOD	31.36	7134.65	276.37	< LOD	36.95	< LOD	15.21	< LOD
90	ppm	C15.2	< LOD	340.8	< LOD	69.3	< LOD	49.78	< LOD	38.13	991660.13	561.35	< LOD	119.37	< LOD	33.15	7336.13	259.96	< LOD	33.51	< LOD	15.52	< LOD
90	ppm	C15.3	< LOD	293.17	< LOD	61.75	< LOD	43.55	< LOD	35.79	965914.81	1108.27	< LOD	134.5	< LOD	31.84	9065.3	334.32	< LOD	39.31	< LOD	15.71	< LOD
90	ppm	C15e-1	< LOD	499.7	< LOD	94.48	< LOD	63.38	< LOD	52.87	995711.75	768.41	< LOD	22.97	< LOD	26.78	< LOD	31.27	< LOD	43.31	< LOD	19.23	< LOD
90	ppm	C15e-2	1206.1	416.6	< LOD	114.07	< LOD	82.45	< LOD	64.4	994997.56	952	< LOD	30.7	< LOD	34.98	< LOD	46.16	< LOD	63.12	< LOD	24.32	< LOD
90	ppm	C15e-3	4066.29	1353.99	< LOD	312.18	< LOD	209.24	< LOD	162.54	987203.5	3341.2	< LOD	173.9	< LOD	178.4	< LOD	287.1	< LOD	372.13	< LOD	133.67	< LOD
90	ppm	C16.1	< LOD	359.62	< LOD	73.98	< LOD	50.82	< LOD	42.54	990800.31	611.92	< LOD	127.15	< LOD	34.44	7623.72	281.62	< LOD	35.93	< LOD	15.5	< LOD
90	ppm	C16.2	639.38	303.88	< LOD	91.96	< LOD	65.46	< LOD	51.13	991453	734.63	< LOD	152.18	< LOD	35.39	7340.63	322.9	< LOD	45.66	< LOD	16.66	< LOD
90	ppm	C16.3	671.79	310	< LOD	92.14	< LOD	60.21	< LOD	51.18	991678.63	759.98	< LOD	142.39	< LOD	33.95	7151.32	318.41	< LOD	47.67	< LOD	17.52	< LOD
90	ppm	C17.1	755.06	397.96	< LOD	112.89	< LOD	76.66	< LOD	59.47	995537.81	859.36	< LOD	113.8	< LOD	26.89	3051.18	176.11	< LOD	58.45	< LOD	18.78	< LOD
90	ppm	C17.2	514.27	283.1	< LOD	85.07	< LOD	55.76	< LOD	46.46	994185.31	685.03	< LOD	96.38	< LOD	24.21	3403.25	155.49	< LOD	40.32	< LOD	15.38	< LOD
90	ppm	C17.3	822.31	369.56	< LOD	103.61	< LOD	73.47	< LOD	57.93	995218.44	840.21	< LOD	109.07	< LOD	35.43	3191.51	180.86	< LOD	58.38	< LOD	19.73	< LOD
90	ppm	C18.1	< LOD	378.34	< LOD	76.56	< LOD	54.17	< LOD	42.69	991385.5	624.96	< LOD	125.17	< LOD	32.19	7279.48	273.67	< LOD	34.93	< LOD	15.46	< LOD
90	ppm	C18.2	< LOD	509.44	< LOD	99.23	< LOD	70.45	< LOD	56.19	992536.69	800.93	< LOD	149.26	< LOD	32.42	6724.17	318.68	< LOD	49.77	< LOD	17.38	< LOD
90	ppm	C18.3	< LOD	309.4	< LOD	64.49	< LOD	43.63	< LOD	34.31	991580.81	507.61	< LOD	110.81	< LOD	27.84	7531.27	245.26	< LOD	29.68	< LOD	13.27	< LOD
90	ppm	C19.1	478.7	231.24	< LOD	67.6	< LOD	48.29	< LOD	38.49	992473.13	560.84	< LOD	104.75	< LOD	29.82	5968.94	212.61	< LOD	32.89	< LOD	15.01	< LOD
90	ppm	C19.2	< LOD	618.69	< LOD	120.73	< LOD	79.61	< LOD	64.8	993022.69	937.81	< LOD	163.9	< LOD	47.7	5932.51	329.82	< LOD	63.65	< LOD	24.74	< LOD
90	ppm	C19.3	< LOD	324.32	< LOD	65.39	< LOD	44.89	< LOD	37.33	992445.13	530.11	< LOD	102.65	< LOD	25.19	5803.39	196.88	< LOD	28.73	< LOD	12.09	< LOD
90	ppm	C20-1	< LOD	433.72	< LOD	88.44	< LOD	62.59	< LOD	44.26	991586.69	709.27	< LOD	126.2	< LOD	43.15	5928.29	250.79	< LOD	41.83	< LOD	20.44	< LOD
90	ppm	C20-2	703.17	266.3	< LOD	77.94	< LOD	54.84	< LOD	46.88	993042.38	624.55	< LOD	114.36	< LOD	29.9	5750.4	230.93	< LOD	38.33	< LOD	16.34	< LOD
90	ppm	C20-3	636.45	265.23	< LOD	83.06	< LOD	55.22	< LOD	43.9	992482.75	654.51	< LOD	124.06	< LOD	33.06	5958.31	246.93	< LOD	42.58	< LOD	15.86	< LOD

User Logi	Hg Error	Au	Au Error	Zn	Zn Error	Cu	Cu Error	Ni	Ni Error	Fe	Fe Error	Cr	Cr Error	V	V Error	Ti	Ti Error	Cl	Cl Error
A01-1	136.67	< LOD	232.4	184.15	88.13	< LOD	269.47	< LOD	226.09	800.16	263.61	< LOD	67.16	< LOD	1475.5	540.19	80.64	< LOD	317.37
A01-2	88.85	< LOD	139.24	257.35	69.56	< LOD	172.85	< LOD	126.09	1231.04	224.2	117.12	36.56	< LOD	1022.68	914.43	77.33	1440.05	188.32
A01-3	82.38	< LOD	127.01	166.58	55.31	< LOD	133.89	< LOD	113.3	194.15	117.98	79.34	35.53	< LOD	930.46	< LOD	72.42	< LOD	223.99
A03.1	42.89	< LOD	65.99	< LOD	40.46	< LOD	83.68	< LOD	72.74	1779.61	175.38	74.8	25.28	< LOD	674.78	547.48	44.99	18649.93	512.02
A03.2	58.64	< LOD	89.78	95.17	40.78	< LOD	110.98	< LOD	93.29	4663.02	306.7	79.18	25.02	< LOD	695.09	1543.55	73.22	6181.39	232.18
A03.3	61.57	< LOD	98.72	129.34	48.82	< LOD	134.12	< LOD	112.36	6924.12	401.87	89.37	23.51	< LOD	727.76	1882.56	87.36	4159.72	187.64
A05-1	83.68	< LOD	121.75	79.72	43.77	< LOD	128.86	< LOD	109.2	< LOD	155.96	< LOD	47.94	< LOD	749.78	< LOD	65.17	< LOD	198.86
A05-2	87.1	< LOD	124.86	79.68	42.83	< LOD	117.53	< LOD	108.95	287.91	118.03	< LOD	46.84	< LOD	760.91	< LOD	65.81	< LOD	203.67
A05-3	126.41	< LOD	185.86	121.49	63.3	< LOD	193.03	< LOD	165.43	< LOD	226.82	< LOD	57.21	< LOD	1038.13	108.83	53.98	< LOD	269.71
A06-1	72.23	< LOD	104.95	104.77	39.82	< LOD	108.46	< LOD	93.49	166.35	93.47	65.45	30.24	< LOD	762.34	< LOD	61.99	< LOD	190.89
A06-2	93.33	< LOD	139.4	< LOD	72.04	< LOD	137.03	< LOD	124.45	313.91	133.66	< LOD	51.58	< LOD	828.99	< LOD	70.79	< LOD	217.73
A06-3	68.36	< LOD	103.67	139.25	42.39	< LOD	108.02	< LOD	88.09	2011.35	212.71	80.95	27.04	< LOD	643.16	808.9	58.26	677.34	154.51
A07-1	23.68	< LOD	33.24	164.26	21.33	< LOD	38.6	< LOD	30.56	792.37	74.63	23.85	14.23	< LOD	324.69	261.55	22.14	< LOD	73.23
A07-2	21.63	< LOD	29.75	154.94	19.35	< LOD	33.97	< LOD	27.36	395.89	52.95	< LOD	20.53	< LOD	292.43	256.08	20.8	484.26	49.65
A07-3	35.09	< LOD	53.28	169.33	29	< LOD	58.87	< LOD	49.73	1083.56	111.67	25.11	16.6	< LOD	447.63	256.37	27.83	< LOD	95.48
A08.1	99.53	< LOD	168.41	172.6	73	< LOD	199.21	< LOD	151.99	431.18	183.82	66.22	40.49	< LOD	1316.13	< LOD	82.69	< LOD	249.46
A08.2	74.73	< LOD	127.51	175.8	58.84	< LOD	161.86	< LOD	139.12	706.54	178.33	< LOD	53	< LOD	1018.05	< LOD	73.77	< LOD	220.31
A08.3	73.59	< LOD	112.35	236.5	56.58	< LOD	144.39	< LOD	107.05	808.84	169.06	66.9	32.43	< LOD	913.35	83.58	46.29	< LOD	196.21
A09.1	77.11	< LOD	123.35	107.23	52.97	< LOD	145.49	< LOD	124.31	227.27	129.82	< LOD	54.9	< LOD	994.62	< LOD	73.01	282.82	157.36
A09.2	81.19	< LOD	139.9	166.43	59.89	< LOD	167.06	< LOD	130.22	279.64	141.13	68.19	38.13	< LOD	1066.91	< LOD	77.51	< LOD	244.34
A09.3	141.13	< LOD	219.65	142.73	83.76	< LOD	250.69	< LOD	216.79	< LOD	301.13	71.26	46.99	< LOD	1504.02	< LOD	95.95	< LOD	325.58
A11-1	75.63	< LOD	107.13	65.25	37.94	< LOD	113.14	< LOD	88.21	< LOD	130.52	< LOD	45.87	< LOD	742.29	< LOD	60.12	< LOD	189.29
A11-2	56.95	< LOD	85.64	87.52	34.03	< LOD	92.23	< LOD	72.8	< LOD	112.07	45.12	26.21	< LOD	619.8	< LOD	51.95	< LOD	162.85
A11-3	73.48	< LOD	109.58	129.32	44.37	< LOD	110.33	< LOD	99.46	694.67	145.63	< LOD	42.24	< LOD	685.39	200.23	41.95	398.45	128.23
A13-1	65.86	< LOD	93.43	< LOD	50.57	< LOD	111.85	< LOD	101.24	199.35	104.88	76.4	30.73	< LOD	918.62	< LOD	105.23	43491.59	1376.77
A13-2	41.55	< LOD	61.03	< LOD	31.06	< LOD	69.44	< LOD	62.41	189.89	72.32	41.9	22.88	653.1	427.58	< LOD	81.96	19422.72	525.33
A13-3	31.5	< LOD	41.18	49.04	17.45	< LOD	47.55	< LOD	41.67	1270.58	108.65	53.06	17.85	737.5	299.83	1012.95	55.07	7100.46	187.45
B01-1	164.26	< LOD	289.57	235.42	109.44	< LOD	311.53	< LOD	264.22	< LOD	281.14	< LOD	99.24	< LOD	1541.67	< LOD	133.97	776.47	316.17
B01-2	196.08	< LOD	303.05	440.79	135.97	< LOD	331.63	< LOD	285.45	< LOD	333.73	113.91	70.64	< LOD	1810.45	< LOD	145.6	1247.22	336.1
B01-3	186.65	< LOD	306.69	367.96	129.93	< LOD	340.06	< LOD	273.39	< LOD	350.32	< LOD	105.94	< LOD	1660.47	< LOD	142.38	773.27	323.48
B04.1	84.45	< LOD	125.18	75.84	45.97	< LOD	132.11	< LOD	103.43	< LOD	168.65	82.69	37.52	< LOD	875.5	< LOD	76.08	2092.5	192.09
B04.2	79.69	< LOD	128.31	< LOD	65.82	< LOD	140.87	< LOD	114.74	< LOD	171.35	< LOD	56.63	< LOD	922.71	< LOD	76.21	< LOD	257.61
B04.3	84.77	< LOD	129.03	< LOD	70.95	< LOD	141.17	< LOD	114.81	< LOD	163.31	98.17	38.91	< LOD	939.51	< LOD	78.59	347.28	173.14
B06.1	56.57	< LOD	91.53	106.41	44.27	< LOD	116.93	< LOD	89.85	< LOD	130.75	78.43	32.83	< LOD	864.2	< LOD	64.79	< LOD	203.65
B06.2	63.77	< LOD	99.61	143.56	46.01	< LOD	120.12	< LOD	98.21	201.63	104.88	94.13	33.61	< LOD	870.03	< LOD	65.43	< LOD	209.1
B06.3	62.46	< LOD	104.62	137.34	47.76	< LOD	122.52	< LOD	100.55	< LOD	151.07	55.29	34.98	< LOD	928.32	< LOD	68.86	421.96	143.53
B07.1	164.28	< LOD	259.67	368.05	112.22	< LOD	281.08	< LOD	246.95	< LOD	332.83	154.33	66.95	< LOD	1425.13	< LOD	142.18	2589.65	359.23
B07.2	233.34	< LOD	374.44	1121.15	211.6	< LOD	397.22	< LOD	326.4	< LOD	441.5	220.2	83.58	< LOD	1616.47	7445.07	530.85	1633.28	341.22
B07.3	162.36	< LOD	260.83	343.22	110.7	< LOD	293.4	< LOD	236.85	359.54	226.89	186.63	66.87	< LOD	1494.13	192.27	94.9	3278.03	374.51

User Logi	Hg Error	Au	Au Error	Zn	Zn Error	Cu	Cu Error	Ni	Ni Error	Fe	Fe Error	Cr	Cr Error	V	V Error	Ti	Ti Error	Cl	Cl Error
B08.1	87.16	< LOD	142.43	< LOD	69.61	< LOD	176.05	< LOD	139.78	322.31	146.73	139.41	44.63	< LOD	1089.98	< LOD	89.86	2180	214.27
B08.2	71.92	< LOD	115.87	< LOD	62.01	< LOD	136.36	< LOD	109.1	209.5	124.52	67.29	39.1	< LOD	1019.87	< LOD	76.04	1625.69	169.82
B08.3	116.56	< LOD	183.48	< LOD	84.48	< LOD	206.72	< LOD	176.76	< LOD	263.04	82.73	52.42	< LOD	1302.6	< LOD	107.42	2069.7	253.84
B09.1	218.06	< LOD	343.5	255.62	122.68	< LOD	359.75	< LOD	312.68	< LOD	392.14	208.69	81.83	< LOD	1704.38	1141.14	149.21	4498.32	485.98
B09.2	137.86	< LOD	227.07	235.97	92.42	< LOD	256.78	< LOD	220.4	< LOD	285.37	103.79	62.58	< LOD	1335.55	2105.41	161.22	712.54	277.24
B09.3	211.95	< LOD	346.9	289.78	131.96	< LOD	375.44	< LOD	302.01	< LOD	394.27	141.84	77.64	< LOD	1645.15	1848.35	182.64	< LOD	493.05
B10.1	103.54	< LOD	167.87	451.95	87.88	< LOD	169.95	< LOD	149.34	378.73	158.27	103.36	45.07	< LOD	1071.96	< LOD	90.03	< LOD	296.69
B10.2	109.42	< LOD	173.01	436.42	89.78	< LOD	179.41	< LOD	159.44	< LOD	205.48	108.7	47.3	< LOD	1182.29	< LOD	96.39	< LOD	300.75
B10.3	134.42	< LOD	222.44	342.21	100.49	< LOD	246.52	< LOD	197.78	< LOD	263.91	91.81	52.2	< LOD	1390.89	< LOD	106.27	< LOD	355.54
C01.1	45.98	< LOD	70.72	135.85	39.98	< LOD	100.1	< LOD	76.62	401.52	112.88	54.17	26.62	< LOD	757.21	936.06	54.76	440.63	103.47
C01.2	50.55	< LOD	80.45	135.18	41.25	< LOD	101.71	< LOD	81.39	207.69	97.53	56.19	27.22	< LOD	796.68	869.29	53.94	< LOD	153.1
C01.3	34.9	< LOD	59.27	174.25	35.46	< LOD	77.66	< LOD	63.6	301.14	86.02	76.5	23.46	< LOD	652.69	982.4	48.5	< LOD	124.08
C02.1	59.44	< LOD	105.67	282.01	57.34	< LOD	116.31	< LOD	90.51	< LOD	152.02	122.54	32.29	< LOD	838.99	< LOD	64.04	< LOD	200.34
C02.2	69.44	< LOD	116.81	298.73	61.87	< LOD	132.94	< LOD	105.46	451.14	138.75	82.97	36.42	< LOD	889.03	< LOD	78.43	< LOD	227.68
C02.3	58.01	< LOD	93.79	244.43	52.09	< LOD	110.56	< LOD	85.48	< LOD	138.32	67.28	31.16	< LOD	786.61	< LOD	60.93	< LOD	193.16
C03.1	83.37	< LOD	137.87	267.65	66.21	< LOD	152.81	< LOD	126.14	< LOD	183.63	< LOD	62.2	< LOD	966.59	< LOD	82.14	< LOD	263.89
C03.2	410.04	< LOD	624.78	< LOD	298.64	< LOD	670.25	< LOD	569.9	< LOD	678.64	< LOD	146.3	< LOD	3106.5	< LOD	209.4	< LOD	786.32
C03.3	77.41	< LOD	123.05	234.66	60.4	< LOD	141.93	< LOD	106.11	< LOD	166.36	124.06	37.74	< LOD	899.21	< LOD	74.41	< LOD	231.68
C04.1	68.93	< LOD	117.47	287.53	62.18	< LOD	133.64	< LOD	107.29	277.79	123.69	90.6	35.76	< LOD	928.7	< LOD	71.7	521.17	150.89
C04.2	70.12	< LOD	112.59	352.99	65.87	< LOD	129.66	< LOD	111.32	183.94	114.85	111.54	35.85	< LOD	891.93	< LOD	71.41	560.83	150.93
C04.3	75.89	< LOD	119.97	279.82	62.22	< LOD	135.09	< LOD	103.94	< LOD	152.03	80.22	36.14	< LOD	892.21	< LOD	71.47	< LOD	232.65
C05.1	62.03	< LOD	107.82	235.62	56.92	< LOD	126.19	< LOD	101.14	< LOD	139.8	64.36	33.49	< LOD	842.56	< LOD	65.97	< LOD	196.97
C05.2	66.81	< LOD	107.4	264.96	57.64	< LOD	126.16	< LOD	101.15	248.89	113.94	65.05	36.04	< LOD	916.46	< LOD	71.9	< LOD	217.39
C05.3	105.67	< LOD	172.95	208.89	73.85	< LOD	196.02	< LOD	154.14	< LOD	236.13	107.72	42.38	< LOD	1193.88	< LOD	86.08	< LOD	274.88
C06.1	72.53	< LOD	123.89	259.41	62.52	< LOD	135.81	< LOD	104.31	243.94	125.79	72.02	37.84	< LOD	933.88	< LOD	76.72	< LOD	243.3
C06.2	79.88	< LOD	134.08	362.31	73.44	< LOD	148.17	< LOD	128.82	< LOD	164.73	117.8	42.79	< LOD	1012.14	< LOD	84.58	< LOD	279.61
C06.3	114.56	< LOD	183.18	333.11	85.72	< LOD	196.76	< LOD	170.55	< LOD	224.79	< LOD	74.71	< LOD	1262.16	< LOD	100.68	< LOD	325.02
C07.1	83.49	< LOD	127.15	302.38	67.38	< LOD	148.14	< LOD	110.11	287.3	135.09	79.01	37.96	< LOD	966.86	< LOD	76.5	< LOD	240.29
C07.2	74.74	< LOD	130.24	329.96	68.41	< LOD	143.73	< LOD	116.91	413.65	144.06	99.16	37.95	< LOD	937.87	< LOD	76.61	< LOD	243.79
C07.3	74.52	< LOD	121.96	278.52	64.4	< LOD	145.26	< LOD	118.42	332.12	136.61	90.61	37.95	< LOD	947.44	< LOD	76.29	< LOD	238.8
C08.1	107.55	< LOD	173	256.31	77.45	< LOD	189.44	< LOD	163.31	< LOD	190.01	77.88	46.36	< LOD	1123.84	< LOD	92.28	< LOD	288.6
C08.2	72.74	< LOD	119.67	305.46	62.96	< LOD	130.08	< LOD	104.91	258.98	121.09	68.19	36.12	< LOD	938.86	< LOD	70.9	302.47	153.09
C08.3	88.97	< LOD	142.88	282.77	68	< LOD	157.46	< LOD	124.29	< LOD	177.06	89.05	43.97	< LOD	1030.9	< LOD	86.52	< LOD	269.22
C09.1	81.13	< LOD	128.65	346.26	71.07	< LOD	150.2	< LOD	123.23	< LOD	184.06	112.59	39.31	< LOD	1074.58	< LOD	81.2	364.65	173.13
C09.2	315.4	< LOD	501.97	< LOD	253.9	< LOD	561.67	< LOD	497.8	< LOD	563.79	< LOD	113.76	< LOD	2271.42	< LOD	160.56	< LOD	603.56
C09.3	75.11	< LOD	127.68	322.2	65.85	< LOD	143.06	< LOD	119.04	< LOD	155.97	< LOD	58.77	< LOD	944.41	< LOD	77.48	< LOD	242.13
C10.1	85.12	< LOD	138.66	278.15	67.78	< LOD	150.9	< LOD	117.46	< LOD	175.14	< LOD	64.55	< LOD	1060.14	< LOD	84.27	< LOD	265.35
C10.2	423.7	< LOD	700.3	< LOD	344.27	< LOD	704.76	< LOD	647.09	< LOD	673.68	< LOD	162.11	< LOD	2910.03	< LOD	229.27	< LOD	854.87
C10.3	83.29	162.15	88.22	328.64	70.15	< LOD	158.49	< LOD	117.8	254.19	133.88	125.32	42.78	< LOD	1053.21	< LOD	86.66	321.07	187.82

User Logi	Hg Error	Au	Au Error	Zn	Zn Error	Cu	Cu Error	Ni	Ni Error	Fe	Fe Error	Cr	Cr Error	V	V Error	Ti	Ti Error	Cl	Cl Error
C11.1	71.05	< LOD	115.45	196.34	55.38	< LOD	129.57	< LOD	105.88	< LOD	161.88	< LOD	57.37	< LOD	914.89	< LOD	76.33	< LOD	237.14
C11.2	128.05	< LOD	206.04	196.36	81.29	< LOD	225.86	< LOD	182.97	< LOD	223.1	< LOD	72.47	< LOD	1373.09	< LOD	99.22	< LOD	308.61
C11.3	59.66	< LOD	101.51	305.72	55.63	< LOD	114.62	< LOD	96.12	193.08	98.44	70.1	32.54	< LOD	849.33	< LOD	63.54	< LOD	203.35
C12.1	74.6	< LOD	120.54	281.14	63.79	< LOD	137.75	< LOD	117.79	< LOD	157.97	86.95	39.09	< LOD	950.61	< LOD	77.26	< LOD	252.78
C12.2	73.45	< LOD	116.43	310.28	63.8	< LOD	135.25	< LOD	105.13	260.19	121.7	94.7	35.78	< LOD	926.82	< LOD	71.84	< LOD	226.43
C12.3	106.41	< LOD	161.79	230.19	73.4	< LOD	200.18	< LOD	155.05	< LOD	194.24	< LOD	63.73	< LOD	1172.34	< LOD	82.75	< LOD	270.73
C13.1	69.25	< LOD	109.85	224.89	57.35	< LOD	128.54	< LOD	108.37	< LOD	157.67	122.31	36.07	< LOD	907.48	< LOD	70.56	< LOD	224.62
C13.2	144.02	< LOD	229.95	215.36	93.87	< LOD	271.48	< LOD	225.27	< LOD	251.82	< LOD	73.81	< LOD	1625.88	< LOD	100.61	< LOD	336.11
C13.3	71.72	< LOD	117.37	202.56	56.48	< LOD	138.42	< LOD	116.09	191.24	118.61	74.64	36.13	< LOD	979.32	< LOD	72.73	< LOD	223.07
C14.1	45.7	< LOD	74.27	154.34	39.59	< LOD	94.45	< LOD	69.15	622	120.62	52.54	26.02	< LOD	735.15	< LOD	51.56	< LOD	147.74
C14.2	38.18	65.11	41.23	158.94	34.9	< LOD	76.49	< LOD	60.02	290.29	86.57	79.28	23.99	< LOD	640.39	< LOD	46.03	< LOD	132.61
C14.3	47.15	< LOD	72.97	130.4	38.78	< LOD	97.52	< LOD	75.03	557.13	118.85	81.45	26.95	< LOD	721.09	69.45	36.86	302.44	106.78
C15.1	57.08	< LOD	83.08	119.85	36.2	< LOD	92.15	< LOD	77.41	500.57	113.51	< LOD	42.07	< LOD	581.19	129.55	40.31	372.91	118.06
C15.2	48.33	< LOD	73.07	158.91	35.88	< LOD	77	< LOD	63.21	155.82	73.44	40.42	26.21	< LOD	518.96	< LOD	52.45	243.59	108.4
C15.3	64.6	< LOD	90.61	141.04	38.63	< LOD	94.02	< LOD	81.63	1178.63	161.97	89.74	29.33	< LOD	621.03	162.72	42.89	23205.76	725.52
C15e-1	83.15	< LOD	137.87	440.84	78.76	< LOD	155.8	< LOD	128.27	996.38	196.24	69.95	39.51	< LOD	964.56	311.67	60.45	1849.72	191.15
C15e-2	120.43	< LOD	201.51	282.07	88.91	< LOD	226.72	< LOD	177.8	1308.98	276.1	< LOD	72.37	< LOD	1174.45	521.38	77.32	1483.66	221.02
C15e-3	720.81	< LOD	1162.82	< LOD	557.18	< LOD	1293.22	< LOD	1106.32	5861.97	1425.76	< LOD	200.92	< LOD	3160.89	1180.72	273.58	< LOD	1038.54
C16.1	56.52	< LOD	80.48	143.56	35.71	< LOD	84.04	< LOD	70.82	422.4	101.15	68.37	27.67	< LOD	558.07	70.27	39.63	495.66	117.75
C16.2	76.38	< LOD	104.26	147.92	44.87	123.92	79.13	< LOD	93.85	161.02	94.23	< LOD	49.77	< LOD	688.41	< LOD	66.06	< LOD	201.55
C16.3	80.64	< LOD	114.08	133.75	46.06	< LOD	112.82	< LOD	89.83	205.56	102.19	< LOD	48.35	< LOD	743.48	< LOD	63.86	< LOD	194.01
C17.1	104.44	< LOD	161.62	< LOD	81.17	< LOD	169.72	< LOD	143.52	374.05	156.85	73.3	40.94	< LOD	946.75	< LOD	83.77	< LOD	266.53
C17.2	67.61	< LOD	108.17	95.66	42.8	< LOD	123.04	< LOD	97.82	1144.21	180.13	60.56	33.63	< LOD	732.83	297.3	52.16	< LOD	214.99
C17.3	102.77	< LOD	164.06	122.44	57.94	< LOD	169.55	< LOD	138.93	308.14	146.38	< LOD	67.47	< LOD	928.33	< LOD	89.07	< LOD	295.66
C18.1	57.01	< LOD	75.34	145.13	35.99	< LOD	87.57	< LOD	72.09	548.44	112.57	52.95	27.29	< LOD	578.41	< LOD	57.53	194.47	112.52
C18.2	84.2	< LOD	123.3	131.36	47.77	< LOD	122.5	< LOD	114.33	166.06	104.52	< LOD	48.4	< LOD	792.44	< LOD	66.23	< LOD	216.42
C18.3	44.93	< LOD	64.67	110.83	28.87	< LOD	67.38	< LOD	55.5	216.23	71.48	64.22	24.26	< LOD	459.26	60.44	32.85	299.6	95.85
C19.1	51.7	< LOD	77	212.57	40.4	< LOD	81.1	< LOD	69.07	482.19	103.61	70.26	26.24	< LOD	549.14	132.09	38.47	< LOD	165.19
C19.2	121.37	< LOD	170.39	220.42	66.74	< LOD	165.57	< LOD	136.95	< LOD	172.11	78.18	40.53	< LOD	944.47	< LOD	86.07	< LOD	255.01
C19.3	44.94	< LOD	63.82	220.61	38.23	< LOD	77.74	< LOD	63.58	625.13	108.13	57.77	24.25	< LOD	521.15	221.46	36.79	280.52	100.74
C20-1	68.93	< LOD	101.46	162.83	46.52	< LOD	111.53	< LOD	86.86	534.72	131.26	51.45	28.85	< LOD	721.12	153.84	42.11	1037.83	128.23
C20-2	65.31	< LOD	95.44	202.45	45.96	< LOD	99.55	< LOD	80.81	165.12	88.89	< LOD	43.87	< LOD	629.87	< LOD	59.83	< LOD	178.49
C20-3	70.07	< LOD	106.61	227.14	49.65	< LOD	103.26	< LOD	89.36	468.5	120.4	63.71	30.46	< LOD	641.48	< LOD	64.42	< LOD	190.55